Ligand Exchange Processes on Solvated Lithium Cations

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Ewa Maria Pasgreta
aus Więcbork (Polen)
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Vorsitzender der Promotionskommission: Prof. Dr. Eberhard Bänsch

Erstberichterstatter: Prof. Dr. Dr. h.c. mult. Rudi van Eldik

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Meiner Familie
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Publications and Conference Contributions

Publications


Conference Contributions

- “$^7$Li NMR Study of the Kinetics of Lithium Ion Complexation by C222, C221 and C211 in different solvents”, 35th International Conference on Coordination Chemistry, Heidelberg, Germany, July 2002, poster presentation.

- “$^7$Li NMR Study of Lithium Ion Complexation by C222, C221 and C211 in different solvents”, Graduiertenkolleg Symposium, Hirschegg-Kleinwalsertal, Austria, March 2003, oral presentation.

- „High Pressure $^7$Li NMR Kinetic Studies of Li$^+$ Complexation by Cryptands in Acetone“, Dalton Discussion Meeting on Inorganic Reaction Mechanisms, Athens, Greece, January 2004, poster presentation.

- “The Mechanism of Ligand Exchange on [Li(H$_2$O)$_n$]$^+$ and [Li(NH$_3$)$_n$]$^+$”, Chemistry Symposium Erlangen-Rennes, Erlangen, Germany, June 2004, poster presentation.

- “$^7$Li NMR Studies of the Kinetics of Lithium Ion Complexation by Cryptands in Gamma-Butyrolactone as Solvent”, The 2004 Younger European Chemists’ Conference, Torino, Italy, August 2004, poster presentation.

- „$^7$Li NMR Studies of the Kinetics of Lithium Ion Complexation by Cryptands in Gamma-Butyrolactone as Solvent“, Catalysis Summer School, Liverpool, Great Britain, September 2005, poster presentation.

- “High Pressure $^7$Li NMR Kinetic Study of Li$^+$ Complexation by Cryptands in Gamma-Butyrolactone”, Dalton Discussion Meeting on Inorganic Reaction Mechanisms, Cracow, Poland, January 2006, poster presentation.

Abbreviations

$\Delta H^\#$  activation enthalpy
$\Delta S^\#$  activation entropy
$\Delta V^\#$  activation volume
$h$  Planck constant, $6.6261 \times 10^{-34}$ J s
$k_b$  Boltzmann constant, $1.3807 \times 10^{-23}$ J K$^{-1}$
$k$  rate constant
$k_{\text{obs}}$  observed rate constant
$k_{\text{on}}$  forward reaction rate constant
$k_{\text{off}}$  backward reaction rate constant
$R$  gas constant, 8.3145 J K$^{-1}$ mol$^{-1}$
$T$  temperature
$t$  time
$A$  associative reaction mechanism
$D$  dissociative reaction mechanism
$I$  interchange reaction mechanism
$I_A$  interchange associative reaction mechanism
$I_D$  interchange dissociative reaction mechanism

C211  4,7,13,18-Tetraoxa-1,10-diazabicyclo[8.5.5]eicosane
C221  4,7,13,16,21-Pentaoxa-1,10-diazabicyclo[8.8.5]tricosane
C222  4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]haxacosane
LiOTf  Lithium Trifluoromethanesulfonate
CH$_3$CN  acetonitrile
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>methanol</td>
</tr>
<tr>
<td>EC</td>
<td>ethylene carbonate</td>
</tr>
<tr>
<td>PC</td>
<td>propylene carbonate</td>
</tr>
<tr>
<td>DMF</td>
<td>N, N-dimethylformamid</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethylsulfoxide</td>
</tr>
<tr>
<td>GBL</td>
<td>γ-butyrolactone</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>B3LYP</td>
<td>Becke’s 3 Parameter Hybrid Functional using Lee-Yang-Paar Correlation</td>
</tr>
<tr>
<td>HF</td>
<td>Hartree-Fock</td>
</tr>
<tr>
<td>MP</td>
<td>Møller-Plesset Perturbation</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>DNMR</td>
<td>dynamic nuclear magnetic resonance</td>
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Lithium, the lightest of all metals and the least reactive, has been the object of numerous experimental and theoretical studies. One might say that lithium chemistry is a branch of chemistry in itself. Anomalous properties of lithium, because of its small size, include such phenomena as the lithium bond (similar to the hydrogen bond), formation of aggregates, and complexation by crown ethers or cryptands.¹

Lithium was first discovered in 1817 by the Swede Johann August Arfvedson and pure lithium metal was first prepared the following year by Davy and Brande by electrolysis of lithium oxide. Lithium’s name originates from Greek word “lithos” meaning stone and it is the lightest of all solids (0.53 g/cm³). The industrial process by which lithium is prepared today is electrolysis of lithium chloride or lithium carbonate. Today, the amount of lithium produced yearly is about 10,000 tons.²

Coordination chemistry of lithium and other alkali metals was viewed until the 1960’s as a rather barren area, made so since the singly charged and relatively large M⁺ ions were held to have rather poor coordinating ability. The majority of the known metal salt complexes were hydrates. Two developments have transformed this research area over past the 40 years. The first began with the Nobel prize-winning discovery by Pedersen, Lehn and Cram of macrocyclic ligands like “crown” ethers, cryptands, and spherands. Such ligands wrap around the metal ion, encapsulating it to greater or lesser degree, and are highly selective regarding which metal cation can be accommodated. This feature has led to important application in cation separation, ion-specific measuring devices, and phase-transfer catalysis, and as mimics of naturally occurring macrocyclic antibiotics. The second major development was brought about by extensive investigation of non-aqueous alkali metal chemistry prompted largely by the importance of lithium reagents in organic synthesis.³
1. Introduction

1.1. A European Project

The research work presented in this thesis has been developed within the framework of the European Research Training Network on *Solvation Dynamics and Ionic Mobility in Conventional Solvents and Plasticizers – by Computational Chemistry and Experiment*. The overall goal of this Network (which involved the collaboration between six European research groups) was to seek firm knowledge about the mechanisms of the dynamical processes present, and their relative importance. The primary scientific aims were:

- to discover unifying and differentiating features in ligand and solvent exchange processes around metal ions in conventional and polymer solvents;
- to study the connection between solvation dynamics and ionic diffusion/conduction mechanism in these systems;
- to help in the search for new applied systems by providing a more detailed understanding of the basic phenomena occurring in model electrolytes

In this thesis these aims are approached from the microscopic point of view, making use of both computer calculations and experimental techniques. The way solvent molecules interact with the ion, and how this interaction affects the physico-chemical properties of the system are studied.

1.2. Outline of this Thesis

The contributions of the present work to the network objectives can be divided into three main topics which constitute the backbone of this thesis:

**Solvation:** how is the first coordination sphere around Li$^+$ constituted; how does the nature of the solvent influence solvation;
Solvent exchange: the exchange process between the first and second coordination spheres of the Li cation is studied; the interplay between diffusion and the exchange mechanism is addressed.

Lithium complexation by cryptands and ligand exchange in conventional solvents and plasticizers: how is Li$^+$ complexed by different cryptands; how do solvents of different properties influence the process of Li$^+$ exchange between complexed and solvated sites.

The Li$^+$ cation remained the centre of our interest: its solvation shell and the way it is solvated. Both experimental and theoretical methods were employed. Solvents of different properties and their influence on the solvation shell were investigated. Questions concerning selective solvation around Li$^+$ and the solvation number of the Li$^+$ cation were studied as a function of the solvent properties. The Gutmann Donor Number was mostly considered as a factor describing the donating abilities of the solvent. However, we were not only interested in thermodynamic phenomena. Kinetic measurements were also of primary importance. Once the solvation shell of the Li cation was known, we wanted to investigate the exchange of certain solvent molecules around Li$^+$. As Li$^+$ is a very labile cation, solvent exchange was found to be very fast on the NMR time scale and this process was therefore also investigated by computational methods.

Solvent exchange is the simplest ligand exchange process, where, in fact, there is no net change in the composition of the first solvation shell. However, this process helps to understand the exchange of Li$^+$ between different environments, i.e. between solvent and another ligand.

Macrocyclic ligands called cryptands were found to bind the alkali and alkaline earth metal ions very efficiently. They have been extensively explored with respect to their structure and binding properties. Although there is a wealth of information about thermodynamic and structural studies on the complexation of metal ions by macrocyclic ligands in different solvents, kinetic and mechanistic studies have received less attention and hence are still poorly understood. For a better understanding of the pronounced selectivities of
1. Introduction

Macrocyclic ligands towards alkali and alkaline earth cations, it is necessary to investigate their mechanisms of formation and dissociation. In this contribution, we were particularly interested in the mechanistic aspects of the Li$^+$ exchange process between cryptands and solvent. In the case of many solvents the exchange was very fast or, on the contrary, in the case of small cavity ligands, there was almost no exchange observed. Therefore, two solvents, viz. acetone and $\gamma$-butyrolactone, were chosen for more detailed mechanistic investigations. They possess different properties and applications, such that the obtained results could be of importance in different application fields.

The experimental method used throughout was $^7$Li NMR. During the past few decades it has been shown that multinuclear NMR is a very powerful technique for the study of alkali complexes with macrocyclic ligands, particularly in non-aqueous solutions. $^7$Li is active in NMR and possesses features that make it convenient for this kind of investigation. Particular attention was given to high pressure $^7$Li NMR, which is the first example reported for this kind of research. High pressure NMR is a powerful tool employed to elucidate details of the reaction mechanism. The determination of activation volumes from the pressure dependence of exchange rates for solvated metal ions is a useful method for the diagnosis of the intimate mechanism.

The outline of this thesis is as follows: Part I is dedicated to introduce the main topics studied and to give a brief introduction of the methods used. Parts II, III, IV and V contain the results and discussion of specific studies on Solvation of the Li Cation in DMSO and DMSO/water mixture, Solvation of the Li Cation in CH$_3$CN and CH$_3$CN/water mixture, Ligand Exchange in Conventional Solvent and Ligand Exchange in Plasticizer, respectively. Finally, concluding remarks are made in Parts VI and VII (in German).
1.3. Lithium

Lithium is the lightest of all metals. It has the highest specific heat of any solid element and therefore is very useful in heat transfer applications. Lithium is also a leading contender as battery anode material due to its high electrochemical potential. The lithium ion is exceptionally small and has, therefore, an exceptionally high charge to radius ratio. As a result, its properties are considerably different from similar ions such as sodium and potassium. Contrarily, its hydrated radius is much larger than similar ions and therefore exhibits different solution properties such as very low vapor pressure, freezing point, and other colligative properties. The large solvation shell around the lithium ion also causes it to have lower mobility in solution. The aforementioned properties of the lithium ion contribute to its unique behavior and effects in a variety of environments. The chloride salt of lithium is one of the most hygroscopic materials known and is therefore used in many air conditioning and drying systems. In general, the lithium ion has been well documented to have profound biological effects of varying intensity on many life forms. Numerous publications confirmed its influence on enzyme activity, metabolism, respiration, and active transport. A prominent effect of lithium on the nervous system can be found in the field of medicine. Here it is used to treat severe mental disorders such as manic-depression by controlling mania and stabilizing mood swings. Although its therapeutic value has been debated, there is no doubt that a number of manic patients have benefited from lithium treatment. The lithium ion seems to counteract the manic symptoms in a specific way, however, little is understood about the mechanism of its therapeutic action. In conclusion, it is evident that lithium can have some profound effects on a variety of chemical and biological systems. Although it has been intensively studied, little is known about the details of the action of lithium including required concentrations and mechanisms by which changes occur.
1. Introduction

1.4. Solvation

Solute-solvents studies involving electrolytes have been a subject of interest to solution chemists for quite sometime. Such studies on the transport properties of electrolytes in aqueous and non-aqueous solvents are of interest in various technologies like high energy density batteries, photo-electrochemical cells, electrodeposition, wet electrolytic capacitors and in electro-organic synthesis.

Ion solvation is a phenomenon of fundamental interest in many aspects of chemistry because solvated ions are almost omnipresent on Earth. Hydrated ions occur in aqueous solution in many chemical and biological systems. Ions solvated in organic solvents or mixtures of water and organic solvents are also very common. Selective solvation occurs when the solvate prefers one of the solvents over the other. This phenomenon can be used to separate different ions from each other, a process known as solvent separation. The exchange of solvent molecules around ions in solution is fundamental to the understanding of the reactivity of ions in solution. Solvated ions also play a key role in electrochemical applications, where for instance the conductivity of electrolytes depends on the ion-solvent interactions.17

A literature survey suggests that the use of mixed solvents involving high permittivity, low viscosity, and a wide liquid range is practicable for use in high energy density batteries, especially lithium batteries. The advantage of using mixed solvents over their pure counterparts in lithium batteries is to manipulate the suitable properties of these solvents for fulfilling the above conditions.

It is known that aprotic solvents show high permittivities, low viscosities, and strong temperature dependences. Hence, in order to develop suitable mixed solvents fulfilling the conditions mentioned above, mixtures of solvents must be prepared to balance the drawbacks of pure solvents. The conductivities of lithium perchlorate in different solvent systems are explained
in terms of solution viscosity and the donor-acceptor properties of the solvents, which mainly govern the ion-solvent interaction.

1.4.1. Conventional Solvents

Solvents and solutes can be broadly classified into polar and non-polar. There are a number of factors describing solvent properties. Polarity can be measured as the dielectric constant or the dipole moment of a compound. Polar solvents can be further subdivided into polar protic solvents (e.g. water or methanol) and polar aprotic solvents (e.g. acetone, acetonitrile, dimethylformamide or dimethylsulfoxide).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>DN, kcal mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-Dichloroethane (reference solvent)</td>
<td>0.0</td>
</tr>
<tr>
<td>Nitromethane</td>
<td>2.7</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>14.1</td>
</tr>
<tr>
<td>Propylene carbonate</td>
<td>15.1</td>
</tr>
<tr>
<td>Ethylene carbonate</td>
<td>16.4</td>
</tr>
<tr>
<td>Acetone</td>
<td>17.0</td>
</tr>
<tr>
<td>γ-Butyrolactone</td>
<td>18.0</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>19.2</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>20.0</td>
</tr>
<tr>
<td>N,N-Dimethylformamide</td>
<td>26.6</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>29.8</td>
</tr>
<tr>
<td>Methanol</td>
<td>30.0</td>
</tr>
<tr>
<td>Water</td>
<td>33.0</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>61.0</td>
</tr>
</tbody>
</table>
1. Introduction

Donor Number (DN) is a qualitative measure of Lewis basicity. It is defined as the negative enthalpy value for 1:1 adduct formation between a Lewis base and the standard Lewis acid SbCl₅, in dilute solution in the non-coordinating solvent 1,2-dichloroethane with a zero DN. The Donor Number describes the ability of a solvent to solvate cations and Lewis acids. The method was developed by V. Gutmann in 1976. Values of DN for common organic solvents are summarized in Table 1.1.

Solvents undergo various weak chemical interactions with the solute. The most usual interactions are the relatively weak van der Waals interactions (induced dipole interactions), the stronger dipole-dipole interactions, and even stronger hydrogen bonds.

The role of a solvent on organometallic substitution reactions cannot be overestimated; even a small modification of the solvent structure may cause a large change in the rate and in the pattern of the processes in solution.

1.4.2. Plasticizers

Battery technology has achieved spectacular progress in recent years. A most successful product is the rechargeable Lithium Ion Battery (LIB), which has reached an established commercial status with a production rate of several millions of units per month. Currently, the lithium salt electrolyte is not held in an organic solvent like in the past models, but in a solid polymer gel electrolyte such as polyacrylonitrile, polyvinylidene fluoride, polyethylene oxide, etc. There are many advantages of this design, for instance, the solid polymer electrolyte is not flammable as the organic solvent that the Li-ion cell uses. Thus, these batteries are less hazardous if mistreated.

The vast majority of electrolytes are the electrolytic solution-types that consist of salts (also called “electrolyte solutes”) dissolved in the solvents (also called plasticizers), either water (aqueous) or organic molecules (non-aqueous), and remain in the liquid state within the service-temperature range. The most used solvents are ethylene carbonate, propylene carbonate and γ-butyrolactone. (Figure 1.1)
Experimentally it has been found that a mixture of two or more plasticizers is more convenient, as it allows optimization of the balance between different features (such as dielectric constant, viscosity, ionic diffusion, salt dissociation, and chemical stability) and thus to enhance the battery performance and cyclability.

The overall goal of the project was to study the solvation dynamics and ionic mobility in conventional solvents and to seek firm knowledge about the mechanisms of the dynamical processes present, and their relative importance. The importance of this mechanism can be illustrated with an example from the polymer field. High molecular-weight poly(ethylene oxide), PEO, with dissolved ions is a polymeric system with low ionic conductivity at room temperature. On the other hand, PEO with dissolved ions and a second, low-molecular weight organic solvent added is an example of a polymeric system with high ionic conductivity at room temperature. The addition of even modest amount of such a small molecule to the pure polymer electrolyte drastically increases the conductivity. The low-molecular weight organic solvent is called plasticizer.
1 Introduction

1.5. Cryptands

Whereas coordination chemistry was almost exclusively concerned with the complexes formed between organic or inorganic ligands and transition metal ions, only scattered examples of alkali cation (AC) complexes were documented. The situation changed entirely with the discovery (around the middle 1960’s in short sequence) of three classes of organic ligands capable of forming strong and selective complexes with alkali, as well as alkaline-earth, cations. First, natural macrocyclic antibiotics (in particular valinomycin) were found to bind and to make membranes permeable to AC’s (namely K⁺), acting as ionophores. Then, it was discovered that macrocyclic polyethers, the crown ethers, formed complexes with AC’s. Thirdly, macrobicyclic receptors, the cryptands, were designed and shown to form even much more stable AC cryptate complexes by inclusion into the three-dimensional molecular cavity. Numerous other ligands were then developed in particular the spherands. Examples of mycrocyclic ligands are illustrated in Figure 1.2. A rich coordination chemistry of AC’s has thus been established, displaying a whole range of complexes of varied structural, thermodynamic and kinetic properties. Strong and selective complexation of AC’s was achieved, yielding for instance stability constants higher than 10⁵ l mol⁻¹ in aqueous solution for the Li⁺, Na⁺ and K⁺ cryptates of the optimal macrobicyclic receptors. Very stable and selective alkaline-earth complexes of macrocyclic and macropoly cyclic ligands were also obtained.²⁰
1. Introduction

Figure 1.2. Structural formulas of crown ethers (a), cryptands (b), and spherands (c).

The chelate effect of acyclic ligands was extended to macrocyclic and cryptate effects defined by special features (such as substrate inclusion, high stability, high selectivity, slow exchange rates, shielding from the environment) presented by macrocyclic and macropolycyclic ligands and their metal ion complexes.

The field of macrocyclic and macropolycyclic chemical compounds has greatly advanced over the last years mainly with the goal of developing complexing-agents, or molecular receptors, capable of binding very efficiently and very selectively a given substrate. Thus, by taking into account specific molecular interactions and the relationship between geometrical structure and binding sites, the chemistry of molecular recognition has been developed, this being a major part of supramolecular chemistry.21
Compared to the usual macrocycles of the crown type which have a two dimensional framework, the cryptands are three dimensional in structure containing an intramolecular cavity (or “crypt”). Cryptands form inclusion complexes, the cryptates, in which the substrate is located inside the cavity.

Several reviews and monographs which contain important information on the structures and applications of macrocyclic complexes with alkali metal ions are available.\textsuperscript{22-29}

Many natural substances have a macrocyclic structure whether or not they exhibit complexing properties, \textit{e.g.}, cyclic antibiotics, cyclodextrins. Since the macrocyclic structure is so widespread in nature, one can conclude that it offers over the linear arrangement certain “useful” properties with respect to the functions performed. The fundamental observation has been incorporated in the chemistry of molecular recognition.

The alkali metal cations are spherical species bearing a positive charge. The recognition of these species involves the selection of a sphere from a collection of spheres of different radii.

In 1975 Lehn and Sauvage\textsuperscript{30} reported stability constants and selectivities for complexation of alkali metal and alkaline earth cations by cryptands. In these multidentate ligands, two nitrogen atoms were linked by three oxygen atom containing bridges. Diameters of the alkali metal cations and the cryptand cavities are recorded in Table 1.2. The cavity size of the cryptand C\textsubscript{211} is appropriate for strong complexation of Li\textsuperscript{+}, but too small to accommodate Na\textsuperscript{+} or any of the other alkali metal cations. Stability constants for complexation of Li\textsuperscript{+}, Na\textsuperscript{+}, and K\textsuperscript{+} by cryptands C\textsubscript{222}, C\textsubscript{221}, and C\textsubscript{211} are summarized in Table 1.3.\textsuperscript{29}
A cation is characterized by its ionic radius, charge and charge density, polarizability, solvation energy, and also the ionization potential of the corresponding metal. Cation complexation is governed by coordination chemistry. The selection of the cation is ensured by a cavity of adequate size, and the bond to the macrocycle arises through the presence of polar interaction sites lining the cavity.

The first macrobicyclic diamines were synthesized by Simmons and Park. These ligands display a particular form of isomerism since the pair at the bridgehead nitrogen may be directed either inwards or outwards with respect to the cavity thus giving rise to three forms: exo-exo or out,out; exo-endo or out,in; endo-endo or in,in. The predominant form depends on the size of the bicyclic system.

Inclusion of a $M^{n+}$ metal cation in the intramolecular cavity of the three possible forms of cryptands should give rise, in principle, to the following three topographies: exo-exo, exo-endo and endo-endo. The endo-endo conformation
is greatly favored because in this case both amine groups participate in stabilizing the complex.

In this study we emphasize the analogy in structure between ion-polymer complexes and ion-macrocyclic ligand complexes. It is suggested that the two types of systems are complementary, in that studies of polymer-salt systems can give information about interactions in mycroyclic ligand-salt systems, and vice versa. Crown ethers have been found to improve the electrical conductivity of solid polymer electrolytes that might be used in lithium batteries. However, there is another way in that the above case makes much closer contact with the practical world of lithium batteries. Poly(ethylene oxide), PEO, has been a prototypical polymer used in studies of lithium battery solid electrolytes. The same –CH₂CH₂O– moiety that appears in the crown ethers and cryptands is the building block of PEO. Thus it is hardly surprising that PEO has a high affinity for alkali metal cations just as crown ethers do.

1.6. Exchange Processes

The exchange of solvent molecules around a metal ion is the simplest ligand substitution process and is fundamental to the understanding of the reactivity of the metal ions in solution. The mechanism of ligand exchange is often discussed in terms of the scheme developed by Merbach et al., which emphasizes a structural definition of the different exchange mechanisms, i.e. the mechanism is defined by the positions of the incoming and leaving ligands relative to the metal ion, as can be seen in Figure 1.3.
The prevailing exchange mechanism can experimentally be deduced from the activation parameters $\Delta S^*$ and $\Delta V^*$. Large negative activation entropies or activation volumes are interpreted as corresponding to an associative mechanism (A) and large positive values as dissociative (D), whereas small values are interpreted as concerted mechanisms ($I_a$, I, or $I_d$).

The pressure dependence of the exchange rate constant leads to the activation volume, $\Delta V^*$, which has become the major tool for the experimental determination of the exchange mechanisms. The volume of activation, $\Delta V^*$, is defined as the difference between the partial molar volumes of the
transition state for the reaction and the reactants and is related to the pressure variation of the rate constant at a constant temperature $T$ by Equation (1.1).

$$\left( \frac{d \ln k}{dP} \right)_T = -\frac{\Delta V^*}{RT}$$

(1.1)

An approximate solution of the above differential Equation (1.1) is Equation (1.2).

$$\ln k = \ln k_{P=0} - \left( \frac{\Delta V^*}{RT} \right)_{P=0} P$$

(1.2)

Solvent and ligand exchange and substitution reactions in liquid solutions are basic chemical processes that in many cases control the rate and efficiency of chemical reactions. This research topic is related to various technological applications both in the polymer electrolyte field and for basic chemical processes. Solvent dynamics is one of the phenomena which enable ionic conductivity in a polymeric salt.

Exchange of a solvent molecule between the first and the second coordination sphere is the simplest reaction that can occur on a metal ion in aqueous and non-aqueous solution. This reaction is fundamental in understanding not only the reactivity of metal ions in chemical and biological systems but also the interaction between the metal ion and the solvent molecules. The displacement of a solvent molecule from the first coordination shell represents an important step in complex-formation reactions of metal cations and in many redox processes. The measured rates of solvent exchange vary extensively with the nature of the metal ion and, to a lesser extend, with that of the solvent. Metal ions of main group elements have filled electron shells, and they differ mainly in electric charge and ionic radius. The number of solvent molecules in the first shell around the ion, commonly called the coordination number, CN, ranges from 4 up to 10. Alkali group ions are very labile, due to the low surface charge density and the absence of ligand field stabilization effects. Solvent exchange at Li$^+$ in water is extremely fast, making it difficult to study directly. An exchange rate constant of
approximately $10^9 \text{ s}^{-1}$ at 25 °C was predicted on the basis of complex-formation data.\textsuperscript{36} (Figure 1.4)

![Graph showing mean lifetimes and water exchange rates](image-url)

**Figure 1.4.** Mean lifetimes, $\tau_{\text{H}_2\text{O}}$, of a particular water molecule in the first coordination shell of a given metal ion and the corresponding water exchange rate $k_{\text{H}_2\text{O}}$ at 298 K. (taken from the recent review\textsuperscript{36})

1.7. *Kinetic Applications of NMR Spectroscopy*

The rates of chemical reactions vary over many orders of magnitude. Some reactions are so slow that they practically do not occur, even though the free energy would decrease considerably. On the other hand, many chemical reactions are so fast that until recently they have been called “immeasurably fast”. During the past 50 years, however, a wealth of techniques have been developed to study reaction times much shorter than one second and well outside the range of conventional analytical methods.\textsuperscript{41}

Figure 1.5 shows various experimental methods and their time scales.
Spectroscopic techniques such as optical spectrophotometry or NMR spectroscopy have often been used to monitor concentration changes as a function of time, thereby allowing the kinetic parameters to be determined. Fast chemical exchange may play a direct role in the optical (or NMR) absorption process itself, changing the line shape of the observed spectra. This kinetic modification of line shapes occurs at complete equilibrium, whereas all other fast reaction techniques require finite deviations from equilibrium. Kinetic information is available from the resulting line broadening. The older CW (continuous wave) NMR technique has been superseded by FT (Fourier transform) NMR.\textsuperscript{41}

Nuclear magnetic resonance (NMR) is one of the most widely used methods for studying rapid intra- and intermolecular equilibrium processes of inorganic, organic, and biochemical systems involving the transfer of
components of ions and molecules or the complete entities between different chemical environments in the liquid state. The only requirement of the method is that the chemical equilibration process must involve the exchange of nuclear spins between different magnetic environments, under which circumstances first order rate constant in the range from $5 \times 10^{-3}$ s$^{-1}$ to $10^6$ s$^{-1}$ are accessible using commercially available NMR spectrometers. In the vast majority of applications, the chemical system studied is at thermal equilibrium and the chemical kinetic parameters are determined from the modification of the NMR spectrum induced by the nuclear spin exchange characterizing the chemical equilibration processes.\textsuperscript{42}

The derivation of the chemical parameters from NMR data requires knowledge of the factors determining spectral line shapes and the sources of spectral modifications induced by nuclear spin exchange accompanying chemical equilibration processes.

Among other spectroscopic techniques, high-pressure NMR especially has found remarkable applications in the investigation of reaction mechanisms. A high-pressure NMR probe designed for a 400 MHz narrow bore NMR spectrometer was developed in our laboratory\textsuperscript{43} and is presented in Figure 1.6(a) The aim of the proposed design was to allow high resolution, high-pressure NMR experiments in a narrow bore magnet system without any modification of the magnet. The probe should be easy and safe to handle. More details are reported elsewhere.\textsuperscript{43} The NMR tubes used for high pressure measurements are presented in Figure 1.6(b)
1.8. Alkali Metal NMR Spectroscopy

The magnitudes of chemical shifts for alkali metal resonances increase markedly from lithium to caesium, and are a further order of magnitude larger for thalium. However the sensitivity of the alkali metal chemical shifts to the environment, specifically the solvation variation, increases in the opposite direction. Chemical shifts depend both on the nucleus and the nature of the solvent. They also, for a given alkali metal cation, depend on the nature of the counterion and the concentration of the salt.44

The properties of 7Li nucleus are quite favorable for NMR studies. (see Table 1.4) The resonance lines of Li+ ion in solutions are exceptionally narrow and chemical shift can be measured with considerable accuracy.45

Lithium consists of two stable isotopes: 6Li and 7Li. The magnetogyric ratio, γ, of 7Li is comparatively high. At a magnetic field strength of 9.4 T (1H: 400 MHz), the correlate Larmor frequency of 7Li is 155.45 MHz. Because of its high
1. Introduction

γ number and its high natural abundance, $^7$Li is a sensitive and easy to detect nucleus. However, many NMR studies on organolithium compounds are now frequently carried out by observing the $^6$Li nucleus, preferably in $^6$Li isotope-enriched samples.$^{46}$

| Table 1.4. Nuclear properties of key isotopes of lithium.$^{46,47}$ |
|---------------------------------|----------|----------|
| Isotope                        | $^6$Li   | $^7$Li   |
| Atomic mass                    | 6.01512  | 7.01600  |
| Natural abundance (%)          | 7.42     | 92.58    |
| Nuclear spin                   | 1        | 3/2      |
| $\nu_0$ at 9.4 T (1H = 40 MHz) | 58.862   | 155.454  |
| Nuclear magnetic moment $\mu$  | +0.82203 | +3.25636 |
| Quadrupole magnetic moment Q ($10^{-28}$ m$^2$) | $-8 \times 10^{-4}$ | $-4.5 \times 10^{-2}$ |
| Receptivity $D_c$ ($^{13}$C = 1.00) | 3.58     | 1540     |
| Width factor ($^7$Li = 1.0)    | $2.0 \times 10^{-3}$ | 1.00     |

Selective solvation of alkali metal ions in mixed solvents can be monitored from the extent to which the chemical shift of the alkali metal nucleus varies with solvent composition.

The linewidth measurements may also give some idea of solvation in mixed solvents. The dependence of the resonance linewidths on solvent composition is investigated in the mixtures containing one good and one poor solvent. The difference in pattern is striking and is attributed to relatively long-lived cation-solvent complexes formed by the strongly coordinating solvents. Such a difference in behavior is reasonable. It is consistent with solvating abilities of the solvents, and with their respective Gutmann donor numbers.
1. Introduction

The exchange of ions between different environments is usually rapid with respect to the NMR time scale, resulting in only one resonance signal at an average frequency determined by the magnetic shielding and lifetime of the nucleus in each of the sites. Alteration of parameters such as concentration, counterions, and solvent produces changes in the relative proportion and type of environment which may be reflected by alteration of the NMR spectra on chemical shift and/or line shape, and/or line width of the observed resonance.\textsuperscript{45}

1.9. Programs

The line widths of the NMR signals can be obtained by fitting Lorentzian functions to the experimental spectra using the NMRICMA 2.7 program.\textsuperscript{48} NMRICMA is a program written for MATLAB to evaluate 1D NMR and EPR spectra. It reads experimental NMR spectra treated with 1D WIN-NMR from Bruker. NMRICMA can fit Lorentzian resonance lines to experimental spectra, fit NMR multiplets (formed by Lorentzian lines) to experimental spectra, fit exchange broadened NMR spectra using Kubo-Sack formalism and simulate exchange broadened NMR spectra.

Complete line-shape analysis based on the Kubo-Sack formalism using modified Bloch equations\textsuperscript{49} was performed with NMRICMA 2.7 to extract rate constants from experimental spectra. In order to elucidate the exchange rate constant between two species, the exchange matrix must be created. In case of a two site exchange, a $2 \times 2$ exchange matrix was created.

\[
D = \begin{bmatrix}
-k_{AB} & k_{AB} \\
\frac{p_A}{k_{AB}} & -\frac{p_A}{k_{AB}}
\end{bmatrix}
\]

34
where: \( k_{AB} \) refers to the rate constant between species A and B, 

\( p_A \) and \( p_A \) represent the populations of the NMR signals referring to the species A and B, respectively.

The exchange matrix is created and saved as the matex file in Matlab:

```matlab
function m = matex2(p,k)
%--------------------------------------------------------------------------
% function subroutine for exchange
%--------------------------------------------------------------------------
% alpha - version; started on january 1994
% © lothar helm, icma université lausanne
% rate constant(s) = k
% populations      = p
%
global xtitle matexfile si td sw sf limits nlimits;
nsites = length(p);
m = zeros(nsites);
m(1,1) = -k(1);
m(1,2) = +k(1);
m(2,1) = p(1)/p(2)*k(1);
m(2,2) = -m(2,1);
```

The adjustable parameters are: resonance frequency, intensity (population), line width and baseline. The temperature and pressure dependent \( ^7Li \) line widths and chemical shifts employed in the line shape analysis were extrapolated from low temperatures where no exchange-induced modification occurred.

The fitting method used throughout was the Lavenberg-Marquard method. The progress of fitting can be followed by observing the MATLAB window. The iteration stops when the maximum number of iterations is reached. The spectrum plot window of NMRICMA shows the result of the fit: experimental and fitted spectra on an overlay plot, difference between fitted and experimental spectrum, and fitting results are given as well as some other
useful information. One example of the output spectrum can be seen in Figure 1.7.

**Figure 1.7.** The output $^7$Li NMR spectrum from the NMRICMA fitting program.

### 1.10. Computational Methods

The theoretical calculations employed in this work were mostly based on quantum chemical methods. They were based either on the wave function or on the electron density of the investigated molecule to calculate its structure and properties. The significance of these two methods can be recognized from two Nobel Prize Awards given in 1998 to J. A. Pople for the development of the computational methods in quantum chemistry and to W. Kohn for the development of the density functional theory.
1. Introduction

The quantum chemical methods based on the wave function come from the Schrödinger equation and describe all relevant electronic, time dependent and relativistic effects. For the purpose of many chemical problems one can often neglect the time dependent and relativistic effects to obtain in this way the time-independent, non-relativistic Schrödinger equation. The fundamental assumption (known as the Born-Oppenheimer approximation) is that, in the adiabatic limit, we can decouple the nuclear and the electronic degrees of freedom; in this way the time-independent electronic Schrödinger equation is obtained.

1.10.1. **Ab-initio Methods**

In order to solve the electronic Schrödinger equation, an additional approximation is introduced: Hartree-Fock (HF) approximation.

The wave function which describes both the single electron spatial distribution and its spin is called *spin orbital*. The fundamental idea of the HF-theory is that the $N$-electrons wave function ($N$ is the number of electrons) is displaced by more single electron wave functions. To a first approximation we can consider that the electrons do not interact. The total Hamiltonian will be the sum of $N$ individual Hamiltonians. The total wave function is the product of $N$ spin orbitals. Since electrons in fact interact with each other, in the Hartree-Fock approximation, the Coulomb interaction among electrons is averaged and the many electrons wave function (and energies) is obtained in an iterative way. In this model one electron is influenced by the presence of...
other electrons. For practical purposes, the unknown spatial molecular orbitals are often transformed into one set of known spatial functions, viz. the basis set. In practice the Hartree-Fock equation is solved by introducing a finite set of $K$ basis functions, which lead to a set of $N$ occupied spin orbitals and $K-N$ virtual ones.

Since there is no correlation in the electron movement in the HF-approximation, this must be considered by means of some other methods. A different procedure to find the correlation energy, which is not variational but size consistent at each level, is the Perturbation Theory (PT). In 1934 Møller and Plesset proposed a perturbation treatment of atoms and molecules in which the unperturbated wave function is the Hartree-Fock function; this is the so called Møller-Plesset (MP) perturbation theory (general: many body perturbation theory). It is based on Rayleigh-Schrödinger perturbation theory where the total Hamiltonian of the system is divided into two parts: a zero-order part which has known eigenvalues and eigenfunctions, and a perturbation operator. Second (MP2) and fourth (MP4) order Møller-Plesset calculations (where we refer to the order of the energies) are standard levels used for small systems and are implemented in many computational chemistry codes.

1.10.2. **Density Functional Theory**

Hohenberg and Kohn in 1964 suggested that the many-electron wave function was a too complicated entity to deal with as the fundamental variable in a variational approach. Firstly, it cannot adequately be described without $\sim 10^{23}$ parameters, and secondly it has the complication of possessing a phase as well as a magnitude. They chose instead to use the electron density as their fundamental variable.

The advent of modern DFT methods for molecular systems has revolutionised computational chemistry, especially for the transition metals. In a nutshell, DFT is based on the fact that all molecular electronic properties can be calculated if the electron density is known. The only blemish is that the exact form of all the components of the functional that gives the energy from
the electron density is unknown. There are, however, a number of approximate functionals available. These can be divided into three classes:

1. Functionals based on the local density approximation (LDA) only depend on the value of the electron density at any given point in space.

2. Functionals that use not only the value of the electron density, but also its gradient (how fast it changes in space) are based on the generalised gradient approximation (GGA).

3. Hybrid density functional techniques combine GGA functionals with a parameterised proportion of the exchange energy calculated by Hartree–Fock (HF) theory. They are thus a cross between DFT and conventional HF ab initio theory. However, hybrid DFT methods are the most accurate of the three classes and, therefore, enjoy great popularity. The best-known hybrid level of theory is Becke’s three-parameter technique with the Lee–Yang–Parr correlation functional (B3LYP).

The two major advantages of DFT calculations are that they give good to excellent results for metal systems, including transition metals, and that they scale relatively well with the size of the system to be calculated, so that large complexes and clusters can be treated. However, DFT shows some serious limitations for studying water-exchange reactions. Hydrogen-bonding and proton-transfer reactions are generally not treated well by DFT. Compared with MP2, even hybrid DFT with an adequate basis set also favors lower coordination numbers.
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1. Introduction


1. Introduction

2. Ligand Exchange Processes on Solvated Lithium Cations. DMSO and Water/DMSO Mixtures

2.1. General remark

The work presented in this chapter was conducted by several authors within a joint project and has been published as:


2.2. Abstract

Solutions of LiClO₄ in solvent mixtures consisting of dimethylsulfoxide (DMSO) and water, or DMSO and γ-butyrolactone, were studied by 7Li NMR spectroscopy. Chemical shifts indicate that the Li⁺ ion is coordinated by four DMSO molecules. In the binary solvent mixture of water and DMSO, no selective solvation is detected, thus indicating that on increasing the water content of the solvent mixture, DMSO is gradually displaced by water in the coordination sphere of Li⁺. The ligand-exchange mechanism of Li⁺ ions solvated by DMSO and water/DMSO mixtures was studied using DFT calculations. Ligand exchange on [Li(DMSO)₄]⁺ was found to follow a limiting associative (A) mechanism. The displacement of coordinated H₂O by DMSO in [Li(H₂O)₄]⁺ follows an associative interchange mechanism. The suggested mechanisms are discussed in reference to available experimental and theoretical data.
2. DMSO and Water/DMSO Mixtures

2.3. Introduction

Lithium salts are widely used in industrial applications, synthesis, and medicine, for example, in psychiatry. Therefore, detailed understanding of fundamental reactions of solvated lithium cations, for example ligand-exchange reactions in different solvents, is essential.

Knowledge of elementary reactions, such as solvent exchange, in different solvents is an important prerequisite for selecting, optimizing and tailoring the ideal solvent and solvent mixture. Whereas experimental methods investigate reactions under real conditions in a whole ensemble of molecules, quantum-chemical calculations can focus on a single molecule in the presence of a small number of solvent molecules, for example, those of the first solvation shell. This complementary approach allows further mechanistic insight to be gained.

Dimethylsulfoxide (DMSO) is a common solvent in chemical laboratories, even though industry tries to avoid it. It is widely used in laboratories due to its ability to dissolve a wide range of chemical compounds (from ionic inorganic salts to purely covalent compounds), because it is an aprotic but highly polar polyfunctional molecule with both a hydrophobic and a hydrophilic site. Moreover, it has the highest dipole moment (4.3 Debye) and highest dielectric constant (48 at 20 °C) of any dipolar aprotic liquid. Furthermore, DMSO is also used as a valuable reactant for example in a number of oxidation reactions, like the Swern oxidation of alcohols to aldehydes and ketones using activated DMSO, or in a Pummerer-type reaction to obtain the Tröger’s bases.

The use of DMSO in human and veterinary medicine is based on its ability to penetrate deeply through skin and other membranes without damaging them, while carrying other compounds deep into a biological system. On the other hand, this effect causes the biggest toxicological concerns.

DMSO possesses very strong donating abilities. This property has also been confirmed by various studies of stability constants of alkali-metal complexes. It is well-known that the solvating ability of the solvent, as expressed by the
Guttmann donor number (DN)\textsuperscript{30} plays a fundamental role in different complexation reactions. DMSO is a solvent of high solvating ability (DN = 29.8) and it can strongly compete with ligands such as crown ethers or cryptands for alkali-metal ion coordination.\textsuperscript{29}

A variety of theoretical and experimental studies on liquid DMSO,\textsuperscript{31-41} water/DMSO mixtures,\textsuperscript{42-47} DMSO/nonaqueous electrolyte solutions\textsuperscript{32, 48-51} and solutions of biomolecules in DMSO\textsuperscript{52-54} have been performed in recent years to understand the physical properties of DMSO solutions. Solutions of alkali-metal ions, mostly Li\textsuperscript{+}, in DMSO have also been investigated experimentally\textsuperscript{55-60} and theoretically,\textsuperscript{32, 61-69} as well as in water/DMSO mixtures\textsuperscript{70-73} and in other solvent combinations.\textsuperscript{74-76} One of the first reports on the utilization of \textsuperscript{7}Li NMR in the investigation of LiClO\textsubscript{4} in various solvents (including DMSO) was published by Maciel et al.\textsuperscript{77} In DMSO, no evidence for contact ion pairing was observed,\textsuperscript{73, 78} as might be expected, for instance, in THF (DN = 7.4).\textsuperscript{79} It was also shown that Li\textsuperscript{+} interacts preferentially with DMSO electrostatically through the oxygen donor of the S=O group.\textsuperscript{76}

The special interest in Li\textsuperscript{+} ions in DMSO and DMSO mixtures with other solvents originates from the use of Li\textsuperscript{+} ions in batteries with high energy densities.\textsuperscript{80-83} Such studies on the transport properties of electrolytes in aqueous and nonaqueous solvents are of interest in various technologies, such as high-energy-density batteries, photo-electrochemical cells, electrodeposition, wet electrolytic capacitors and in electro-organic synthesis.\textsuperscript{82} Electrochemical technologies search for electrolyte solutions with optimized properties for the special tasks which they must fulfill in devices and processes.\textsuperscript{83} A literature survey suggests that the use of mixed solvents involving high permittivity, low viscosity and wide liquid range is practicable for use in high-energy-density batteries, especially lithium batteries. The advantage of using mixed solvents over using their pure counterparts in lithium batteries is to be able to manipulate the suitable properties of these solvents for fulfilling the above conditions.
While many studies explored the behaviour of Li\(^+\) in DMSO and water/DMSO mixtures, to our knowledge, no attempts have been made to investigate the ligand-exchange mechanism of solvated Li\(^+\) in DMSO and water/DMSO mixtures. Herein, we extend our combined quantum-chemical and experimental investigations of the ligand-exchange mechanism around Li\(^{7+}\) and focus on DMSO and water/DMSO mixtures.

### 2.4. Experimental Section

#### 2.4.1. General Procedures

All transformations were carried out in an Ar or N\(_2\) atmosphere using standard Schlenk techniques, in an Ar atmosphere in a drybox, or under vacuum. Lithium perchlorate (Aldrich, battery grade) was vacuum-dried at 120 °C for 48 h and then stored under dry nitrogen. DMSO (Acros, extra dry, with molecular sieves, water < 50 ppm) was used as received. \(\gamma\)-Butyrolactone (Aldrich) was dried over anhydrous CaSO\(_4\), then fractionally distilled under vacuum and stored under nitrogen over Linde 3Å molecular sieves. Solutions of LiClO\(_4\) were prepared under dry nitrogen. For \(\gamma\)Li NMR studies, these solutions were sealed in Ar atmosphere in 5-mm NMR tubes.

#### 2.4.2. \(\gamma\)Li NMR Spectroscopy

Fourier-transform \(\gamma\)Li NMR spectra were recorded at 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 outer diameter 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 an Ar to a Wilmad screw-cup NMR tube equipped with a poly(tetrafluoroethylene) septum. All samples were prepared in the same fashion.
2.4.3. Quantum-Chemical Calculations

All structures were fully optimized using the B3LYP hybrid density functional\textsuperscript{84-86} and the LANL2DZp basis set, that is, with pseudo-potentials on sulfur and the valence basis set augmented with polarization functions,\textsuperscript{87-91} and characterized as minima or transition-state structures by computation of vibrational frequencies (for minima, all frequencies are positive, NImag = 0; for transition structures, exactly one imaginary frequency is present, NImag = 1). Structures were subsequently refined at B3LYP/6-311+G**,\textsuperscript{84-86, 92} that is, with diffuse functions on non-hydrogen atoms, in order to minimise the basis set superposition error (BSSE).\textsuperscript{93} Zero-point energies and contributions to enthalpy and entropy were computed for a temperature of 298 K at B3LYP/LANL2DZp or B3LYP/6-311+G**, as indicated. The influence of the bulk solvent was evaluated via single-point calculations using the CPCM (conductor-like polarizable continuum model)\textsuperscript{94, 95} formalism, that is, B3LYP(CPCM)/6-311+G**//B3LYP/6-311+G** and water as solvent. Structure optimizations at this level, probed for selected system, were found to yield essentially the same results. The approximation of solvent effects by the polarizable continuum model (PCM)\textsuperscript{96} or the isodensity molecular surface polarizable continuum model (IPCM)\textsuperscript{97} unfortunately failed for some systems, [see \textsuperscript{98, 99} but where successful, they agreed with CPCM results. The Gaussian 03 suite of programs was used throughout.\textsuperscript{100}

2.5. Results and Discussion

2.5.1. Coordination Number of Li\textsuperscript{+} in DMSO

To determine the coordination number of Li\textsuperscript{+} in DMSO, the cation should be dissolved in a solvent mixture that consists of a weakly and strongly coordinating component. The method is based on monitoring the resonance frequency of \textsuperscript{7}Li nucleus as a function of DMSO-to-metal ion molar ratio while keeping the metal ion concentration constant and varying the concentration of DMSO over a wide range. This kind of study might be hampered by limited solubilities of Li salts in solvent mixtures or limited miscibility of mixture
components. There are a few conditions that must be obeyed: 1) A weakly coordinating solvent must be available, which will dissolve all solution components. 2) A measurable parameter must exist which is a function of solvent composition. 3) The formation constant of the solvate must be sufficiently large that a limiting value of the parameter may be obtained. In this case, the parameter was the Li$^+$ NMR signal. Its position in the NMR spectrum depends on the solvation shell of the solvated ion. Typical alkali-metal salts are not appreciably soluble in truly non-coordinating solvents. Therefore, it was necessary to select a solvent with a weak interaction toward DMSO and the alkali-metal ions.$^{101}$

γ-Butyrolactone was found to represent a good compromise for the various requirements. Contrary to DMSO, it is a rather weak donor ($DN = 18.0$)$^{102}$ that appreciably dissolves alkali-metal salts, and its interaction with DMSO is much weaker than that between DMSO and a metal cation. The molar ratio data confirmed the “inertness” of the solvent and indicated that it is in fact sufficiently unreactive for the purpose of this investigation.

![Figure 2.1](image)

**Figure 2.1.** $^7$Li NMR chemical-shift variation as a function of the DMSO/LiClO$_4$ molar ratio in γ-butyrolactone solution.
2. DMSO and Water/DMSO Mixtures

Figure 2.1 shows the molar-ratio plot of the DMSO/LiClO₄ system in γ-butyrolactone solution, where the LiClO₄ concentration was kept constant at 0.05 M. A clear break can be observed at the DMSO/Li⁺ ratio of 4:1, indicating a solvation number of 4 for Li⁺ in DMSO.

2.5.2. Selective Solvation of Li⁺

Selective solvation of Li⁺ in H₂O/DMSO mixture was studied by Emons et al.,⁷³ using Raman spectroscopy. Their results suggest that Li⁺-ion coordination by DMSO is stronger than by water. On the other hand, the Gutmann donor number for water (33³⁰) is higher than for DMSO (29.8), which would suggest the opposite.

We performed ⁷Li NMR measurements keeping the concentration of LiClO₄ constant (0.1 M) and varying the composition of the mixture of H₂O/DMSO by increasing the percentage of H₂O from 0 to 100 % (molar ratio). For each sample, the ⁷Li NMR spectrum was recorded. The chemical shift varied gradually from 4.35 ppm (DMSO) to 5.07 ppm (water; see Figure 2.2), and the plot of chemical shift versus solvent composition (Figure 2.3) shows no clear inflection like that observed for the DMSO/γ-butyrolactone system in Figure 2.1. Thus, the composition of the first coordination sphere around Li⁺ in mixtures of H₂O and DMSO depends only on the ratio of these solvents. DMSO and water are equally strong ligands in the coordination of Li⁺.
2. DMSO and Water/DMSO Mixtures

**Figure 2.2.** $^7$Li NMR spectra of LiClO$_4$ in H$_2$O/DMSO for different mixture compositions.

**Figure 2.3.** Chemical-shift variation as a function of water content in LiClO$_4$ solutions of H$_2$O/DMSO mixtures.
Model calculations (B3LYP(CPCM)/6-311+G**//B3LYP/6-311+G**) corroborate these results (Table 2.1). The exchange reactions in the stepwise conversion of [Li(H2O)4]+ + 4 DMSO to [Li(DMSO)4]+ + 4 water are computed to be essentially thermoneutral. Only for the exchange of the last water molecule by DMSO is the computed reaction enthalpy somewhat larger (–3.4 kcal/mol).

### Table 2.1. Calculated energies for the stepwise conversion of [Li(H2O)4]+ to [Li(DMSO)4]+.[a]

<table>
<thead>
<tr>
<th></th>
<th>( \Delta E_{\text{DFT}} ) [b]</th>
<th>( \Delta H_{\text{CPCM}} ) [c]</th>
<th>( \Delta G_{\text{CPCM}} ) [c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Li(H2O)4]+ + 4 DMSO</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>[Li(DMSO)(H2O)3]+ + H2O + 3 DMSO</td>
<td>–13.3</td>
<td>–0.5</td>
</tr>
<tr>
<td>3</td>
<td>[Li(DMSO)2(H2O)2]+ + 2 H2O + 2 DMSO</td>
<td>–24.6</td>
<td>0.8</td>
</tr>
<tr>
<td>4</td>
<td>[Li(DMSO)3(H2O)]+ + 3 H2O + DMSO</td>
<td>–33.4</td>
<td>–0.8</td>
</tr>
<tr>
<td>5</td>
<td>[Li(DMSO)4]+ + 4 H2O</td>
<td>–42.6</td>
<td>–4.2</td>
</tr>
</tbody>
</table>

[a] Energies in kcal/mol relative to [Li(H2O)4]+ and 4 DMSO; [b] B3LYP/6-311+G**, including \( \Delta ZPE \) computed at B3LYP/6-311+G**; [c] B3LYP(CPCM)/6-311+G**//B3LYP/6-311+G** with thermodynamic contributions calculated at B3LYP/6-311+G**

The Gibbs free energy values might be interpreted as predicting the exchange reactions to be endergonic. However, due to inherent inaccuracies, the error interval of the computed entropy contributions is too large to draw any conclusions here. Note also the importance of including the effect of the bulk solvent: in the gas-phase calculations, all solvent-exchange steps are significantly exothermic.

Calculations at the B3LYP(IPCM)/6-311+G**//B3LYP/6-311+G** level, that is, employing the isodensity surface polarizable continuum model, were successful only for [Li(H2O)4]+ and [Li(DMSO)4]+ (Table 2.1, entries 1 and 5). However, the computed reaction enthalpy for the complete solvent exchange, –5.3 kcal/mol, agrees well with the CPCM result.
2.5.3. **Ligand Exchange on Solvated Li⁺**

Exchange of a solvent molecule between the first and the second coordination shell is the simplest reaction that can occur on a metal ion in solution. This reaction is of fundamental importance in understanding not only the reactivity of the metal ion in chemical and biological systems but also the interaction between the metal ion and the solvent molecule. The displacement of a solvent molecule from the first coordination shell presents an important step in complex-formation reactions of metal cations and in many redox processes. Mechanistically, associative (A), interchange (I) and dissociative (D) pathways are conceivable. Solvent exchange on Li⁺ in water is extremely fast, making it difficult to study directly. An exchange rate constant of approximately $10^9$ s⁻¹ at 25 °C was predicted on the basis of complex-formation data. As shown above, DMSO coordinates to Li⁺ with a similar strength as water. Its exchange process is also very fast and therefore impossible to be studied experimentally. All alkali-metal ions and the large alkaline-earth-metal ions are very labile due to the low surface charge density and the absence of ligand field stabilization effects.

2.5.4. **Computed Mechanisms of Solvent Exchange**

Experimental (*vide supra*) and previous theoretical studies agree with the present study that the first coordination shell around Li⁺ consists of four tightly bound DMSO molecules. The computed Li-O distance is 1.96 Å. An additional DMSO molecule does not coordinate to the lithium cation but instead is only weakly bound, mainly by electrostatic interactions. The Li···O distance is well over 5 Å (see Figure 2.4), and the computed gas-phase binding energy for the fifth DMSO molecule in [Li(DMSO)₄(DMSO)]⁺ is 7.6 kcal/mol. When the influence of the bulk solvent is taken into account, at B₃LYP(CPCM)/6-311+G**//B₃LYP/6-311+G**, this binding energy (computed for the gas-phase structure) vanishes. Optimization of the precursor complex at B₃LYP(CPCM)/6-311+G** resulted in only minimal changes in structure and energy.
In a previous study, we found a limiting associative (A) mechanism for water exchange around Li\(^{+}\). Mechanistic details are very similar for DMSO exchange. The reaction proceeds through a distorted trigonal-bipyramidal reactive intermediate \([\text{Li(DMSO)}_5]^+\) that is reached via a late transition state. The enthalpy profile (Figure 2.4, B3LYP(CPCM)/6-311+G**\(_2\)) thermodynamic contributions computed at B3LYP/LANL2DZp) is in line with the experimental observation (\textit{vide supra}) of a very fast exchange process: the five-coordinate intermediate is computed to be 7.9 kcal/mol less stable than \([\text{Li(DMSO)}_4]^+\) and free DMSO, while an overall activation barrier of only 8.4 kcal/mol is computed. Obviously, the intermediate will be extremely short-lived, since its barrier toward loss of DMSO is only 0.5 kcal/mol. Note that with the obvious exception of the binding energy for the fifth DMSO molecule in the precursor complex (\textit{vide supra}), the influence of the bulk solvent on the energy profile is minor.
2. DMSO and Water/DMSO Mixtures

One might argue that this energy difference is smaller than the accuracy of the computational method and thus meaningless. However, whereas the value of the (small) barrier may indeed vary, the shape of the potential-energy surface usually does not (see also ref. 7). In the present case, zero-point energy and thermodynamic corrections do not change the energetic order of the structures. Inclusion of entropy contributions (we believe these to be sufficiently accurate, in view of the similarity of the structures calculated for intermediate and transition states) even stabilises the intermediate: a free energy barrier of 1.8 kcal/mol is computed. We therefore consider the mechanistic conclusion of associative (A) exchange to be reliable.

We also investigated in detail the mechanism of the exchange of a water ligand by DMSO. The enthalpy profile, calculated at B3LYP(CPCM)/6-311+G** with thermodynamic contributions computed at B3LYP/6-311+G**, is shown in Figure 2.5. B3LYP/6-311+G** gas-phase energy values, corrected for ΔZPE at this level, are included for comparison.

**Figure 2.5.** Reaction profile for the water/DMSO exchange around [Li(H₂O)₄]⁺; enthalpy: B3LYP(CPCM)/6-311+G** including thermodynamic contributions at B3LYP/6-311+G**; gas-phase energy values: B3LYP/6-311+G** including ΔZPE, in parentheses. T.S. = transition state.
The reaction involves a precursor complex, in which the incoming DMSO molecule is weakly bound to two water ligands through hydrogen bonds. As in the case of water exchange\textsuperscript{7} and DMSO exchange (\textit{vide supra}), the gas-phase binding energy for this complex is exaggerated. Otherwise, the influence of the bulk solvent on the energy profile is minor.

The two H\textsubscript{2}O ligands with hydrogen bonds to the DMSO oxygen move to axial positions while DMSO approaches the lithium cation (Figure 2.5). In the distorted trigonal-bipyramidal transition structure, one hydrogen bond to the leaving water molecule remains. Note that the reaction proceeds with \textit{cis} stereochemistry. The activation barrier is 6.9 kcal/mol, relative to the precursor complex, or 3.3 kcal/mol relative to separated [Li(H\textsubscript{2}O)\textsubscript{4}]\textsuperscript{+} and DMSO. The computed normal mode vector for the imaginary frequency clearly corresponds to a ligand substitution: the Li–O\textsubscript{water} bond length increases upon shortening of the Li–O\textsubscript{DMSO} bond (2.29 Å; 0.4 Å longer than in the product). The Li–O\textsubscript{water} bond is elongated by only 0.16 Å in the transition structure. We conclude that the reaction will be very fast (cf. ref.\textsuperscript{105}) and proceeds through an associative interchange mechanism. No stable five-coordinate intermediate structure could be found, despite extensive searches.

The reaction proceeds to a product complex in which the leaving water molecule has hydrogen bonds to two water ligands and to DMSO; this arrangement is 3.6 kcal/mol less stable than the precursor complex. Breaking the bond to DMSO leads to a second, somewhat more stable complex, from which the water molecule is released.

\textbf{2.6. Conclusions}

It was confirmed both experimentally and theoretically that Li\textsuperscript{+} has a coordination number of four in pure DMSO and in water/DMSO mixtures. In the binary mixture of water and DMSO, both solvents coordinate equally strongly by the Li\textsuperscript{+} ion. Displacement of DMSO by water in the coordination sphere of solvated Li\textsuperscript{+} occurs gradually, indicating that the two compounds have similar donor strengths. In the solvent mixture consisting of DMSO and
2. DMSO and Water/DMSO Mixtures

\[\gamma\text{-butyrolactone, the latter component is weakly coordinating and can be considered as a diluent for DMSO and alkali-metal ions. Computational studies suggest that ligand exchange on } [\text{Li(DMSO)}_4]^+ \text{ follows a limiting associative mechanism, whereas displacement of coordinated water by DMSO seems to follow an associative interchange mechanism.}\]
2.7. References

2. DMSO and Water/DMSO Mixtures


2. DMSO and Water/DMSO Mixtures

2. DMSO and Water/DMSO Mixtures


2. **DMSO and Water/DMSO Mixtures**


3. Ligand Exchange Processes on Solvated Lithium Cations. Acetonitrile and Hydrogen Cyanide

3.1. General remark

The work presented in this chapter was conducted by several authors within a joint project and has been published as:


3.2. Abstract

Solutions of LiClO₄ 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(H₂O)₄]⁺. The solvent-exchange mechanism of [Li(L)₄]⁺ (L = CH₃CN and HCN) was studied 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.
3.3. Introduction

The ongoing discussion on sustainability in chemistry is partly focused on the role of solvents and especially on alternatives for common organic solvents. Such alternatives could be, for example, ionic liquids\textsuperscript{1-4} or supercritical carbon dioxide.\textsuperscript{5-8} 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\textsuperscript{9, 10} or in the investigation of complexation phenomena and complex-formation constants.\textsuperscript{11-25} 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\textsubscript{4} are highly soluble in hydrogen cyanide, most likely because of its high dielectric constant of 123 (at 15.6 °C).\textsuperscript{26-30} However, HCN serves as an excellent simplified model of CH\textsubscript{3}CN and thus can be used instead in quantum chemical studies of CH\textsubscript{3}CN.

The behaviour of pure acetonitrile and acetonitrile mixtures was studied experimentally\textsuperscript{31, 32} and computationally.\textsuperscript{31, 33} Since an ion in solution strongly disturbs the local solvent structure, a detailed knowledge of the environment is an essential prerequisite for understanding reactions in the neighbourhood of the ion. Several studies investigated solvated Li\textsuperscript{+} ions in acetonitrile both experimentally with various spectroscopic techniques\textsuperscript{34-44} and computationally with different classical molecular dynamics (MD) methods\textsuperscript{45-52} and Monte Carlo simulations on solvated alkali and halide ions in CH\textsubscript{3}CN.\textsuperscript{53} Over the past decade, DFT and ab initio calculations on [Li(CH\textsubscript{3}CN)\textsubscript{n}]\textsuperscript{+} and related clusters were also performed by different groups.\textsuperscript{37, 54-57}

There has been a special interest in the properties of Li salts, such as conductivity,\textsuperscript{58-64} transport ability,\textsuperscript{65-67} viscosity,\textsuperscript{68} and osmotic behaviour,\textsuperscript{69} in
solvents and solvent mixtures because of the use of Li$^+$ ions in batteries of high energy density.\textsuperscript{70} Such studies are not restricted to liquid systems. Li$^+$ mobility in potential solid electrolytes was also investigated intensively both experimentally and theoretically.\textsuperscript{71-73}

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,\textsuperscript{74, 75} quantum chemical calculations focus on one molecule and a small number of solvent molecules, for example, the first solvent shell.\textsuperscript{76-82} 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 HCN, as well as in CH$_3$CN/H$_2$O and HCN/H$_2$O 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.

\textbf{3.4. Experimental Section}

\textbf{3.4.1. General Procedures}

All transformations were carried out under an 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.\textsuperscript{83} Solutions of LiClO$_4$ were prepared under dry nitrogen. For $^7$Li NMR spectroscopic studies, these solutions were sealed under an Ar atmosphere in 5-mm NMR tubes.
3.4.2. \( ^7\text{Li} \) NMR Spectroscopy

Fourier transform \( ^7\text{Li} \) 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 cup NMR tube equipped with a poly(tetrafluoroethylene) septum. All samples were prepared in the same way.

3.4.3. Quantum-Chemical Calculations

All structures were fully optimized at the B3LYP/6-311+G**\(^84-87\) 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;\(^88\) the influence of the bulk solvent was probed by using the IPCM\(^89\) and CPCM\(^90,91\) 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**.\(^92\) The Gaussian 03 suite of programs was used throughout.\(^93\)

3.5. Results and Discussion

3.5.1. 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),\(^94\) and on the basis of IR spectroscopic intensities measured for the acetonitrile CN stretching vibrations.\(^95,96\) Even compounds with mixed
coordination of a counterion and acetonitrile were reported to be four-coordinate, namely \([\text{Li(CH}_3\text{CN})_3\text{Br}]\) formed from 0.58 M LiBr in CH\(_3\)CN.\(^{42}\) Extensive concentration-dependent ion-pairing was also found for weak coordinating counterions, such as in LiBF\(_4\)\(^{37}\) and LiClO\(_4\)\(^{95}\) by studying the CN vibration.\(^{97}\) These findings for the coordination number are in good agreement with published X-ray structures.\(^{98-100}\)

However, Sajeevkumar and Singh found the average coordination number to be 4.7,\(^{101}\) whereas Megyes et al. found up to six acetonitrile molecules surrounding the Li\(^+\) ion in the gas phase by means of mass spectrometry.\(^{102}\) Therefore, we reinvestigated the maximum coordination number of \([\text{Li(CH}_3\text{CN})_n]^{+}\) both experimentally and computationally, and purely quantum chemically for \([\text{Li(NCH})_n]^{+}\).

In order to determine the coordination number of Li\(^+\) by using NMR techniques, the concentration of LiClO\(_4\) was kept constant and the CH\(_3\)CN 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 mole 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\(_3\)CN and the alkali metal ion.\(^{103}\)

Nitromethane (Gutmann donor number \(DN = 2.7\))\(^{104}\) represents a good compromise for the various requirements. It appreciably dissolves alkali metal
3. Acetonitrile and Hydrogen Cyanide

salts and its interaction with Li⁺ is much weaker than that between CH₃CN (Gutmann donor number $DN = 14.1$) and a metal cation. The mole 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 3.1 and Figure 3.2 illustrate the results obtained from the ⁷Li NMR spectroscopic study. Figure 3.2 shows a plot of the chemical shift as a function of the mole ratio of the CH₃CN/LiClO₄ system; the LiClO₄ concentration was kept at 0.05 M in nitromethane. A clear break can be observed at a [CH₃CN]/[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 3.1.** ⁷Li NMR spectra recorded as a function of CH₃CN/LiClO₄ mole ratio (0.05 M LiClO₄ in the CH₃CN/nitromethane mixture) at 25 °C.
3.5.2. **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.\(^{105}\)

We performed the measurements by keeping the concentration of LiClO₄ constant (0.1 M) and by changing the composition of the H₂O/CH₃CN mixtures. The concentration of H₂O (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 3.2.** ⁷Li NMR shift measured for 0.05 M LiClO₄ in CH₃CN/nitromethane solvent mixtures.
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% H₂O). The chemical shift value then increased slightly and remained almost constant when the amount of water was changed from 10 to 100% (see Figures 3.3 and 3.4). 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.

**Figure 3.3.** ³⁷Li NMR spectra of 0.1 M LiClO₄ in H₂O/CH₃CN mixtures.
3.5.3. **Ligand Exchange on Solvated Li**

It was not possible to follow the exchange process for CH$_3$CN 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$_3$CN 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.

3.5.4. **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$_3$CN-solvated lithium cation. As mentioned before, HCN was employed as a simplified working model to perform quantum chemical calculations on CH$_3$CN. Our calculations corroborated the results of the experimental study in solution (*vide supra*)$^{35}$ and in the solid state,$^{100}$ which
showed that the first coordination sphere around Li$^+$ consists of four tightly bound CH$_3$CN 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 3.5).

**Figure 3.5.** Energy profile (RB3LYP/6-311+G**) for the exchange of HCN on [Li(NCH)$_4$]$^+$.

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 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 changes in the computed energies, except in those for the intermediate ([Li(L)₄(L)]⁺) (see Table 3.1). 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.¹⁰⁶,¹⁰⁷ 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 3.1 and Figure 3.5). 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(NCCH₃)₄]⁺ shows the same topology; only the energy differences are somewhat smaller. 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(NCCH₃)₄(NCCH₃)]⁺ because of the rotation of methyl groups, and IPCM calculations show the well-documented problems in reaching an energy convergence.³,¹⁰⁸
### 3. Acetonitrile and Hydrogen Cyanide

Table 3.1. Calculated relative energies (in kcal/mol) for the exchange of L at [Li(L)$_4$]$^+$ (L: HCN, CH$_3$CN).

<table>
<thead>
<tr>
<th>L: HCN</th>
<th>[Li(L)$_4$]$^+$ + L</th>
<th>[Li(L)$_4$:$^\cdots$(L)]$^+$ ts</th>
<th>[Li(L)$_4$(L)]$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP</td>
<td>8.9</td>
<td>0.0</td>
<td>5.5</td>
</tr>
<tr>
<td>MP2(full)</td>
<td>9.5</td>
<td>0.0</td>
<td>3.2</td>
</tr>
<tr>
<td>IPCM</td>
<td>-2.8</td>
<td>0.0</td>
<td>-2.6</td>
</tr>
<tr>
<td>CPCM</td>
<td>-0.4</td>
<td>0.0</td>
<td>1.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>L: H$_3$CCN</th>
<th>B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6.1</td>
</tr>
</tbody>
</table>

[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**; IPCM: B3LYP/(CPCM: water)/6-311+G**//B3LYP/6-311+G**

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 Li$^+$, 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$_2$O exchange process exemplarily for [Li(NCH)$_4$]$^+$ to [Li(NCH)$_3$(H$_2$O)]$^+$ (Table 3.2). 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
Acetonitrile and Hydrogen Cyanide

A water-coordinated Li⁺ complex. This can be reproduced for HCN as model by quantum chemical calculations (RB3LYP/6-311+G**).

### Table 3.2
Calculated energies for the subsequent reactions of [Li(NCH)₄]⁺ with water.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Gas phase</th>
<th>IPCM: acetonitrile</th>
<th>IPCM: water</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Li(NCH)₄]⁺ + H₂O → [Li(H₂O)(H₂O)₃]⁺ + NCH</td>
<td>-0.5</td>
<td>+1.7</td>
<td>+1.6</td>
</tr>
<tr>
<td>[Li(H₂O)(NCH)₃]⁺ + H₂O → [Li(H₂O)₂(NCH)₂]⁺ + NCH</td>
<td>-0.5</td>
<td>-1.4</td>
<td>-1.6</td>
</tr>
<tr>
<td>[Li(H₂O)₂(NCH)₂]⁺ + H₂O → [Li(H₂O)₃(NCH)]⁺ + NCH</td>
<td>-0.3</td>
<td>-3.6</td>
<td>-3.9</td>
</tr>
<tr>
<td>[Li(H₂O)₃(NCH)]⁺ + H₂O → [Li(H₂O)₄]⁺ + NCH</td>
<td>+0.1</td>
<td>-0.9</td>
<td>-1.2</td>
</tr>
<tr>
<td>∑</td>
<td>-1.3</td>
<td>-4.2</td>
<td>-5.1</td>
</tr>
</tbody>
</table>

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.

**Figure 3.6.** Energy profile (RB3LYP/6-311+G**) for the HCN/water exchange around [Li(NCH)₄]⁺.
3. Acetonitrile and Hydrogen Cyanide

We investigated the mechanism for the first reaction step in detail (see Figure 3.6). As shown before, 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 H₂O molecule in [Li(NCH)₄…(OH₂)]⁺ 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 H₂O in the axial position. 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 position and the H₂O molecule together with the two remaining HCN molecules in the equatorial positions. The bonds for the axial molecules are 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 will form a hydrogen bond with the nearest hydrogen atom, one would expect the product [Li(NCH)₃(H₂O)…(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 3.3).
### Table 3.3.
Calculated relative energies for the exchange of H$_2$O/NCH at [Li(NCH)$_4$]$^+$ (L = HCN; W = H$_2$O).\textsuperscript{[a]}

<table>
<thead>
<tr>
<th>L:HCN; W: H$_2$O</th>
<th>[Li(L)$_4$–W]$^+$</th>
<th>ts</th>
<th>[Li(L)$_2$(W)(L)$_2$]$^+$</th>
<th>ts</th>
<th>[Li(L)$_3$(W)--L]$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B$_3$LYP</td>
<td>0.7</td>
<td>7.8</td>
<td>4.1</td>
<td>4.2</td>
<td>0.0</td>
</tr>
<tr>
<td>MP2(full)</td>
<td>0.9</td>
<td>6.1</td>
<td>0.6</td>
<td>1.2</td>
<td>0.0</td>
</tr>
<tr>
<td>IPCM</td>
<td>0.1</td>
<td>2.8</td>
<td>1.3</td>
<td>1.8</td>
<td>0.0</td>
</tr>
<tr>
<td>CPCM</td>
<td>0.1</td>
<td>5.6</td>
<td>1.0</td>
<td>1.5</td>
<td>0.0</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} B$_3$LYP: B$_3$LYP/6-311+G**// B$_3$LYP/6-311+G**; MP2(full): MP2(full)/6-311+G**//B$_3$LYP/6-311+G**; IPCM: B$_3$LYP/(IPCM: Acetonitrile)/6-311+G**//B$_3$LYP/6-311+G**

Whereas MP2(full)/6-311+G**//B$_3$LYP/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.

### 3.6. 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.
3.7. References

3. Acetonitrile and Hydrogen Cyanide


3. Acetonitrile and Hydrogen Cyanide

3. Acetonitrile and Hydrogen Cyanide


3. Acetonitrile and Hydrogen Cyanide

92. In the CPCM formalism some molecules failed while using symmetry in the molecular cavity generation. This problem was solved successfully by the keyword “nosymm”.

4. Ligand Exchange Processes on Solvated Lithium Cations. Complexation by Cryptands in Acetone as Solvent

4.1. General remark

The work presented in this chapter was conducted by several authors within a joint project and has been published as:


4.2. Abstract

Kinetic studies on Li⁺ exchange between the cryptands C222 and C221 and acetone as solvent were performed as a function of ligand-to-metal ratio, temperature and pressure using ⁷Li NMR spectroscopy. Temperature and pressure dependence measurements were performed in the presence of an excess of Li⁺. The rate and activation parameters for the exchange process are: C222: \( k_{298} = (1.7 \pm 0.5) \times 10^3 \text{ s}^{-1}, \Delta H^\# = 24 \pm 1 \text{ kJ mol}^{-1} \text{ and } \Delta S^\# = -105 \pm 4 \text{ J K}^{-1} \text{ mol}^{-1}; \) C221: \( k_{298} = 2.24 \pm 0.09 \text{ s}^{-1}, \Delta H^\# = 29 \pm 2 \text{ kJ mol}^{-1} \text{ and } \Delta S^\# = -141 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1}. \) The influence of pressure on the exchange rate is insignificant for both ligands, such that the activation volume is around zero within the experimental error limits. The reported activation parameters suggest that the exchange of Li⁺ between solvated and chelated ions follows an associative interchange mechanism.
4. Complexation by Cryptands in Acetone as Solvent

4.3. Introduction

Following the work of Pedersen on two-dimensional crowns, Lehn and coworkers developed in the late 1960s a range of three-dimensional, polycyclic ligand systems which they named cryptands (Greek: cryptos = cave). Until today this class of compounds has been intensively explored and extended in different directions in terms of cavity size, donor atoms, and metalla-topomers. Because cryptands readily form complexes with a wide range of metal ions and NH$_4^+$, provided the ion involved is not too large to be contained in the macrocyclic cavity, they find their application in various areas like catalysis, medicine, biomimetic research, and as receptors and electrides. Studies on the complexes (cryptates) formed between alkali-metal ions and cryptands, have revealed a substantial understanding of the effects of metal-ion size and cryptand-cavity size on the structure, stability and lability of cryptates, and the mechanism of the cryptate complex-formation processes. Such selective complexation has led to many biological and chemical studies.

Kinetic studies on macrocyclic complex-formation reactions with alkali cations not only result in important information on the rates and mechanisms of complex-formation reactions, but also lead to a better understanding of the high selectivity of these ligands toward different cations. The broad impact of such studies spans from the theory of complexation to cation transport through membranes, and makes the ability to control cation selectivity via tactical structural changes in the complexing agent of prime importance. Polyoxo macrobicyclic diamines, represented by the structure in Figure 4.1, are able to form metal-ion complexes in which the metal ion is located in the cavity of the macromolecule and two nitrogen donors along with the oxygen donors participate in binding the metal cation. All complexes have a 1:1 stoichiometry with the metal ion positioned at the center of the ligand cavity.
In case of crown ethers and cryptands in non-aqueous solutions, the rates of complex-formation \((k_i)\) with alkali-metal cations are in general diffusion-controlled and, consequently, the complexation selectivities are governed by the decomplexation rates \((k_d)\).\(^{26}\) These reactions have received significant attention, initially from Lehn and co-workers and more recently from Popov et al.\(^{27-29}\) and Lincoln et al.\(^{30-37}\) Many examples have been included in a series of review articles.\(^{38-41}\) It has been reported that ligand structure and solvent properties have considerable effects on the reaction rates, activation parameters, and exchange mechanism of cations between the solvated and complexed sites. We have now extended our earlier studies\(^{42}\) on Li\(^+\) exchange reactions to acetone as solvent.

Non-aqueous solvents and their mixtures combined with Li\(^+\) are often used in secondary lithium batteries.\(^{43, 44}\) Li\(^+\) in acetone is also known to catalyze Diels-Alder-reactions\(^{45}\) and the ene reaction.\(^{46}\) The behavior of Li\(^+\)-ions in different solvents is therefore an important research area.\(^{47-57}\) A variety of studies on solutions of Li\(^+\) in acetone have been mainly studied experimentally\(^{52, 55, 58-63}\) and some theoretically,\(^{64, 65}\) as well as for solvent/acetone combinations\(^{53}\) or chelator/acetone combinations.\(^{53, 66}\) In this contribution, we focus on acetone as a solvent and the competition between solvated and endohedral complexed Li\(^+\), report kinetic parameters for the exchange of Li\(^+\) between solvated and complexed states in acetone under ambient and elevated pressure conditions, and discuss the mechanistic implications.
4.4. Experimental Section

4.4.1. General Procedures

The preparation of test solutions was carried out under an Ar or N₂ using standard Schlenk techniques, under an Ar in a glove box, or under vacuum. Lithium perchlorate (Aldrich, battery grade) was vacuum-dried at 120 °C for 48 h and then stored under dry nitrogen. The cryptands C222 (purchased from Fluka), C221 and C211 (purchased from Aldrich) were dried under vacuum for 48 h and stored under dry nitrogen. Acetone (Acros, extra dry, water < 50 ppm) was used as received. Solutions of LiClO₄, C222, C221 and C211 in acetone were prepared under dry nitrogen. For the ⁷Li NMR measurements the solutions were sealed in 5-mm NMR tubes under Ar. In order to study the kinetics of the exchange of Li⁺ between C222 and C221 and acetone as solvent, three solutions of different concentration ratio were prepared for each system. The concentration of lithium perchlorate in each solution was kept constant at 0.04 M, whereas the concentration of ligand was varied between 0.01 M and 0.032 M. In this way the measurements were always performed in the presence of an excess of Li⁺.

4.4.2. ⁷Li NMR Spectroscopy

Variable-temperature and variable-pressure Fourier transform ⁷Li 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 tubes (5 mm) were used with a 1-mm o.d. melting point capillary inserted coaxially in the spinning tube and filled with an external reference solution (1 M LiClO₄ in acetonitrile). The temperature dependence measurements were performed over a wide as possible temperature range for each system. We did not use a temperature calibration by insertion of a capillary filled with methanol (low temperature calibration) or ethylene glycol (high temperature calibration) into the sample tube, as the corresponding signals of these solvents would disturb the NMR spectra in the region of interest. In such a case a temperature-calibrated NMR probe has to be used in
4. Complexation by Cryptands in Acetone as Solvent

order to determine the temperature of the sample accurately. Methanol was used for the low-temperature calibration of the NMR probe, whereas ethylene glycol was used for high-temperature calibration. The actual sample temperature can be calculated from the chemical shift differences. If there is any difference between the sample temperature and the temperature detected by the thermocouple of the probe, the probe can be calibrated by using standard Bruker Topspin software.

A homemade high-pressure probe described in the literature was used for the variable-pressure experiments which were conducted at a selected temperature and at ambient, 30, 60, 75, 90, 120 and 150 MPa pressure. A standard 5-mm NMR tube cut to a length of 45 mm was used for the sample solution. The high-pressure NMR tube was sealed with a MACOR plug and an O-ring made of VITON. The plug and O-ring were shown to be stable in the employed solvent. The pressure was transmitted by the movable MACOR piston to the sample, and the temperature of the sample was controlled with a Pt-100 resistor. The probe itself was externally heated with a thermostatted circulating fluid that was pumped through a double helix that was cut into the outer surface of the autoclave. Because the sample is embedded in the high-pressure transmitting fluid that serves as a thermostating bath, a reliable temperature setting is guaranteed.

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 test samples were prepared in the same way.

4.4.3. Programs

The line widths of the NMR signals were obtained by fitting Lorentzian functions to the experimental spectra using the NMRICMA 2.7 program for Matlab. The adjustable parameters were the resonance frequency, intensity, line width and baseline. Complete line-shape analysis based on the Kubo-Sack formalism using modified Bloch equations was also performed with NMRICMA 2.7 to extract rate constants from experimental spectra. The temperature and pressure dependent 7Li line widths and chemical shifts
employed in the line shape analysis were extrapolated from low temperatures where no exchange-induced modification occurred.

**4.4.4. Quantum-Chemical Calculations**

All structures were optimized with the B3LYP\textsuperscript{71-73} and the basis set D95Vp\textsuperscript{74,75} or with 6-311+G** with no constraints other than symmetry, and confirmed to be minima by computation of vibrational frequencies. Relative energies were corrected for zero point vibrational energy differences. The D95V basis set, augmented with polarization functions (D95Vp), was used.\textsuperscript{76} If not otherwise mentioned, calculations were done without a solvent model. The influence of bulk solvent was probed using the CPCM formalism and water as solvent, \textit{i.e.}, B3LYP(CPCM)/D95Vp//B3LYP/D95Vp. The Gaussian 03 suite of programs was used throughout.\textsuperscript{77}

**4.5. Results and Discussion**

**4.5.1. Spectroscopic and Kinetic Observations**

In preliminary experiments we investigated the Li\textsuperscript{+} exchange in different solvents. In water and methanol the exchange process was too fast to be studied by \textsuperscript{7}Li NMR (only a single signal was observed). The process became slower in acetonitrile, and in acetone two completely separated signals were observed at low temperature. We, therefore, investigated Li\textsuperscript{+} exchange between the selected cryptands and acetone as solvent. A similar system was also investigated before by Popov et al..\textsuperscript{28} Although they reported a significantly negative value for the activation entropy, they suggested the operation of a dissociative exchange mechanism. We realized that it would be worth to perform a reinvestigation of this system in acetone in order to clarify this apparent discrepancy, in particular by means of high pressure \textsuperscript{7}Li NMR spectroscopy.

Initially, a series of \textsuperscript{7}Li NMR measurements for the Li\textsuperscript{+}-cryptand system in acetone were performed. For each of the cryptands C222, C221 and C211, molar ratio dependent measurements were performed by variation of both the
cryptand/Li⁺ and Li⁺/cryptand molar ratios. The results enabled us to observe the distribution of particular species on variation of the concentration ratio. Basically, two signals of varying intensity were observed in the ⁷Li NMR spectra that refer to solvated Li⁺ and Li⁺ bound inside the cryptand cavity. In case of the smallest chelate C211, however, an additional signal appeared which can be ascribed to Li⁺ bound outside the cryptand and being partially solvated. In the case of Li(C211)⁺, the complex is very stable and almost no exchange takes place. A detailed study of the observed rate constant, \( k_{\text{obs}} \), for the exchange of Li⁺ as a function of temperature and pressure was therefore undertaken only for C221 and C222. The lithium exchange reaction between cryptand and acetone was studied for three solutions with different ligand-to-metal ratios in the presence of an excess of Li⁺.

Three signals can be observed in Figure 4.2; viz. one coming from the reference (\( \delta = 5.8 \) ppm) and the other two from the exchanging sites (\( \delta = 9.0 \) ppm for solvated Li⁺ and 6.6 ppm for complexed Li⁺). At low temperature the signals are sharp and completely separated due to very slow or no exchange. Because the formation constant for Li(C221)⁺ is very high,²⁴ the concentration of bound lithium equals the amount of cryptand added. At ca. 283 K, the signals start to broaden and the exchange process takes place. The linear temperature dependence for the temperature range in which exchange takes place can be seen in Figure 4.5. In the case of C222 (Figure 4.3), the exchange process is faster due to the larger cavity of the cryptand. The signals that refer to solvated and complexed Li cation (8.7 and 6.8 ppm, respectively at 223 K) coalescence at ca. 263 K and at high temperature (>313 K) only one sharp signal at 7.7 ppm was observed as a consequence of a very fast exchange process. An accurate temperature dependence for C222 over a large temperature range can be observed in Figure 4.6.
4. Complexation by Cryptands in Acetone as Solvent

**Figure 4.2.** $^7$Li NMR spectra recorded as a function of temperature for the mole ratio $C_{221}/LiClO_4 = 0.5$.

**Figure 4.3.** $^7$Li NMR spectra recorded as a function of temperature for the mole ratio $C_{222}/LiClO_4 = 0.5$.

The rate of the exchange reaction increased not only with increasing cavity size of the cryptand but also with increasing concentration of the chelate, as
can be recognized from the shape of the signals at 223 K in Figure 4.4 and from the values of $k_{\text{obs}}$ in Table 4.1 (see Figure 4.5 and Figure 4.6).

**Figure 4.4.** $^7$Li NMR spectra of C222 and LiClO$_4$ in acetone. Temperature dependence for the sample ratios C222/LiClO$_4$ = 0.25, 0.5 and 0.75, respectively.

**Figure 4.5.** Eyring plots for $k_{\text{obs}}$ as a function of temperature for C221 in the temperature range in which exchange was observed for the concentration ratios C221/LiClO$_4$ = 0.5, 0.65 and 0.8, respectively.

**Figure 4.6.** Eyring plots for $k_{\text{obs}}$ as a function of temperature for C222 for the concentration ratios C222/LiClO$_4$ = 0.25, 0.5 and 0.75, respectively.
4. Complexation by Cryptands in Acetone as Solvent

### Table 4.1.
Values of the observed rate constants ($k_{\text{obs}}$) and activation parameters calculated from the line-shape analysis for the exchange of Li$^+$ between solvated and chelated sites at 25 °C.

<table>
<thead>
<tr>
<th>Molar ratio [L]:[Li$^+$]</th>
<th>$k_{\text{obs}}$ at 298 K, s$^{-1}$</th>
<th>$\Delta H^\circ$, kJ mol$^{-1}$</th>
<th>$\Delta S^\circ$, J K$^{-1}$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C221</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>2.10 ± 0.04</td>
<td>41 ± 3</td>
<td>-102 ± 12</td>
</tr>
<tr>
<td>0.65</td>
<td>4.5 ± 0.1</td>
<td>37 ± 1</td>
<td>-109 ± 3</td>
</tr>
<tr>
<td>0.8</td>
<td>19.4 ± 0.8</td>
<td>31 ± 1</td>
<td>-116 ± 4</td>
</tr>
<tr>
<td>C222</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>1001 ± 20</td>
<td>33.3 ± 0.5</td>
<td>-76 ± 1</td>
</tr>
<tr>
<td>0.5</td>
<td>3263 ± 98</td>
<td>34.1 ± 0.4</td>
<td>-64 ± 1</td>
</tr>
<tr>
<td>0.75</td>
<td>6346 ± 254</td>
<td>29 ± 1</td>
<td>-75 ± 2</td>
</tr>
</tbody>
</table>

4.5.2. **Suggested Exchange Mechanism**

Two mechanisms should be considered for the decomplexation processes of cryptand-alkali-metal complexes: unimolecular (dissociative) and bimolecular (associative) cation exchange. The solvent plays a major role in the unimolecular mechanism and this mechanism is therefore favored in strong donor solvents.40

Lincoln et al.30-37 investigated many similar systems where the Li$^+$ cation was exchanged between different cryptands or crown ethers and common solvents. In case of crown ethers and cryptands in non-aqueous solutions, the rates of formation ($k_c$) for their interaction with alkali-metal cations are generally diffusion controlled and, consequently, the complexation selectivities are governed by the decomplexation rates ($k_d$). They proposed the operation of a monomolecular mechanism for the decomplexation of Li$^+$ from the cryptand, notwithstanding the fact that decomplexation is characterized by very negative activation entropies.
According to Popov et al.,28 there are two possible mechanisms that need to be considered for the exchange of Li⁺ cation between the solvated and the complexed sites, viz. bimolecular (associative) (I) and unimolecular (dissociative) (back reaction in II) cation exchange processes, where S presents solvent and L the employed chelate.28, 78 (In this description we have added the terms ‘associative’ and ‘dissociative’ because this is implied by the mechanistic interpretation offered by the authors).

\[ *\text{Li}(S)^+ + \text{Li}(L)^+ \xrightleftharpoons[k_{-1}]{k_1} \text{Li}(S)^+ + *\text{Li}(L)^+ \]  
(I)

\[ \text{Li}(S)^+ + L \xrightleftharpoons[k_{-2}]{k_2} \text{Li}(L)^+ + S \]  
(II)

At equilibrium

\[ k_1[*\text{Li}(S)][\text{Li}(L)] = k_{-1}[*\text{Li}(L)][\text{Li}(S)] \]

\[ k_2[\text{Li}(S)][L] = k_{-2}[\text{Li}(L)][S] \]

Therefore see Equation (4.1) and Equation (4.2)

\[-\frac{d}{dt}[\text{Li}(S)] = k_{\text{obs}}[\text{Li}(S)] = k_1[\text{Li}(S)][\text{Li}(L)] + k_{-2}[\text{Li}(L)][S] \]  
(4.1)

and

\[ k_{\text{obs}} = k_1[\text{Li}(L)] + \frac{k_{-2}[\text{Li}(L)][S]}{[\text{Li}(S)]} \]  
(4.2)

An alternative form of Equation (4.2) is Equation (4.3), which was used to fit the data in Figure 4.7 and Figure 4.9.

\[ \frac{k_{\text{obs}}}{[\text{Li}(L)]} = k_1 + k_{-2} \cdot \frac{1}{[\text{Li}(S)]} \]  
(4.3)
Plots of $k_{obs}/[\text{Li(L)}]$ vs. $1/[\text{Li(S)}]$ were found to be linear with varying slopes ($k_{-2}' = k_{-2}[S]$) and intercepts ($k_1$) (see Figure 4.7 and Figure 4.9). The plots indicate that both pathways compete with each other and the competition is controlled by temperature and the nature of the cryptand. In the case of C222 (Figure 4.7), the plots at low temperature exhibit no meaning intercept, whereas the plots at high temperature exhibit very large intercepts. Thus the contribution from $k_1$ increases significantly with temperature. In the case of C221 (Figure 4.9), all the plots exhibit almost no intercept, such that the exchange process is mainly controlled by $k_{-2}$. The corresponding Eyring plots are shown in Figure 4.8 and Figure 4.10, respectively, and the thermal activation parameters are summarized in Table 4.2.

Figure 4.7. Plots of $k_{obs}/[\text{Li(L)}]$ vs. $1/[\text{Li(S)}]$ for C222 as a function of temperature.
4. Complexation by Cryptands in Acetone as Solvent

Figure 4.8. Eyring plots for $k_1$ and $k_{-2}$ as a function of temperature for C222.

Figure 4.9. Plots of $k_{obs}/[\text{Li(L)}]$ vs. $1/[\text{Li(S)}]$ for C221 as a function of temperature.
Figure 4.10. Eyring plot for $k_2$ as a function of temperature for C221.

Table 4.2. Thermal activation parameters obtained from the values of $k_1$ and $k_2$ as a function of temperature.

<table>
<thead>
<tr>
<th>Chelate</th>
<th>$k_1^{298}$, M$^{-1}$ s$^{-1}$</th>
<th>$k_2^{298}$, s$^{-1}$</th>
<th>$\Delta H^s$, kJ mol$^{-1}$</th>
<th>$\Delta S^s$, J K$^{-1}$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C221</td>
<td>2.24 ± 0.09</td>
<td>29 ± 2</td>
<td>-141 ± 5</td>
<td></td>
</tr>
<tr>
<td>C222</td>
<td>(1.7 ± 0.5) x 10$^3$</td>
<td>24 ± 1</td>
<td>-105 ± 4</td>
<td></td>
</tr>
<tr>
<td>C222</td>
<td>(6 ± 3) x 10$^4$</td>
<td>54 ± 4</td>
<td>+29 ± 15</td>
<td></td>
</tr>
</tbody>
</table>

The activation parameters derived from the temperature dependence of $k_1$ are rather inaccurate due to the large error limits of the intercepts and the reported activation entropy has no mechanistic meaning. On the basis of the values of $k_2$ and the significantly negative activation entropies obtained for this pathway, the activation parameters support an associative type of exchange process. $k_2$ for C222 is almost three orders of magnitude larger than for C221. Furthermore, the activation parameters are very similar to those obtained directly from the values of $k_{obs}$ as a function of temperature. This
would be in a good agreement with that postulated by Lincoln, who assumed that only the decomplexation process contributes to the observed reaction under the given experimental conditions. The negative activation entropies found for the decomplexation reactions of both C221 and C222 strongly suggest that attack of the solvent on the complexed Li⁺ must play an important role in the decomplexation process, i.e. decomplexation follows an associative mechanism (see theoretical calculations).

The reported activation parameters are within the range of those reported by Popov et al. for closely related systems. However, it should be pointed out that they used a different rate law than the one proposed by Shchori et al. and the one used in the present study, which complicates a direct comparison of the reported activation parameters. Nevertheless, although they proposed another mechanism, the values of the activation parameters obtained from their study are very similar to ours, as shown in Table 4.3 below.

### Table 4.3. Comparison of activation parameters.

<table>
<thead>
<tr>
<th></th>
<th>( k_b ), s⁻¹</th>
<th>( \Delta H^\circ ), kJ mol⁻¹</th>
<th>( \Delta S^\circ ), J K⁻¹ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Popov et al.²⁸</td>
<td>794 ± 42</td>
<td>20 ± 1</td>
<td>-121 ± 3</td>
</tr>
<tr>
<td>This work</td>
<td>1724 ± 484</td>
<td>24 ± 1</td>
<td>-105 ± 4</td>
</tr>
</tbody>
</table>

It is reasonable to expect that solvents such as acetonitrile, acetone and γ-butyrolactone, due to their similar properties as expected from their rather similar Gutmann donor numbers (\( DN = 14.1, 17.0 \) and 18.0, respectively) should coordinate to Li⁺ in a similar way and should have a similar influence on the exchange mechanism. This observation corresponds to that reported by Shamsipur et al. for the exchange of Li⁺ between C221 and acetonitrile/nitromethane mixtures. In all solvent mixtures used, Li⁺ exchange was found to occur through an associative mechanism, as expected for weakly donor solvents (\( DN = 14.1 \) and 2.7 for acetonitrile and nitromethane, respectively).
4.5.3. **High Pressure $^7$Li NMR Measurements**

Additional mechanistic information on the intimate nature of the exchange mechanism can in principle be obtained from the effect of pressure on the Li$^+$ exchange process.$^{82-85}$ A systematic pressure dependence study was performed to determine the volume of activation for the Li$^+$ exchange process for both chelates. Pressure-dependent NMR spectra were recorded for each sample over the pressure range of 0.1 to 150 MPa at 313.2 K. The higher temperature had to be chosen, since in case of C221 the exchange process hardly occurs at room temperature, whereas in case of C222 the signals are broad at room temperature due to coalescence and it was difficult to observe line broadening that resulted from increasing pressure. There are two signals to be seen in Figure 4.11: one for the solvated Li at 8.8 ppm and the one for Li complexed by C221 at 6.5 ppm. It can be observed that there is a very small difference in the shape of the NMR spectra recorded at various pressures. The same effect was observed for the second ligand, C222 (Figure 4.12), where only one signal appears due to the fast exchange. Its shape almost does not change with the varying pressure for any of the three samples. The rate constants calculated for each pressure were very similar within the experimental error limits and resulted in a practically zero value for $\Delta V^\#_{\text{obs}}$ for both ligands, which points to a concerted interchange type of exchange mechanism.$^{86}$ In terms of an interchange mechanism, bond formation and bond cleavage occur in a concerted fashion without the formation of a distinct intermediate of higher or lower coordination number. In addition, decomplexation will be accompanied by charge creation due to the release of Li$^+$, which in turn will lead to an increase in electrostriction which will offset the intrinsic volume changes.
4. Complexation by Cryptands in Acetone as Solvent

Figure 4.11. $^7$Li NMR spectra recorded as a function of pressure at 313.2 K for the mole ratio C221/LiClO$_4$ = 0.5.

Figure 4.12. $^7$Li NMR spectra of C222 and LiClO$_4$ in acetone. Pressure dependence for the sample ratios C222/LiClO$_4$ = 0.25, 0.5, and 0.75, respectively, at 313.2 K.

4.5.4. **Theoretical Calculations**

For the closely related $\gamma$-butyrolactone and Li$^+$/\$\gamma$-butyrolactone high level ab initio studies were recently performed by Rey et al.\textsuperscript{87} For acetone and Li$^+$/acetone only Hartree-Fock calculations were performed.\textsuperscript{65} In our DFT calculations we found that the Li$^+$ cation coordinates to the carbonyl oxygen with an almost co-linear configuration relative to the carbon-oxygen bond, as for \$\gamma$-butyrolactone. This configuration holds for clusters of up to four
molecules and also in the solid phase, where a tetrahedral first solvation (coordination) sphere was found (see Table 4.4).66

Table 4.4. Calculated bond length for Li⁺ solvated in actone.

<table>
<thead>
<tr>
<th>Bond length [Å]</th>
<th>PG</th>
<th>B3LYP/D95Vp</th>
<th>B3LYP/6-311+G**</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Li(acetone)]⁺</td>
<td>$C_2$</td>
<td>1.77</td>
<td>1.75</td>
</tr>
<tr>
<td>[Li(acetone)₂]⁺</td>
<td>$D_2$</td>
<td>1.81</td>
<td>1.79</td>
</tr>
<tr>
<td>[Li(acetone)₃]⁺</td>
<td>$D_3$</td>
<td>1.88</td>
<td>1.86</td>
</tr>
<tr>
<td>[Li(acetone)₄]⁺</td>
<td>$C_1$</td>
<td>1.96 (averaged)</td>
<td>1.96 (averaged)</td>
</tr>
</tbody>
</table>

Experimentally, a decrease in the cavity size of the cryptands hampers the exchange of Li⁺ between the cryptand and the solvent. We were able to observe it in the case of γ-butyrolactone and again we can see it in the present case. The improved binding of Li⁺ in a smaller cavity is visible from the structure and the following model reaction [Equation (4.4)] that describes the energy required for the dechelation process. Application of the CPCM solvent model strengthens this trend significantly (see Table 4.5).

$$ [\text{Li} \subset \text{Cryptand}]^+ + 4 \text{ solvent} \rightarrow [\text{Li(solvent)₄}]^+ + \text{Cryptand} \quad (4.4) $$

In agreement with previous studies by Wipff et al.,⁵ we also found only a limited flexibility for the investigated cryptands in our DFT calculations, therefore all cryptands were calculated within the highest possible symmetry (Table 4.5). We recently demonstrated that reaction (4.4) is a valuable tool to determine ion selectivity as a function of the ionic radii⁸⁸ and to examine cavity size of the cryptands as a variable.⁴²
4. Complexation by Cryptands in Acetone as Solvent

### Table 4.5. Dechelation energy, $E_{\text{dechelation}}$, for the reaction outlined in Equation (4.4).\(^{[a]}\)

<table>
<thead>
<tr>
<th>Acetone</th>
<th>C222</th>
<th>C221</th>
<th>C211</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{dechelation}}$ (DFT) [kcal/mol]</td>
<td>-8.6</td>
<td>+2.0</td>
<td>+3.0</td>
</tr>
<tr>
<td>$E_{\text{dechelation}}$ (CPCM) [kcal/mol]</td>
<td>+5.4</td>
<td>+13.6</td>
<td>+20.4</td>
</tr>
<tr>
<td>$\gamma$-Butyrolactone</td>
<td>C222</td>
<td>C221</td>
<td>C211</td>
</tr>
<tr>
<td>$E_{\text{dechelation}}$ (DFT) [kcal/mol](^{[a]})</td>
<td>-16.8</td>
<td>-11.6</td>
<td>-5.3</td>
</tr>
</tbody>
</table>

\(^{[a]}\) DFT: B3LYP/D95Vp, CPCM: B3LYP(CPCM)/D95Vp//B3LYP/D95Vp.

### Table 4.6. Calculated (RB3LYP/D95Vp) and X-ray bond lengths (in Å).

<table>
<thead>
<tr>
<th>d [Å]</th>
<th>C222</th>
<th>C221</th>
<th>C211</th>
<th>[Li(OH$_2$)$_4$]$^+$</th>
<th>[Li(acetone)$_4$]$^+$</th>
<th>[Li(NH$_3$)$_4$]$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-O</td>
<td>2.14</td>
<td>-</td>
<td>2.11</td>
<td>1.95</td>
<td>1.96</td>
<td>-.--</td>
</tr>
<tr>
<td></td>
<td>2.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li-N</td>
<td>2.22</td>
<td>2.28</td>
<td>2.38</td>
<td>-.--</td>
<td>-.--</td>
<td>2.13</td>
</tr>
<tr>
<td>PG</td>
<td>C$_3$</td>
<td>C$_1$</td>
<td>C$_2$</td>
<td>$T$</td>
<td>$C_1$</td>
<td>$C_1$</td>
</tr>
<tr>
<td>X-ray</td>
<td>89</td>
<td>90</td>
<td>91</td>
<td>$92$</td>
<td>$93$</td>
<td></td>
</tr>
<tr>
<td>Li-O</td>
<td>-.--</td>
<td>2.06</td>
<td>2.08</td>
<td>1.96</td>
<td>1.94, 1.91, 1.93,</td>
<td>-.--</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.95</td>
<td></td>
</tr>
<tr>
<td>Li-N</td>
<td>-.--</td>
<td>2.40</td>
<td>2.29</td>
<td>-.--</td>
<td>-.--</td>
<td>2.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.44</td>
</tr>
</tbody>
</table>

In agreement with the experimental kinetic data, the smaller cryptand binds Li$^+$ better and slows down its exchange rate (Table 4.2). On comparing the calculated Li-O and Li-N bond lengths of the three structures with the bond length in [Li(OH$_2$)$_4$]$^+$ and [Li(NH$_3$)$_4$]$^+$, the trend can easily be understood (see Table 4.6 and Figure 4.11). In C222, Li$^+$ is four-fold weakly...
coordinated in a trigonal-pyramidal shape by one Li-N and three Li-O interactions all clearly elongated (0.2 and 0.1 Å, respectively). The Li\(^+\) cation in C221 is five-fold coordinated (distorted trigonal-bipyramidal structure) by one nitrogen and four oxygen bonds all extended by around 0.15 Å. The coordinating bonds in \([\text{Li} \subset \text{C211}]^+\) are even more extended, but the Li-O bonds form a somewhat distorted tetrahedral coordination sphere for the lithium monocation, while the stronger elongated Li-N bonds form a kind of second coordination sphere. Therefore, the lithium ion can formally adopt a six-coordinate state, which strongly supports the proposed associative character of the decomplexation process that involves binding of external solvent molecules as suggested by the very negative activation entropies. A comparison of the calculated and X-ray bond lengths shows a good agreement. A comparison between the calculated data for γ-butyrolactone and acetone shows the same trend for both solvents. Li\(^+\) is better coordinated in the smaller cavities of the smaller cryptands, as expected.

To draw a conclusion on solvation abilities from a direct comparison of the dechelating energies in acetone and γ-butyrolactone, is risky. The calculated dechelating energies can not be considered as a proof of the rule of Madrakian et al., that there is an inverse relationship between the stability of the complexes and the solvating ability of the solvent.\(^{66}\) The different values can be attributed to the different number of non-hydrogen atoms in both solvents. Acetone has only four non-hydrogen atoms, while γ-butyrolactone has six and can therefore stabilize charge much better.
4. Complexation by Cryptands in Acetone as Solvent

Figure 4.13. Optimized structures for $[\text{Li} \subset \text{C222}]^+$, $[\text{Li} \subset \text{C221}]^+$, $[\text{Li} \subset \text{C211}]^+$ and $[\text{Li}(\text{Acetone})_4]^+$.

4.6. Conclusions

It can be concluded from the results of the present study that for the Li$^+$ exchange process between C222, C221 and acetone as solvent, two pathways, viz. bimolecular (associative) and unimolecular (dissociative) compete with each other. The pressure dependence of the exchange process suggests the operation of a pure interchange mechanism, whereas the negative activation entropy values favor an associative interchange process for the decomplexation reaction. The basic idea of an interchange process involves concerted bond
formation and bond cleavage, which is in agreement with the consideration that acetone is a rather weak donor. The results are in good agreement with that expected on the basis of a systematic comparison with data reported in the literature for solvents of similar donor strength.
4. Complexation by Cryptands in Acetone as Solvent

4.7. References

4. Complexation by Cryptands in Acetone as Solvent

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4. Complexation by Cryptands in Acetone as Solvent

5. Complexation by Cryptands in γ-Butyrolactone as Solvent

5. Ligand exchange processes on solvated lithium cations. Complexation by Cryptands in γ-Butyrolactone as Solvent

5.1. General remark

The work presented in this chapter was conducted by several authors within a joint project and has been published as:


5.2. Abstract

Kinetic studies on Li⁺ exchange between the cryptands C222 and C221 and γ-butyrolactone as solvent were performed as a function of ligand-to-metal ratio, temperature and pressure using 7Li NMR. The thermal rate and activation parameters are: C222: \( k_{298} = (3.3 \pm 0.8) \times 10^4 \, \text{M}^{-1} \text{s}^{-1}, \Delta H^\circ = 35 \pm 1 \, \text{kJ mol}^{-1} \) and \( \Delta S^\circ = -41 \pm 3 \, \text{J K}^{-1} \text{mol}^{-1} \); C221: \( k_{298} = 105 \pm 32 \, \text{M}^{-1} \text{s}^{-1}, \Delta H^\circ = 48 \pm 1 \, \text{kJ mol}^{-1} \) and \( \Delta S^\circ = -45 \pm 2 \, \text{J K}^{-1} \text{mol}^{-1} \). Temperature and pressure dependence measurements were performed in the presence of an excess of Li⁺. The influence of pressure on the exchange rate is insignificant for both ligands, such that the value of activation volume is around zero within the experimental error limits. The activation parameters obtained in this study indicate that the exchange of Li⁺ between solvated and chelated Li⁺ ions follows an associative interchange mechanism.
5. Complexation by Cryptands in γ-Butyrolactone as Solvent

5.3. Introduction

Following the work of Pedersen on two-dimensional crowns, Lehn and coworkers developed in 1969 a range of three-dimensional, polycyclic ligand systems which they named cryptands (Greek: *cryptos* = cave).\textsuperscript{1, 2} Until today this class of compounds has been intensively explored and extended in different directions\textsuperscript{3-4} in terms of cavity size,\textsuperscript{5-6} donor atoms,\textsuperscript{7} and metalla-topomers.\textsuperscript{8-11} Since cryptands readily form complexes with a wide range of metal ions and \(\text{NH}_4^+\),\textsuperscript{12} provided the ion involved is not too large to be contained in the macrocyclic cavity,\textsuperscript{13} they find their application in various areas like catalysis, medicine, biomimetic research,\textsuperscript{14-21} and as receptors\textsuperscript{22} and electrides.\textsuperscript{23} Studies on the complexes (cryptates) formed between alkali metal ions and cryptands, have revealed a substantial understanding of the effects of metal ion size and cryptand cavity size on the structure, stability and lability of cryptates, and the mechanism of the cryptate complex-formation processes.\textsuperscript{24-28} Such selective complexation has led to many biological and chemical studies.

Kinetic studies on macrocyclic complex-formation reactions with alkali cations not only result in important information on the rates and mechanisms of complex-formation reactions, but also lead to a better understanding of the high selectivity of these ligands toward different cations. The broad impact of such studies spans from the theory of complexation to cation transport through membranes, and makes the ability to control cation selectivity via tactical structural changes in the complexing agent of prime importance.\textsuperscript{18} Polyoxo macrobicyclic diamines, represented by the structure in Figure 5.1, are able to form metal ion complexes in which the metal ion is located in the cavity of the macromolecule and two nitrogen atoms along with the oxygen atoms participate in binding the metal cation. All complexes have 1:1 stoichiometry with the metal ion positioned in the center of the ligand cavity.\textsuperscript{24}
5. Complexation by Cryptands in \( \gamma \)-Butyrolactone as Solvent

Figure 5.1. Chelate structures. C211: \( m = 0, n = 1 \). C221: \( m = 1, n = 0 \). C222: \( m = 1, n = 1 \).

In case of crown ethers and cryptands in non-aqueous solutions, the rates of complex-formation \((k_f)\) for the interaction with alkali-metal cations are generally diffusion-controlled and, consequently, the complexation selectivities are governed by the decomplexation rates \(k_d\). These reactions have received significant attention, initially from Lehn and co-workers and more recently from Popov et al. and Lincoln et al. These and other groups performed a series of detailed kinetic studies and found that two mechanisms need to be considered for the decomplexation process of cryptand-alkali metal cation complexes, viz., bimolecular associative (I) and unimolecular dissociative (back reaction in II) cation exchange processes, where S presents solvent and L the employed chelate.

\[
\begin{align*}
  *\text{Li}(S)^+ + \text{Li}(L)^+ & \quad \xrightarrow{k_1} \quad \text{Li}(S)^+ + *\text{Li}(L)^+ \quad (I) \\
  \text{Li}(S)^+ + L & \quad \xrightarrow{k_2} \quad \text{Li}(L)^+ + S \quad (II)
\end{align*}
\]

The solvent plays a major role in the unimolecular mechanism II, which is therefore favored in strong donor solvents. Many examples have been included in a series of review articles. It has been reported that ligand structure and solvent properties have considerable effects on the reaction rates, activation parameters, and exchange mechanism of cations between the
solvated and complexed sites. We have now extended the study of Li+ exchange to γ-butyrolactone (see Figure 5.2) as solvent.

Figure 5.2. Structure of γ-butyrolactone.

γ-Butyrolactone was chosen as solvent due to its relevance in lithium batteries and capacitors. It is a model cyclic ester used as a major chemical compound with extensive application in pharmaceuticals, pesticides and petrochemicals. The butyrolactone ring is an integral building block of many natural products of biological activity, like the sesquiterpene lactones, flavor components, alkaloids, antileukemics, and pheromones. γ-Butyrolactone is one of the important intermediates in fine chemical industrial practices, for example in the synthesis of pyrrolidine, herbicides and rubber additives. It is also used as a solvent for surface treatment of textiles and metal coated plastics, as a paint remover, in photochemical etching, in vitamin and pharmaceutical preparations.

Recently, computational studies on γ-butyrolactone and Li+/γ-butyrolactone have been performed by Rey et al.. It was found that the Li+ cation coordinates to the carbonyl oxygen with an almost co-linear configuration relative to the carbon-oxygen bond but with a slight tilting toward the lactone oxygen. This configuration holds for clusters of up to four molecules and also in the liquid phase, where a tetrahedral first solvation (coordination) sphere was found.

In this contribution, we report kinetic parameters for the exchange of Li+ in γ-butyrolactone under ambient and elevated pressure conditions, and discuss their mechanistic implications.
5. Complexation by Cryptands in γ-Butyrolactone as Solvent

5.4. Experimental Section

5.4.1. General Procedures

The preparation of test solutions was carried out under an Ar or N₂ atmosphere using standard Schlenk techniques, under an Ar atmosphere in a glove box, or under vacuum. Lithium perchlorate (Aldrich, battery grade) was vacuum-dried at 120 °C for 48 h and then stored under dry nitrogen. The cryptands C222 (purchased from Fluka), C221 and C211 (purchased from Aldrich) were dried under vacuum for 48 h and stored under dry nitrogen. γ-Butyrolactone (Aldrich) was dried over anhydrous CaSO₄, then fractionally destilled under vacuum and stored under nitrogen over Linde 3Å molecular sieves. Solutions of LiClO₄, C222, C221 and C211 in γ-butyrolactone were prepared under dry nitrogen. For the ⁷Li NMR measurements the solutions were sealed in 5 mm NMR tubes under an Ar atmosphere. In order to study the kinetics of the exchange of Li⁺ between C222 and C221 and γ-butyrolactone as solvent, four solutions of different concentration ratio were prepared for each system. The concentration of lithium perchlorate in each solution was kept constant at 0.05 M, whereas the concentration of ligand was varied between 0.0175 M and 0.04 M. In this way the measurements were always performed in the presence of an excess of Li⁺.

5.4.2. ⁷Li NMR Spectroscopy

Variable-temperature and variable-pressure Fourier transform ⁷Li 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. 5 mm spinning 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 LiClO₄ in DMF). The temperature dependence measurements were performed over a wide as possible temperature range for each system. A homemade high-pressure probe described in the literature was used for the variable-pressure experiments which were conducted at a selected temperature and at ambient, 30, 60, 90, 120 and 150 MPa pressure. A
5. Complexation by Cryptands in γ-Butyrolactone as Solvent

A standard 5 mm NMR tube cut to a length of 45 mm was used for the sample solution. The high-pressure NMR tube was sealed with a MACOR plug and an O-ring made of VITON. The plug and O-ring were shown to be stable in the employed solvent. The pressure was transmitted by the movable MACOR piston to the sample, and the temperature was controlled as described elsewhere. For a typical kinetic run, 0.8 ml of solution was transferred under an Ar atmosphere to a Wilmad screw-cap NMR tube equipped with a poly(tetrafluoroethylene) septum. All test samples were prepared in the same way.

5.4.3. Programs

The line widths of the NMR signals were obtained by fitting Lorentzian functions to the experimental spectra using the NMRICMA 2.7 program for Matlab. The adjustable parameters were the resonance frequency, intensity, line width and baseline. Complete line-shape analysis based on the Kubo-Sack formalism using modified Bloch equations was also performed with NMRICMA 2.7 to extract rate constants from experimental spectra. The temperature and pressure dependent 7Li line widths and chemical shifts employed in the line shape analysis were extrapolated from low temperatures where no exchange-induced modification occurred.

5.4.4. Quantum-Chemical Calculations

All structures were optimized at the B3LYP/D95Vp hybrid DFT level with no constraints other than symmetry and confirmed to be minima by computation of vibrational frequencies. Relative energies were corrected for zero point vibrational energy differences. The D95V basis set, augmented with polarisation functions (D95Vp), was used. The Gaussian suite of programs was used throughout.
5. Complexation by Cryptands in γ-Butyrolactone as Solvent

5.5. Results and Discussion

5.5.1. Spectroscopic Observations

In preliminary experiments, a series of 7Li NMR measurements for the Li+-cryptand system in γ-butyrolactone as solvent were performed. For each of the cryptands C222, C221 and C211, mole ratio dependent measurements were performed by variation of both the cryptand:Li+ and Li+:cryptand molar ratios. The results enabled us to observe the distribution of particular species on increasing the amount of chelate or lithium salt. Basically, two signals of varying intensity were observed in the 7Li NMR spectra that refer to solvated Li+ and Li+ bound inside the cryptand cavity. In case of the smallest chelate C211, however, an additional signal appeared which can be ascribed to Li+ bound outside the cryptand and being partially solvated. The distribution plot for the various species in a solution of C211 and LiClO4 in γ-butyrolactone is presented in Figure 5.3. The concentration of LiClO4 was kept constant at 0.01 M and the concentration of C211 was varied in the range 0 to 0.04 M. Initially only the signal of free (solvated) Li+ is observed, and then with increasing amount of C211, the signals referring to the complexed Li+ appear. Contrary to the larger cryptands, there are two signals that refer to bound Li+; one for Li+ inside the cavity and another of low intensity (max. 15 %) for Li+ presumably bound outside the cryptand and being partially solvated. The latter signal, however, disappears once the C211/LiClO4 molar ratio gets to 1, and then all the Li+ is bound as internal complex. Due to the facts that the exchange process among the three species cannot be clearly defined, Li(C211)+ is very stable and there is almost no exchange taking place, a detailed study of the observed rate constant, $k_{obs}$, for the exchange of Li+ as a function of temperature and pressure was undertaken only for C221 and C222. The lithium exchange reaction between cryptand and γ-butyrolactone was studied for four solutions with different ligand-to-metal ratios in the presence of an excess of Li+. 

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Three signals can be observed in Figure 5.4; one comes from the reference (6.6 ppm) and the other two from the exchanging sites (6.0 ppm solvated Li⁺ and 4.8 ppm complexed Li⁺). At low temperature the signals are narrow and completely separated due to very slow or no exchange. Since the formation constant for Li(C221)⁺ is very high, the concentration of bound lithium is equal to the amount of cryptand added. At ca. 358 K the signals start to coalescence and at 388 K only one broad signal (at 5.3 ppm) can be observed due to fast exchange. In the case of C222 (Figure 5.5), the exchange process is faster due to the larger cavity of the cryptand. The signals that refer to solvated and complexed Li cation (8.3 ppm and 6.8 ppm, respectively at 218 K) coalescence at a lower temperature (ca. 268 K), and at high temperature (368 K) only one sharp signal at 7.7 ppm was observed as a consequence of a very fast exchange process. An accurate temperature dependence for C222 over a large temperature range can be observed in Figure 5.7.
5. Complexation by Cryptands in γ-Butyrolactone as Solvent

Figure 5.4. $^7$Li NMR spectra recorded as a function of temperature for the mole ratio C221:LiClO$_4$ = 0.65.

Figure 5.5. $^7$Li NMR spectra recorded as a function of temperature for the mole ratio C222:LiClO$_4$ = 0.65.

The rate of the exchange reaction increased not only with increasing cavity size of the cryptand but also with increasing concentration of the chelate, as can be recognized from the shape of the signals at 338 K in Figure 5.6 and from the values of $k_{obs}$ in Table 5.1.
5. Complexation by Cryptands in $\gamma$-Butyrolactone as Solvent

Figure 5.6. $^7$Li NMR spectra of C222 and LiClO$_4$ in GBL. Temperature dependence for the sample ratios C222:LiClO$_4$ = 0.35, 0.45, 0.55 and 0.65.

Figure 5.7. Eyring plots for $k_{obs}$ as a function of temperature for C222 for the concentration ratios C222:LiClO$_4$ = 0.35, 0.45, 0.55 and 0.65, respectively.
5. Complexation by Cryptands in γ-Butyrolactone as Solvent

Table 5.1. Values of the observed rate constants ($k_{obs}$) calculated from the line shape analysis for the exchange of Li$^+$ between solvated and chelated sites at 25°C.

<table>
<thead>
<tr>
<th>Mole ratio C221:Li$^+$</th>
<th>$k_{obs}$, s$^{-1}$</th>
<th>Mole ratio C222:Li$^+$</th>
<th>$k_{obs}$, s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>2.68 ± 0.05</td>
<td>0.35</td>
<td>654 ± 13</td>
</tr>
<tr>
<td>0.5</td>
<td>4.3 ± 0.1</td>
<td>0.45</td>
<td>851 ± 25</td>
</tr>
<tr>
<td>0.65</td>
<td>6.9 ± 0.3</td>
<td>0.55</td>
<td>1282 ± 51</td>
</tr>
<tr>
<td>0.8</td>
<td>9.6 ± 0.5</td>
<td>0.65</td>
<td>1352 ± 68</td>
</tr>
</tbody>
</table>

5.5.2. Suggested Exchange Mechanism

As mentioned above, there are two possible mechanisms for the exchange of the lithium ion between the solvated and the complexed sites, namely bimolecular associative (I) and unimolecular dissociative (II) mechanisms.

At equilibrium

\[ k_1[^*\text{Li(S)}][\text{Li(L)}] = k_{-1}[^*\text{Li(L)}][\text{Li(S)}] \]

\[ k_2[\text{Li(S)}][\text{L}] = k_{-2}[\text{Li(L)}][\text{S}] \]

Therefore

\[ -\frac{d}{dt}[\text{Li(S)}] = k_{obs}[\text{Li(S)}] = k_1[\text{Li(S)}][\text{Li(L)}] + k_{-2}[\text{Li(L)}][\text{S}] \quad (5.1) \]

and

\[ k_{obs} = k_1[\text{Li(L)}] + \frac{k_{-2}[\text{Li(L)}][\text{S}]}{[\text{Li(S)}]} \quad (5.2) \]

An alternative form of Equation (5.2) is Equation (5.3), which was used to fit the data in Figure 5.8 and Figure 5.10.

\[ \frac{k_{obs}}{[\text{Li(L)}]} = k_1 + k_{-2}, \frac{1}{[\text{Li(S)}]} \quad (5.3) \]
Plots of $k_{\text{obs}}/[\text{Li(L)}]$ vs. $1/[\text{Li(S)}]$ were found to be linear with negligible slopes ($k_{-2} = k_{-2}[S]$) (especially at low temperature) and significant intercepts ($k_1$) (see Figures 5.8 and 5.10). This indicates that the exchange mechanism has a more associative character for both C221 and C222. This led us to take only the values of $k_1$ into consideration, from which it follows that the exchange process is much faster for C222 than for C221. The corresponding Eyring plots for $k_1$ are shown in Figures 5.9 and 5.11, respectively, and the thermal activation parameters are summarized in Table 5.2.

![Figure 5.8](image-url)

**Figure 5.8.** Plots of $k_{\text{obs}}/[\text{Li(L)}]$ vs $1/[\text{Li(S)}]$ for C222 as a function of temperature.
5. Complexation by Cryptands in γ-Butyrolactone as Solvent

Figure 5.9. Eyring plot for $k_1$ as a function of temperature for C222.

Figure 5.10. Plots of $k_{obs}/[\text{Li(L)}]$ vs $1/[\text{Li(S)}]$ for C221 as a function of temperature.
Complexation by Cryptands in γ-Butyrolactone as Solvent

\[ Y = A + B \times X \]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (error)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>18.36172 (0.29829)</td>
</tr>
<tr>
<td>B</td>
<td>-5766.54595 (97.29293)</td>
</tr>
</tbody>
</table>

\( \ln (k_1/T) \) vs. \( 1/T, \text{K}^{-1} \)

**Figure 5.11.** Eyring plot for \( k_1 \) as a function of temperature for C221.

**Table 5.2.** Thermal activation parameters obtained from the values of \( k_1 \) as a function of temperature.

<table>
<thead>
<tr>
<th>Chelate</th>
<th>( k_{298}^1, \text{M}^{-1} \text{s}^{-1} )</th>
<th>( \Delta H^#, \text{kJ mol}^{-1} )</th>
<th>( \Delta S^#, \text{J K}^{-1} \text{mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C221</td>
<td>105 ± 32</td>
<td>48 ± 1</td>
<td>-45 ± 2</td>
</tr>
<tr>
<td>C222</td>
<td>((3.3 ± 0.8) \times 10^4)</td>
<td>35 ± 1</td>
<td>-41 ± 3</td>
</tr>
</tbody>
</table>

Based on the significantly negative activation entropy, the activation parameters support an associative interchange type of exchange process. Furthermore, the reported activation parameters are within the range of those reported by Popov et al. for closely related systems, viz. \( k_{298} = 680 ± 42 \ \text{M}^{-1} \text{s}^{-1} \), \( \Delta H^# = 28 ± 1 \ \text{kJ mol}^{-1} \) and \( \Delta S^# = -101 ± 2 \ \text{J K}^{-1} \text{mol}^{-1} \) for Li\(^+\)/C221 in acetonitrile, and \( k_{298} = 892 ± 50 \ \text{M}^{-1} \text{s}^{-1} \), \( \Delta H^# = 26 ± 1 \ \text{kJ mol}^{-1} \) and \( \Delta S^# = -109 ± 2 \ \text{J K}^{-1} \text{mol}^{-1} \) for Li\(^+\)/C221 in propylene carbonate, for which the authors also postulated an associative character for the Li\(^+\) exchange process. In the case of Li\(^+\) exchange between C222 and solvents such as acetonitrile, propylene carbonate and acetone, these authors found the mechanism to have more of a dissociative character. However, it should be pointed out that they used a different rate law than the one proposed by Shchori et al. and that used in the present study, which complicates a direct comparison of the reported
activation parameters with ours. It is reasonable to expect that solvents such as propylene carbonate, ethylene carbonate and $\gamma$-butyrolactone, together considered as a class of solvents that play an important role in polymer-gel lithium-ion batteries,\textsuperscript{66-70} due to their similar structure and properties as expected from their rather similar Gutmann donor numbers ($DN = 15.1, 16.4$ and 18.0, respectively\textsuperscript{71}), should coordinate to Li$^+$ in a similar way and should have a similar influence on the exchange mechanism. This observation corresponds to that reported by Shamsipur \textit{et al.}\textsuperscript{72} for the exchange of Li$^+$ between C221 and acetonitrile-nitromethane mixtures. In all solvent mixtures used, Li$^+$ exchange was found to occur via an associative mechanism, as expected for weakly donor solvents ($DN = 14.1$ and 2.7 for acetonitrile and nitromethane, respectively). The same group reported another case, where Li$^+$ exchange occurred between C221 and mixtures of nitromethane (low donor ability) and dimethylformamide (high DN = 26.6), where it was found that the associative mechanism predominates in nitromethane, whereas a dissociative pathway prevails in dimethylformamide solution.

\textbf{5.5.3. High Pressure $^7$Li NMR Measurements}

Additional mechanistic information on the intimate nature of the exchange mechanism can in principle be obtained from the effect of pressure on the Li$^+$ exchange process.\textsuperscript{73-76} A systematic pressure dependence study was performed to determine the volume of activation for the Li$^+$ exchange process for both chelates. Pressure dependent NMR spectra were recorded for each sample over the pressure range of 0.2 to 150 MPa at 316.5 K. The effect of pressure was found to be not very significant for these systems. There was a very small difference in the shape of the NMR spectra recorded at various pressures as can be seen in Figure 5.12. The rate constants calculated for each pressure were very similar within the experimental error limits and resulted in a practically zero value for $\Delta V^*_{obs}$, which points to a concerted interchange type of exchange mechanism.\textsuperscript{77} In terms of an interchange mechanism, bond formation and bond cleavage occur in a concerted fashion without the formation of a distinct intermediate of higher or lower coordination number.
5. Complexation by Cryptands in γ-Butyrolactone as Solvent

Figure 5.12. 7Li NMR spectra recorded as a function of pressure at 316.5 K for the mole ratio C221:LiClO$_4$ = 0.65.

5.5.4. Influence of Water

The rate of the exchange process was also investigated in a mixture of γ-butyrolactone and water in order to probe the impact of the solvent polarity and donor ability on the rate of the exchange reaction. The exchange measurements were repeated for one of the samples (C222:LiClO$_4$ = 0.35) with 1μl H$_2$O added to the 0.8 ml of γ-butyrolactone solution. It was observed that the exchange rate increased significantly as compared to the value obtained for the sample in the absence of water. The values of $k_{obs}$ increase from 27 to 75 s$^{-1}$ at 248 K, from 654 to 1282 s$^{-1}$ at 298 K, and from 5945 to 12895 s$^{-1}$ at 358 K, on addition of water. This can be accounted for by the higher donor strength of water compared to γ-butyrolactone. It follows that the presence of water plays an important role in the exchange rate of Li$^+$ between cryptand and solvent.

5.5.5. Theoretical Calculations

Experimentally a decrease in the cavity size hampers the exchange of Li$^+$ between the cryptand and the solvent. The improved binding of Li$^+$ in a smaller cavity should become visible from the structure and the following model reaction that describes the energy required for the dechelation process (Table 5.3).
Complexation by Cryptands in $\gamma$-Butyrolactone as Solvent

$[\text{Li} \subset \text{Cryptand}]^+ + 4\gamma$-Butyrolactone $\rightarrow [\text{Li}(\gamma$-Butyrolactone)$_4]^+ + \text{Cryptand} (5.4)$

It is noteworthy that in agreement with previous studies by Wipff et al.,$^5$ we also found only a limited flexibility for the investigated cryptands in our DFT calculations, justifying that all cryptands were calculated within the highest possible symmetry. In earlier work we demonstrated that eq. (5.4) is a valuable tool to determine ion selectivity as a function of the ionic radii.$^7$ We therefore examined the cavity size of the cryptands as a variable.

Table 5.3. Dechelation energy, $E_{\text{dechelation}}$, for the reaction outlined in (5.4).

<table>
<thead>
<tr>
<th>$\gamma$-Butyrolactone</th>
<th>C222</th>
<th>C221</th>
<th>C211</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{dechelation}}$ [kJ/mol]</td>
<td>-70.3</td>
<td>-48.6</td>
<td>-22.2</td>
</tr>
</tbody>
</table>

Table 5.4. Calculated (RB3LYP/D95Vp) and x-ray bond lengths (in Å).

<table>
<thead>
<tr>
<th>d [Å]</th>
<th>C222</th>
<th>C221</th>
<th>C211</th>
<th>[Li(OH$_2$)$_4$]$^+$</th>
<th>[Li($\gamma$-butyrolactone)$_4$]$^+$</th>
<th>[Li(NH$_3$)$_4$]$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-O</td>
<td>2.14</td>
<td>-</td>
<td>2.11</td>
<td>1.95</td>
<td>1.94</td>
<td>-.--</td>
</tr>
<tr>
<td></td>
<td>2.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li-N</td>
<td>2.22</td>
<td>2.28</td>
<td>2.3</td>
<td>-.--</td>
<td>-.--</td>
<td>2.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PG</td>
<td>$C_3$</td>
<td>$C_1$</td>
<td>$C_2$</td>
<td>$T$</td>
<td>$C_1$</td>
<td>$C_1$</td>
</tr>
<tr>
<td>X-ray</td>
<td>79</td>
<td>80</td>
<td>81</td>
<td>82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li-O</td>
<td>-.--</td>
<td>2.06</td>
<td>2.0</td>
<td>1.96</td>
<td>-.--</td>
<td>-.--</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.10</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li-N</td>
<td>-.--</td>
<td>2.40</td>
<td>2.29</td>
<td>-.--</td>
<td>-.--</td>
<td>2.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.44</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

In agreement with the experimental kinetic data, the smaller cryptand binds Li$^+$ better and slows down its exchange rate (Table 5.2). On comparing
the calculated Li-O and Li-N bond lengths of the three structures with the bond distance in [Li(OH$_2$)$_4$]$^+$ and [Li(NH$_3$)$_4$]$^+$, the trend can easily be understood (see Table 5.4 and Figure 5.13). In C222, Li$^+$ is four times weakly coordinated in a trigonal pyramidal shape by one Li-N and three Li-O interactions all clearly elongated (0.2 and 0.1 Å, respectively). The Li$^+$ cation in C221 is coordinated five times (distorted trigonal bipyramidal structure) by one nitrogen and four oxygen bonds all extended by around 0.15 Å. The coordinating bonds in [Li⊂C211]$^+$ are even more extended, but the Li-O bonds form a somewhat distorted tetrahedral coordination sphere for the lithium mono cation, while the stronger elongated Li-N bonds form a kind of second coordination sphere. Therefore, the lithium ion is formally six-coordinate. A comparison of the calculated and x-ray bond lengths shows a good agreement.

**Figure 5.13.** Optimized structures for [Li⊂C222]$^+$, [Li⊂C221]$^+$, [Li⊂C211]$^+$ and [Li(γ-Butyrolactone)$_4$]$^+$. 

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5.6. Conclusions

It can be concluded from the results of the present study that for the Li\(^+\) exchange process between C222, C221 and \(\gamma\)-butyrolactone as solvent, two pathways, viz. bimolecular associative and unimolecular dissociative, compete with each other. The pressure dependence of the exchange process suggests the operation of a pure interchange mechanism, whereas the negative activation entropy values favor an associative interchange process. The basic idea of an interchange process involves concerted bond-formation and bond-cleavage, which is in agreement with the consideration that \(\gamma\)-butyrolactone is a rather weak donor. The results are in good agreement with that expected on the basis of a systematic comparison with data reported in the literature for solvents of similar donor strength.
5. Complexation by Cryptands in γ-Butyrolactone as Solvent

5.7. References

5. Complexation by Cryptands in γ-Butyrolactone as Solvent

5. Complexation by Cryptands in $\gamma$-Butyrolactone as Solvent

5. Complexation by Cryptands in γ-Butyrolactone as Solvent


5. Complexation by Cryptands in γ-Butyrolactone as Solvent


5. Complexation by Cryptands in γ-Butyrolactone as Solvent

6. Summary

In this work the solvation process of Li\(^+\) ion, as well as solvent and ligand exchange reactions on Li\(^+\) ion were studied. Li\(^+\) ions possess interesting properties and like other alkali metal ions are known to form complexes with macrocyclic ligands called cryptands. In this summary, an overview over the insights gained in the factors that control the reactivity of Li\(^+\) complexes with respect to the solvent and cryptand properties is presented.

Three main questions were addressed:

- How does the nature of the solvent influence the first coordination sphere around the Li\(^+\) ion?
- How is solvent exchanged between the first and second coordination spheres of the Li\(^+\) ion?
- How is the Li\(^+\) ion complexed by different cryptands and what is the nature of the Li\(^+\) exchange mechanism between cryptand and solvent?

In this thesis these aims were approached from the microscopic point of view, making use of both theoretical calculations and experimental techniques. The first two topics mentioned above constitute the contents of Chapters 2 and 3, whereas the third objective was approached and the results are reported in Chapters 4 and 5.

The experimental method used throughout was \(^{7}\text{Li}\) NMR. It was shown that \(^{7}\text{Li}\) NMR is a very powerful technique for the study of alkali complexes with macrocyclic ligands, particularly in non-aqueous solutions. Particular attention was given to high pressure \(^{7}\text{Li}\) NMR, which represents the first example reported for this kind of research. It could be demonstrated that \(^{7}\text{Li}\) NMR is a very convenient method for the estimation of the coordination number on Li\(^+\) ion as well as for investigation of the selective solvation of Li\(^+\) in a mixture of solvents. This method was also used for mechanistic studies, specifically for Li\(^+\) exchange between two environments: solvated and chelated species.
6. Summary

Solvents of different properties and their influence on the solvation shell were investigated. Questions concerning selective solvation around Li\(^+\) and the solvation number of the Li\(^+\) cation were studied as a function of the solvent properties. The Gutmann Donor Number \((DN)\) was mostly considered as a factor to describe the donor properties of the solvent. It reflects the ease of donation of the solvent molecule’s lone electron pair.

In order to determine the coordination number of Li\(^+\), the cation was dissolved in a solvent mixture that consisted of a weakly and strongly coordinating component. It could be shown in Chapter 2 that the Li\(^+\) ion in DMSO is coordinated by 4 solvent molecules. \(\gamma\)-Butyrolactone was found to be a convenient diluent in this kind of study. Contrary to DMSO \((DN = 29.8)\), it is rather a weak donor \((DN = 18.0)\) which appreciably dissolves alkali metal salts and its interaction with DMSO is much weaker than that between DMSO and a metal cation. By plotting the chemical shift of the obtained \(^7\)Li NMR signal vs. the DMSO/LiClO\(_4\) mole ratio, a clear brake point could be observed at a DMSO/Li\(^+\) ratio of 4:1, indicating that the solvation number of Li\(^+\) in DMSO is 4. Using the same method for the solvent mixture of acetonitrile \((DN = 14.1)\) and nitromethane \((DN = 2.7)\), it was found that also in this case the Li\(^+\) ion is coordinated by four acetonitrile molecules, as reported in Chapter 3.

Selective solvation of alkali metal ions in mixed solvents can be monitored from the extent to which the chemical shift of the alkali metal nucleus varies with solvent composition. In the binary solvent mixture of water and DMSO reported in Chapter 2, no selective solvation was observed, indicating that on increasing the water content of the solvent mixture, DMSO is gradually displaced by water in the coordination sphere of Li\(^+\). We did not observe any rapid change in the position of the NMR signal when the amount of water was increased. DMSO is a solvent of high solvating ability which can strongly coordinate to the Li\(^+\) ion and can compete with water in the first coordination sphere of the Li\(^+\) ion. It could be concluded that the composition of the first coordination sphere in mixtures of H\(_2\)O/DMSO gradually changes from \([\text{Li(DMSO)}_4]^+\) to \([\text{Li(H}_2\text{O)}_4]^+\) on increasing the water content of the solvent.
This is a consequence of the rather similar donor strength of these solvents as expressed by their donor numbers.

In the binary water/acetonitrile mixture, however, water is coordinated stronger to Li\(^+\) than acetonitrile such that addition of water immediately leads to the formation of [Li(H\(_2\)O\(_4\))\(^+\)]. It was observed that the position of the NMR signal moved significantly (from 4.5 to 6.4 ppm) even if the amount of added water is very small (only 10 % H\(_2\)O). Then the chemical shift value increased slightly and stayed almost constant while the amount of water was changed from 10 to 100 %. This observation confirms that water coordinates much stronger to the Li\(^+\) ion than acetonitrile (Chapter 3).

Once the solvation shell of the Li\(^+\) ion was known, we wanted to investigate the exchange of certain solvent molecules around Li\(^+\). The Li\(^+\) ion, however, is very labile due to the low surface charge density and the absence of ligand field stabilization effects. Solvent exchange on Li\(^+\) is therefore extremely fast, making it difficult to study experimentally. The ligand exchange mechanism of Li\(^+\) ions solvated by DMSO and water/DMSO mixtures was studied using DFT calculations. Ligand exchange on [Li(DMSO)\(_4\)]\(^+\) was found to follow a limiting associative mechanism, whereas the displacement of coordinated H\(_2\)O by DMSO in [Li(H\(_2\)O)\(_4\)]\(^+\) follows an associative interchange mechanism.

In Chapter 3, we have extended our combined quantum chemical and experimental investigations of the ligand coordination and ligand exchange on Li\(^+\) in acetonitrile (CH\(_3\)CN) and HCN, as well as in CH\(_3\)CN/H\(_2\)O and HCN/H\(_2\)O mixtures.

We studied the ligand exchange process in more detail and report computational evidence for a limiting associative exchange mechanism on the HCN and CH\(_3\)CN solvated lithium cation. HCN was employed here as a simplified model to perform quantum chemical studies on CH\(_3\)CN. Our calculations corroborated the experimental work that the first coordination sphere around Li\(^+\) consists of four tightly bound CH\(_3\)CN and HCN molecules. Ligand exchange reactions on Li\(^+\) most probably follow an associative
mechanism as indicated by the formation of stable five-coordinate intermediates.

The class of ligands that were found to form stable complexes with alkali metals are macrocyclic ligands called cryptands. They were designed and shown to form stable alkali metal (i.e. lithium) cryptate complexes by inclusion into the three-dimensional molecular cavity. Here three cryptands, viz. C211, C221, and C222 were investigated.

In this work, we were particularly interested in the mechanistic aspects of the Li\(^+\) exchange process between cryptands and solvent. In preliminary experiments we investigated the Li\(^+\) exchange in different solvents. It was shown that the stability of the cryptate varies with the nature of the solvent. The stability tends to decrease as \(DN\) increases. In water and methanol the exchange process was too fast to be studied by \(^7\)Li NMR (only a single signal was observed). The process became slower in acetonitrile, and in acetone and \(\gamma\)-butyrolactone two completely separated signals were observed at low temperature. Therefore, these two solvents, viz. acetone and \(\gamma\)-butyrolactone, were chosen for more detailed mechanistic investigations.

In Chapter 4 we focused on acetone as a solvent and the competition between solvated and endohedral complexed Li\(^+\), reported kinetic parameters for the exchange of Li\(^+\) between solvated and complexed states in acetone under ambient and elevated pressure conditions, and discussed the mechanistic implications.

Initially, a series of \(^7\)Li NMR measurements for the Li\(^+\)-cryptand system in acetone were performed. The results enabled us to observe the distribution of particular species on variation of the concentration ratio. Basically, two signals of varying intensity were observed in the \(^7\)Li NMR spectra that refer to solvated Li\(^+\) and Li\(^+\) bound inside the cryptand cavity. In the case of the smallest chelate (C211), however, an additional signal appeared which could be ascribed to Li\(^+\) bound outside the cryptand and being partially solvated. This complex is very stable and almost no exchange took place. A detailed study of the observed rate
constant, \( k_{obs} \), for the exchange of Li\(^+\) as a function of temperature and pressure was therefore undertaken only for C221 and C222.

Stabilities of the cryptates increase in the sequence Li(C222)\(^+\) < Li(C221)\(^+\) < Li(C211)\(^+\), consistent with the six donor atoms of the C211 cavity and the optimal fit of Li\(^+\) \((r = 1.48 \, \text{Å})\) into the C211 cavity \((r = 1.6 \, \text{Å})\) in inclusive Li(C211)\(^+\), generating the largest stability. The increase in stability Li(C222)\(^+\) < Li(C221)\(^+\) indicates that the effect of the decrease in electrostatic interaction with Li\(^+\) resulting from the decrease in the number of donor atoms from 8 in C222 to 7 in C221 is offset by the smaller cavity size of C221, with the consequence that Li(C221)\(^+\) is the more stable cryptate. The more open and flexible structure of C222 accounts for the larger \( k_{obs} \) values that characterize Li(C222)\(^+\) by comparison with those of the relatively rigid inclusive Li(C211)\(^+\). These comparisons illustrate the interplay of the effects of the number of donor atoms and cryptand flexibility which produce variations in cryptate stability and lability.

Two mechanisms were considered for the decomplexation processes of cryptand-alkali metal complexes: bimolecular and unimolecular cation exchange.

The obtained results indicate that both pathways compete with each other and the competition is controlled by temperature and the nature of the cryptand. However, the unimolecular pathway seems to dominate, indicating the nonparticipation of solvated Li\(^+\) in the rate-determining step, resulting in the first order rate constant \( k_{-2} \). Based on the values of \( k_{-2} \) and the significantly negative activation entropies obtained for this pathway, the activation parameters support an associative type of exchange process. \( k_{-2} \) for C222 is almost three orders of magnitude larger than for C221. The negative activation entropies found for the decomplexation reactions of both C221 and C222 strongly suggest that attack of the solvent on the complexed Li\(^+\) must play an important role in the decomplexation process, i.e. decomplexation follows an associative mechanism.
6. Summary

Additional mechanistic information on the intimate nature of the exchange mechanism can in principle be obtained from the effect of pressure on the Li$^+$ exchange process. It could be observed that there was a very small difference in the shape of the NMR spectra recorded at various pressures. The observed rate constants calculated for each pressure were very similar within the experimental error limits and resulted in a practically zero value for $\Delta V^\ast_{\text{obs}}$ for both ligands, which points to a concerted interchange type of exchange mechanism. In terms of an interchange mechanism, bond formation and bond cleavage occur in a concerted fashion without the formation of a distinct intermediate of higher or lower coordination number. In addition, decomplexation will be accompanied by charge creation due to the release of Li$^+$, which in turn will lead to an increase in electrostriction which will offset the intrinsic volume changes.

It is not invariably the case that the unimolecular mechanism operates in cryptate systems. This is exemplified by the system in $\gamma$-butyrolactone, for which the Li$^+$ exchange process follows rather the bimolecular mechanism in which also solvated Li$^+$ is involved and therefore the concentration of Li$^+$ is taken into account in the rate law.

In Chapter 5, we report kinetic parameters for the exchange of Li$^+$ in $\gamma$-butyrolactone under ambient and elevated pressure conditions, and discuss their mechanistic implications. $\gamma$-Butyrolactone was chosen as solvent due to its relevance in lithium batteries where it is used as plasticizer.

It could also be seen in this system that both pathways, bimolecular and unimolecular compete with each other. However, the bimolecular pathway seems to predominate, indicating participation of solvated Li$^+$ in the rate-determining step, resulting in the second order rate constant $k_1$. Involvement of the solvent in the decomplexation process was found to be less pronounced than it was in the case of acetone. This is probably due to the fact that although both solvents, acetone and $\gamma$-butyrolactone should coordinate to the naked Li$^+$ cation comparatively strongly, it cannot be observed in the process in which Li$^+$ must be released from the cryptand cavity. In this case the steric hindrance
should be taken into account, \textit{i.e.} acetone as a sterically less demanding molecule has probably better access to the Li\textsuperscript{+} complexed by the cryptand as \(\gamma\)-butyrolactone does. Therefore, second order rate constants were obtained for both ligands, as a consequence of participation of the solvated Li\textsuperscript{+} in the decomplexation process.

Based on the values of \(k_1\) and the significantly negative activation entropies obtained for this pathway, the activation parameters support an associative interchange type of exchange process. The effect of pressure was found to be not very significant for these systems and resulted in a practically zero value for \(\Delta V^\#_{\text{obs}}\), which points to a concerted interchange type of exchange mechanism.

This work clearly demonstrated that the ligand structure and solvent properties have considerable effects on the reaction rate and the exchange mechanism of the cation between the solvated and the complexed sites. The stability of the cryptate complexes depends to a large extent on the size relationship between the three-dimensional cavity of the cryptand and the diameter of the complexed ion. The relative stabilities of cryptates depend on the electrostatic interactions between metal ions and cryptands, the solvation energies of metal ions and cryptands, and the fit of the metal ion into the cryptand cavity.

In general it can be concluded that the present thesis has shown in a systematic manner that the combination of experimental (dynamic \(^7\text{Li} \text{NMR})\) and theoretical (DFT) methods represents a powerful tool that enabled us to gain valuable qualitative and quantitative insight into mechanistic details of the coordination behavior of lithium cations and cryptands in different solvents. To the best of our knowledge, this was for the first time that mechanistic investigations on complex-formation reactions by cryptands were carried out using high pressure NMR techniques, in particular \(^7\text{Li} \text{NMR}.\) The results presented here give a promising outlook in terms of the possibility to investigate further lithium ion technologically relevant systems by the methods used in this study.
7. Zusammenfassung


Folgende drei grundsätzliche Fragen wurden angegangen:

Wie wird die erste Koordinationssphäre um das Lithiumion von der Natur des Lösungsmittels beeinflusst?

Wie wird das Lösungsmittel zwischen der ersten und der zweiten Koordinationssphäre des Lithiumions ausgetauscht?

Wie wird das Lithiumion von verschiedenen Kryptanden komplexiert und wie ist der Mechanismus des Lithiumaustausches zwischen Kryptand und Lösungsmittel.

Die gesteckten Ziele wurden aus der mikroskopischen Perspektive angegangen. Anwendung fanden hier sowohl experimentelle Methoden (\(^7\)Li NMR) als auch quantenchemische Rechnungen. Die ersten beiden oben genannten Fragestellungen bilden den Kern der Kapitel 2 und 3, während die erhaltene Ergebnisse des dritten Themas in den Kapitel 4 und 5 beschrieben sind.

Wie aus der Literatur bereits bekannt war, stellt \(^7\)Li NMR Spektroskopie eine sehr leistungsstarke Methode zur Untersuchung von Alkalimetallionen in makrozyklischen Liganden, besonders in nichtwässrigen Lösungen dar. In der vorgelegten Arbeit wird hierbei besondere Aufmerksamkeit der Hochdruck \(^7\)Li NMR Spektroskopie gewidmet. Sie wird hier zum ersten Mal für Untersuchungen an Kryptaten benutzt. Es wurde weiterhin gezeigt, dass die \(^7\)Li
NMR Spektroskopie eine sehr leistungsstarke Methode zur Bestimmung der Koordinationszahl des Lithiumions als auch zur Untersuchung der selektiven Solvatation in gemischten Lösungsmitteln ist. Diese Methode wurde auch für mechanistische Untersuchungen benutzt, hier konkret für den Lithiumionenaustausch zwischen solvatisierten und chelatisierten Spezies.

Lösungsmittel von verschiedenen Eigenschaften und ihr Einfluss auf die Solvatationshülle wurden untersucht. Das Problem der selektiven Solvatation um das Lithiumion und die Koordinationszahl des Lithiumions wurden als Funktion der Lösungsmittel Eigenschaften studiert. Die Donorzahl nach Gutmann \((DN)\) wurde meistens als der Faktor eingesetzt, der die Fähigkeit des Lösungsmittels als Donor zu agieren charakterisiert.

Um die Koordinationszahl des Lithiumkations zu bestimmen, wurde eine Lösung vorbereitet, die aus einem Gemisch von schwach und stark koordinierenden Lösungsmitteln bestand. In Kapitel 2 wurde gezeigt, dass das Lithiumion in DMSO von 4 Lösungsmittelmolekülen koordiniert wird. Wir konnten zeigen, dass \(\gamma\)-Butyrolakton ein gut geeignetes Verdünnungsmittel für derartige Untersuchungen ist. Im Gegensatz zu DMSO \((DN = 29.8)\), stellt \(\gamma\)-Butyrolakton einen eher schwachen Donor \((DN = 18.0)\) dar. Es löst die Salze der Alkalimetalle in merklicher Weise, wobei die Wechselwirkung mit den DMSO-Molekülen wesentlich schwächer ist als die zwischen DMSO und den Metallkationen. Durch graphische Auftragung der chemischen Verschiebung des \(^7\)Li NMR Signals gegen das Molverhältniss von DMSO/LiClO\(_4\) konnte ein deutlicher Bruch in der Kurve bei einem Molverhältniss von 4:1 beobachtet werden. Dies deutet auf eine Koordinationszahl von 4 für Li\(^+\) in DMSO hin. Die Anwendung dieser Methode auf ein Lösungsmittelgemisch bestehend aus Acetonitril \((DN = 14.1)\) und Nitromethan \((DN = 2.7)\) ergab ebenfalls eine vierfache Koordination des Lithiumkations in Acetonitril Lösung, wie im Kapitel 3 berichtet wird.

Selektive Solvatation der Alkalimetallionen in Lösungsmittelgemischen kann anhand der Veränderung der chemischen Verschiebung des Alkalimetallkerns in Abhängigkeit mit der Zusammensetzung des
7. Zusammenfassung


DMSO ist ein Lösungsmittel mit großer Solvatationsfähigkeit, das das Lithiumion stark koordinieren kann, und deswegen mit Wasser in der ersten Koordinationssphäre des Lithiumions konkurriert. Es kann die Schlussfolgerung gezogen werden, dass sich die Zusammensetzung der ersten Koordinationssphäre in Gemischen von $\text{H}_2\text{O}/\text{DMSO}$ mit zunehmendem Wassergehalt im Lösungsmittelgemisch schrittweise von $[\text{Li(DMSO)}_4]^+$ zu $[\text{Li(H}_2\text{O)}_4]^+$ ändert. Dies lässt auf eine ähnliche Donorstärke dieser Lösungsmittel schließen, wie sie sich auch aus ihren Donorzahlen ergibt.

In binären Gemischen von Wasser und Acetonitril ist jedoch Wasser zum Lithiumion stärker koordiniert als Acetonitril, so dass die Zugabe von Wasser sofort zur Bildung von $[\text{Li(H}_2\text{O)}_4]^+$ führt. Wir beobachteten, dass sich die Position des NMR-Signals signifikant ändert (4.5 zu 6.4 ppm) sogar wenn die Menge des zugegebenen Wassers sehr gering ist (nur 10 % $\text{H}_2\text{O}$). Danach erhöhte sich die chemische Verschiebung nur moderat und blieb konstant während die Menge des Wassers von 10 % auf 100 % gesteigert wurde. Diese Beobachtung bestätigt, dass Wasser viel stärker als Acetonitril an das Lithiumion koordiniert (Kapitel 3).

Nachdem die Solvatationshülle des Lithiumions aufgeklärt wurde, wollten wir den Austausch von bestimmten Lösungsmittelmolekülen um das Lithiumion untersuchen. Das Lithiumkation ist jedoch wegen seiner geringen Oberflächenladungsdichte und fehlenden Ligandenfeldstabilisierungseffekten sehr labil. Der Lösungsmittelau斯塔usch am Lithiumion ist deswegen extrem schnell und experimentell schwierig zu untersuchen. Der Ligandenaustauschmechanismus an dem von DMSO und Wasser/DMSO-
Gemischen solvatisierten Lithiumion wurde mittels DFT-Rechnungen untersucht. Es wurde gefunden, dass der Lösungsmittelaustausch an $[\text{Li(DMSO)}_4]^+$ durch einen reinen assoziativen Mechanismus (A) erfolgt, während die Substitution von koordiniertem Wasser durch DMSO in $[\text{Li(H}_2\text{O)}_4]^+$ durch einen assoziativen Interchange Mechanismus erfolgt.

Im Kapitel 3 erweiterten wir unsere kombinierten quantenchemischen und experimentellen Untersuchungen der Ligandenkoordination und des Ligandenaustausches auf das Lithiumion in CH$_3$CN und HCN, wie auch auf CH$_3$CN/H$_2$O und HCN/H$_2$O Gemische.

Wir studierten die Ligandenaustauschprozesse detaillierter und konnten quantenchemische Hinweise für einen reinen assoziativen Austauschmechanismus an dem von HCN und CH$_3$CN solvatisierten Lithiumion finden. HCN wurde hier als ein vereinfachtes Modell für quantenchemische Untersuchungen von CH$_3$CN eingesetzt. Unsere Rechnungen untermauerten zusätzlich die experimentellen Ergebnisse, dass die erste Koordinationssphäre um das Lithiumion aus vier koordinierten CH$_3$CN- und HCN-Molekülen besteht. Ligandenaustauschreaktionen am Lithiumion erfolgen am wahrscheinlichsten durch einen assoziativen Mechanismus, worauf die Bildung von stabilen fünffach-koordinierten Intermediaten hindeutet.

Wie bereits ausgeführt, bilden Kryptanden mit Alkalimetallionen stabile Komplexe, sog. Kryptate. Wir haben drei Kryptanden untersucht: C211, C221 und C222.

7. Zusammenfassung

In Acetonitril ist der Prozess langsamer geworden, und in Aceton und γ-Butyrolakton konnten zwei vollständig getrennte Signale bei tiefen Temperaturen beobachtet werden. Infolgedessen wurden diese zwei Lösungsmittel (Aceton und γ-Butyrolakton) für weitere detaillierte mechanistische Untersuchungen ausgewählt.

Im Kapitel 4 konzentrierten wir uns auf Aceton als Lösungsmittel und auf die Konkurrenz zwischen solvatisiertem und endohedral komplexiertem Lithiumion. Darüber hinaus wird in diesem Kapitel über kinetische Parameter für den Lithiumionenaustausch zwischen solvatisiertem und komplexiertem Zustand in Aceton unter Umgebungs- und Hochdruckbedingungen berichtet und mechanistische Folgerungen werden gezogen.

Zunächst wurde eine Serie von 7Li NMR-Messungen für das System Li+/Kryptand durchgeführt. Die erhaltenen Ergebnisse ermöglichten uns die Verteilung konkreter Spezies in Abhängigkeit von Konzentrationsänderungen zu beobachten. Es wurden zwei Signale von variierender Intensität in den 7Li NMR-Spektren beobachtet, die auf das solvatisierte und das im Kryptandenhohlraum gebundene Lithiumion zurückgeführt werden können. Im Falle des kleinsten Kryptanden (C211) erschien aber auch ein zusätzliches drittes Signal, das auf das von außen gebundene und damit nur teilweise solvatisierte Lithiumion zurückgeführt werden könnte. Der Li(C211)-Komplex ist sehr stabil und es fand fast kein Austausch statt. Eine detaillierte Studie der beobachteten Geschwindigkeitskonstante \( k_{obs} \) für den Lithiumionenaustausch als Funktion von Temperatur und Druck wurde deswegen nur für C221 und C222 durchgeführt.

Die Stabilität der Kryptate nimmt in der Reihenfolge Li(C222)+ < Li(C221)+ < Li(C211)+ zu. Dies ist im Einklang mit den sechs Donoratomen des Hohlraums von C211 und damit, dass das Lithiumion (\( r = 1.48 \text{ Å} \)) optimal in den Hohlraum von C211 (\( r = 1.6 \text{ Å} \)) passt. Die zunehmende Stabilität Li(C222)+ < Li(C221)+ < Li(C211)+ weist darauf hin, dass die Abnahme der Anzahl der Donoratome von 8 in C222 auf 7 in C221 durch den kleineren Hohlraum von C221 ausgeglichen wird. Dementsprechend ist Li(C221)+ der stabilere Kryptat.
Die flexiblere Struktur von C222 hat den größeren \( k_{\text{obs}} \)-Wert zu Folge, der für Li(C222)\(^+\) charakteristisch ist, im Vergleich zu den Werten für den relativ starren Li(C211)\(^+\) Einschlußkomplex. Diese Vergleiche stellen die Folgen der unterschiedlichen Zahl von Donoratomen in Kombination mit der Flexibilität des Kryptanden gut dar. Sie haben eine unterschiedliche Stabilität bzw. Labilität der Kryptate zur Folge.

Es wurden zwei Mechanismen für den Dekomplexierungsprozess von Alkalimetal-Kryptatkomplexen in Aceton in Betracht gezogen: der bimolekulare und der unimolekulare Kationenaustausch. Die Ergebnisse deuten darauf hin, dass beide Prozesse miteinander konkurrieren und von der Temperatur und der Natur des Ligandes gesteuert werden. Allerdings scheint der unimolekulare Prozess dominant zu sein, was auf die Nichtbeteiligung des solvatisierten Lithiumions im geschwindigkeitsbestimmenden Schritt hindeutet und was in einer Geschwindigkeitskonstante erster Ordnung resultiert. Basierend auf den für diesen Prozess erhaltenen Geschwindigkeitskonstanten und signifikant negativen Aktivierungsentropien, kann auf einen assoziativen Austauschprozess geschlossen werden. Die Geschwindigkeitskonstante für C222 ist fast um drei Größenordnungen größer als für C221. Die negativen Aktivierungsentropien, die für die Dekomplexierungsreaktionen von C221 und C222 beobachtet wurden, deuten stark darauf hin, dass der Angriff des Lösungsmittels auf das komplexierte Lithiumion eine wichtige Rolle im Dekomplexierungsprozess spielt, d.h. die Dekomplexierung erfolgt durch einen assoziativen Mechanismus.

7. Zusammenfassung

Bildung und Spaltung der Li-Donor-Bindungen erfolgen konzertiert ohne Bildung eines eindeutigen Intermediats mit höherer oder niedrigerer Koordinationszahl. Durch die Dekomplexierung der Li⁺-Ionen erfolgt eine Freisetzung von beweglichen Landungsträgern, was auf der anderen Seite zu zunehmender Elektrostriktion führt, die die intrinsische Volumenänderungen ausgleicht.

Im Gegensatz zum unimolekularen Lithiumionenaustauschprozess bei in Aceton gelösten Li-Kryptatkomplexen finden wir im Fall von in γ-Butyrolacton gelösten Kryptaten eher einen bimolekularen Mechanismus. Dieser wird auch durch die Konzentration der solvatisierten Lithiumionen beeinflusst, dementsprechend muß auch die Lithiumkonzentration in die Geschwindigkeitsberechnung einbezogen werden.

Im Kapitel 5 berichten wir über kinetische Parameter für den Lithiumionenaustausch an in γ-Butyrolacton gelösten Kryptaten unter verschiedenen Drücken und diskutieren ihre Folgen für den Mechanismus. Die Wahl von γ-Butyrolacton als Lösungsmittel ergab sich aus dessen Bedeutung für Lithiumbatterien.

Hier wurde ebenfalls beobachtet, dass beide Prozesse, der bimolekulare und der unimolekulare, miteinander konkurrieren. Allerdings, ist in diesem Fall der bimolekulare Prozess dominant, was auf die Beteiligung des solvatisierten Lithiumions am geschwindigkeitsbestimmenden Schritt hindeutet und in einer Geschwindigkeitskonstante zweiter Ordnung resultiert. Die Beteiligung des Lösungsmittels am Dekomplexierungsprozess war geringer als im Falle des Acetons. Beide Lösungsmittel, Aceton und γ-Butyrolacton, koordinieren nicht komplexierte Lithiumkationen gleich gut. In Konkurrenz zwischen den hier untersuchten Kryptanden und den Lösungsmittelmolekülen um die Komplexierung kann dies jedoch nicht beobachtet werden. Da γ-Butyrolacton im Gegensatz zu Aceton sterisch anspruchsvoller ist, muß der Angriff auf ein im Kryptanden endohedral komplexiertes Li⁺-Ion als sterisch behindert angesehen werden. Somit spielen solvatisierte Li⁺-Ionen bei den Austauschprozessen eine größere Rolle als im Fall des Acetons. Dies zeigt die
für beide Liganden, C221 und C222, erhaltene Geschwindigkeitskonstanten zweiter Ordnung.

Die für diesen Prozess erhaltenen Geschwindigkeitskonstanten und die signifikant negativen Entropien, untermauern den assoziativen Interchange Charakter der untersuchten Reaktionen. Es konnte hierbei kein signifikanter Druckeinfluss beobachtet werden. Die $\Delta V_{\text{obs}}^*$-Werten sind nahezu Null und legen zusätzlich einen Interchange-Mechanismus (I) nahe.


Lebenslauf

Persönliche Daten:

Name: Ewa Maria Pasgreta
Geburtsdatum: 11. März 1976
Geburtsort: Więcbork (Polen)
Eltern: Urszula und Stefan Pasgreta
Staatsangehörigkeit: polnisch
Familienstand: ledig

Schulbildung:

September 1983 - Juni 1991 Grundschule in Runowo Krajeńskie, Polen
September 1991 - Juni 1995 Gymnasium in Bydgoszcz, Polen (abgeschlossen mit Abitur)

Studium:

Oktober 1995 - Juni 2001 Universität in Toruń, Polen
Chemiestudium mit dem Abschluss Dipl.-Chem.

November 2001 – December 2006 Friedrich-Alexander Universität Erlangen-Nürnberg,
Anfertigung der Promotion bei Prof. Dr. Dr. h.c. mult. Rudi van Eldik an der Institut für Anorganische Chemie

März 2007 Abschluss mit Promotion zum Dr. rer. nat.