

^7Li NMR Spectroscopy: a Tool for Determining Dimerization Constants and Averaged Dimerization Constants of the Monomer/Dimer Equilibrium of Hierarchical Helicates

Tobias Krüchel⁺,^[a] Steffen Schauerte⁺,^[a] Jinbo Ke,^[a] Marcel Schlottmann,^[a] Sandra Bausch,^[a] Xiaofei Chen,^[a] Christoph Räuber,^[a] Igor d’Anciães Almeida Silva,^[b] Thomas Wiegand,^[b, c] and Markus Albrecht^{*[a]}

^7Li nuclear magnetic resonance (NMR) spectroscopy is an ideal tool to study hierarchically assembled helicates of the form $\text{Li}[\text{Li}_3\text{L}_6\text{Ti}_2]$. Internally bound and external lithium ions can be well distinguished by solution- or solid-state NMR spectroscopy

and dimerization constants of the monomer/dimer equilibrium can be easily determined in solution. Averaged dimerization constants can be estimated in case of statistical mixtures of helicates formed from mixtures of ligands.

Introduction

Supramolecular chemistry may be described as multi-component chemistry. Two or more molecular species interact by non-covalent interactions to form well defined aggregates.^[1] If the assembly process of a supramolecular entity proceeds in a stepwise fashion with successive aggregation steps depending on each other, it represents an example of hierarchical (self)assembly. Such hierarchical assembly processes are important in nature as well as in chemistry. They offer an easy entry into the formation of complex functional structures starting from simple building blocks. Therefore it is important to gain a deeper understanding in basic principles of hierarchical assembly.^[2]

Since some time, we are studying hierarchically formed helicates.^[3,4,5] In contrast to related complexes described by others in the literature,^[6] our system shows a monomer-dimer equilibrium in solution.^[7] This allows to thoroughly investigate the energetics of the equilibrium and to use the equilibrium as a solvent-dependent molecular switch.^[8] Based on this, a

molecular balance^[9] for the estimation of solvent effects^[10] and for the determination of London dispersion effects in solution^[11] has been developed.^[12] In addition, the hierarchical helicates have been used as platform for switching selectivity of reactions and catalytic processes,^[13,14] for dendrimer assembly^[15] or for lithium dependent^[16] expandable/compressible spring-like^[17] switches^[18] (Figure 1).

Our hierarchical helicates are obtained from carbonyl substituted catechol ligands and appropriate metal ions (e.g. titanium(IV)) in the presence of lithium cations. Over the years a broad variety of differently substituted catechol ligands has been used.^[19]

In the crystal, the hierarchical helicates are exclusively present as the triple lithium bridged coordination compounds –

[a] T. Krüchel,⁺ S. Schauerte,⁺ J. Ke, Dr. M. Schlottmann, S. Bausch, Dr. X. Chen, Dr. C. Räuber, Prof. M. Albrecht
Institut für Organische Chemie
RWTH Aachen University
Landoltweg 1, D-52074 Aachen, Germany
E-mail: markus.albrecht@oc.rwth-aachen.de

[b] Dr. I. d’A. Almeida Silva, Prof. Dr. T. Wiegand
Max-Planck Institut für chemische Energiekonversion
Stiftstr. 34–36, D-45470 Mülheim/Ruhr, Germany

[c] Prof. Dr. T. Wiegand
Institut für Technische und Makromolekulare Chemie
RWTH Aachen University
Worringerweg 2, D-52074 Aachen, Germany

[⁺] Equally contributed to this article.

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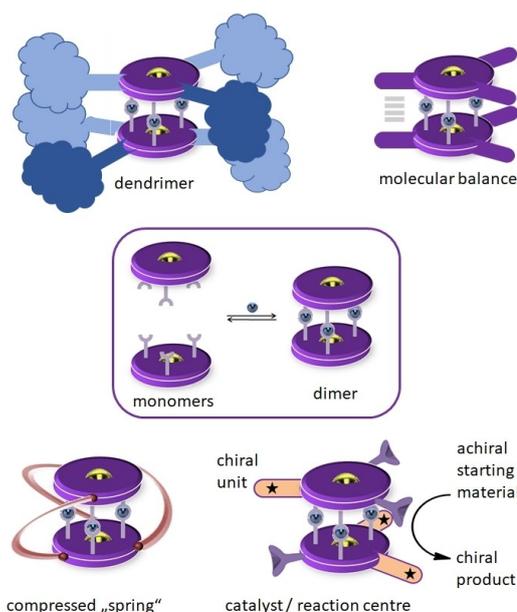
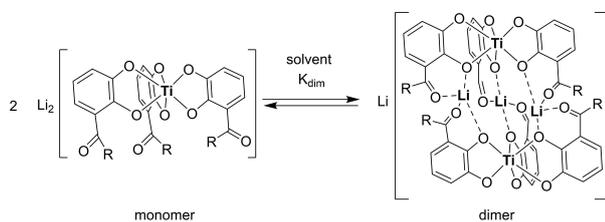


Figure 1. Schematic representation of the monomer-dimer equilibrium of catecholate based hierarchical helicates and use of the system for different purposes.

the “dimers”. In solution, a monomer-dimer equilibrium is observed which strongly depends on the substituent R at the catecholate ligand (R=H: aldehyde, R=R': ketone, R=OR': ester, R=SR': thioester). In addition, the solvent exerts considerable influence on the equilibrium (Scheme 1).^[7,19]

When the dimeric helicates are dissolved, they slowly dissociate into the monomer and finally the thermodynamic equilibrium is reached.^[20] Depending on this equilibrium, different ratios of coordinated and solvated lithium cations are present in solution. As exemplified in a very early study, the different lithium cations of $\text{Li}[\text{Li}_3\text{L}_6\text{Ti}_2]$ (R=H) can be distinguished by ^7Li solution-state NMR (in THF-d_6) for which resonances at $\delta=1.80$ (bridging/“bound” Li^+) and 0.41 ppm (solvated/“free” Li^+) have been observed.^[7] After this early study, ^7Li NMR has not been used again for the evaluation of the hierarchical helicates. This is unfortunate, because ^7Li NMR provides an excellent tool to explore the neighborhood of the bridging lithium cations^[21] and to determine dimerization constants of the hierarchical helicates. It is even possible to obtain averaged dimerization constants for mixtures of helicates formed from mixtures of ligands.^[22] In here, thorough ^7Li NMR spectroscopic studies in solution, as well as in the solid state are presented for hierarchically assembled catecholate based triple-lithium bridged titanium(IV) helicates.



Scheme 1. The monomer-dimer equilibrium of catecholate based hierarchical helicates showing solvated as well as bridging lithium cations. The bound lithium cations are shown in bold.

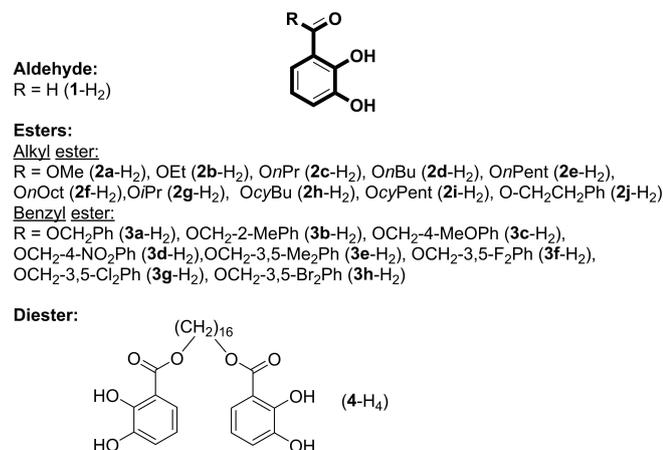


Figure 2. Catechol-based ligands discussed in this study.

Results and Discussion

^7Li Solution-State NMR Spectroscopy of Triple Lithium Bridged Hierarchical Helicates

A series of hierarchical helicates $\text{Li}[\text{Li}_3\text{L}_6\text{Ti}_2]$ with aldehyde 1 and ester-based ligands (2, 3) as well as a bridged complex $\text{Li}[\text{Li}_3\text{L}'_3\text{Ti}_2]$ (4) are investigated herein by ^7Li NMR spectroscopy (Figure 2).

The complexes $\text{Li}[\text{Li}_3\text{L}_6\text{Ti}_2]$ obtained from ligands 1-H₂-3-H₂ and $\text{Li}[\text{Li}_3\text{L}'_3\text{Ti}_2]$ from 4-H₄ were studied by using ^7Li solution-state NMR spectroscopy in methanol-d₄, acetone-d₆ and DMSO-d₆.

Chemical-Shift Effects Observed by ^7Li Solution-State NMR Spectroscopy

Two signals are typically observed by ^7Li NMR for the hierarchical helicates $\text{Li}[\text{Li}_3\text{L}_6\text{Ti}_2]$, a high-field shifted resonance corresponding to the solvated (“free”) and a low-field shifted one for the encapsulated (“bound”) lithium cations (Figure 3).^[7]

For example, the ^7Li NMR signals of the methyl ester $\text{Li}[\text{Li}_3\text{2a}_6\text{Ti}_2]$ ⁷ are observed at $\delta=1.36$ and -1.05 ppm (in methanol-d₄, Figure 3), 1.28 and -1.52 (DMSO-d₆) or at 1.50 and 1.21 ppm (acetone-d₆). Hereby, the separation of the chemical-shift values of the bound and free lithium cations strongly depends on the chosen solvent. Nevertheless, the chemical shift serves as a measure of the magnetic shielding of the lithium cation within the hierarchical helicate in comparison to the free cations. Figure 4 shows the representation of chemical-shift differences $\Delta\delta$ of complexes $\text{Li}[\text{Li}_3\text{L}_6\text{Ti}_2]$ as determined in methanol-d₆ (a), acetone-d₆ (b) or DMSO-d₆ (c) sorted by increasing $\Delta\delta$.

The $\Delta\delta$ -values depend on the solvents as well as on the substituents R. For ester-substituents in methanol-d₄, $\Delta\delta$ is ranging in-between 2.2–2.7 ppm, which is comparable to DMSO-d₆; with $\Delta\delta=2.5$ –3.0 ppm. Only acetone-d₆ shows significantly smaller values for $\Delta\delta=0.2$ –0.6 ppm.

The esters may be grouped into two different subclasses:

The **alkyl esters**^[11] (including the 2-phenylethyl ester) $\text{Li}[\text{Li}_3\text{2}_6\text{Ti}_2]$ show relatively small signal separations $\Delta\delta$

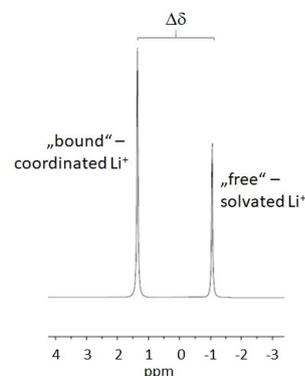


Figure 3. ^7Li NMR spectrum of $\text{Li}[\text{Li}_3\text{2a}_6\text{Ti}_2]$ in methanol-d₄.

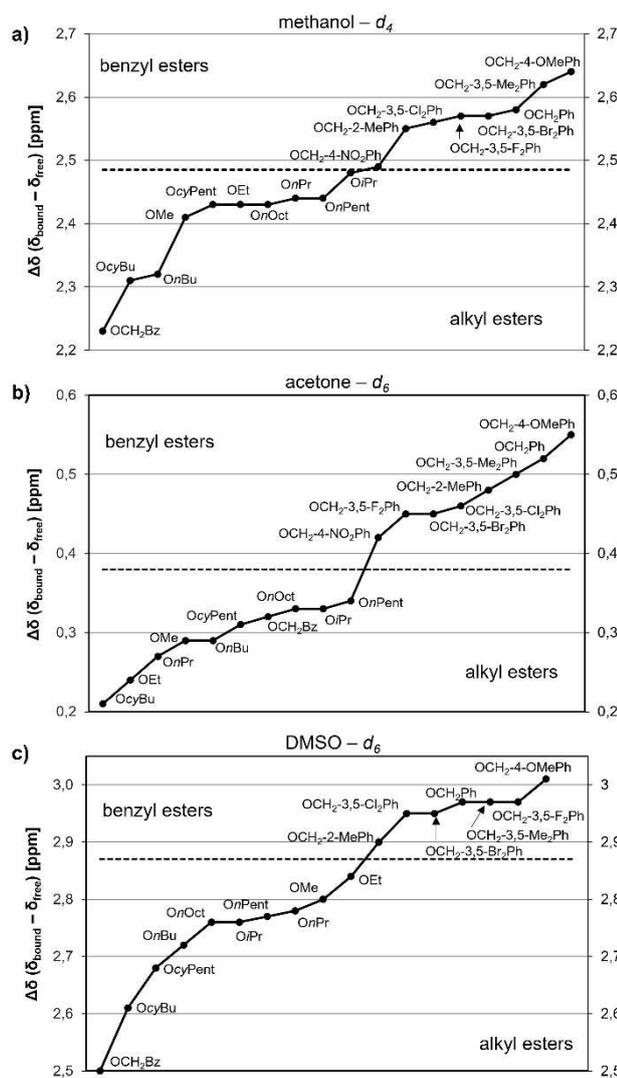


Figure 4. ^7Li NMR shift differences $\Delta\delta$ between the resonances of bound and free lithium cations of $\text{Li}[\text{Li}_3\text{L}_6\text{Ti}_2]$ as determined in methanol- d_4 (a), acetone- d_6 (b) and DMSO- d_6 (c).

(<2.5 ppm in methanol- d_4 , <0.4 ppm in acetone- d_6 and <2.9 ppm in DMSO- d_6).

The $\Delta\delta$ -values of the **benzyl esters**^[19] $\text{Li}[\text{Li}_3\text{C}_6\text{Ti}_2]$ are observed above the threshold given for the alkyl esters. The larger splitting of the resonances of the free and bound lithium cations in the benzylic-derivatives $\text{Li}[\text{Li}_3\text{C}_6\text{Ti}_2]$ is either due to an anisotropic effect of the phenyl group which probably is located in close proximity of the lithium cations. Alternatively, the electronic polarization at the benzylic methylene unit may influence the ^7Li NMR shift. With the elongated $\text{CH}_2\text{CH}_2\text{Ph}$ unit of $\text{Li}[\text{Li}_3\text{J}_6\text{Ti}_2]$ a similar orientation or electronic effect is not possible, since this substituent behaves like an alkyl group.

In addition, it is remarkable that $\Delta\delta$ of the benzylic systems $\text{Li}[\text{Li}_3\text{C}_6\text{Ti}_2]$ for sterically comparable moieties increases with increasing electron density at the aromatic unit (4- NO_2Ph ($\text{Li}[\text{Li}_3\text{3d}_6\text{Ti}_2]$) < Ph ($\text{Li}[\text{Li}_3\text{3a}_6\text{Ti}_2]$) < 4-MeOPh ($\text{Li}[\text{Li}_3\text{3c}_6\text{Ti}_2]$)). In DMSO- d_6 the dimer $\text{Li}[\text{Li}_3\text{3d}_6\text{Ti}_2]$ (4- NO_2Ph) was not observed, therefore $\Delta\delta$ could not be determined.

The aldehyde complex $\text{Li}[\text{Li}_3\text{1}_6\text{Ti}_2]/\text{Li}_2[\text{1}_3\text{Ti}]^7$ in methanol- d_4 as well as in DMSO- d_6 leads to the by far smallest $\Delta\delta$ -value (2.13 ppm in methanol- d_4 , 2.16 ppm in DMSO- d_6), while relative to the esters a much higher one is observed for the aldehyde in acetone- d_6 (0.28 ppm).

^7Li Solution-State NMR Spectroscopy for the Determination of Dimerization Constants

^7Li NMR also is a valuable tool for the evaluation of dimerization constants of hierarchical helicates. The resonances of bound and free lithium cations appear well separated and can be easily integrated. Thus, in a solution with a well-known concentration the lithium cations of the dimer show two signals with three ions bound in the complex (at low field) and one being a solvated counter-cation (at high field). The remaining integral of the signal of solvated ions is due to the presence of the monomer. From the ratio of monomer and dimer the dimerization constant is calculated from the equations shown in Scheme 2 (see also SI for more details).

Figure 5 depicts as representative examples of ^7Li NMR spectra the ones of $\text{Li}[\text{Li}_3\text{3d}_6\text{Ti}_2]$ ($\text{R} = \text{OCH}_2\text{-4-NO}_2\text{Ph}$) in DMSO- d_6 and of $\text{Li}[\text{Li}_3\text{2e}_6\text{Ti}_2]$ ($\text{R} = \text{On-pent}$) in methanol- d_4 ; as well as in DMSO- d_6 ; at concentrations of 2 mmol/L (the concentration corresponds to the initially introduced amount of dimer).

For $\text{Li}[\text{Li}_3\text{3d}_6\text{Ti}_2]$ in DMSO- d_6 only one signal is observed by ^7Li NMR at $\delta = -1.58$ ppm. This resonance corresponds to “free” solvated lithium cations. Here only the monomer $\text{Li}_2[\text{3d}_3\text{Ti}]$ is present in solution.

In case of $\text{Li}[\text{Li}_3\text{2e}_6\text{Ti}_2]$ two signals are found at $\delta = 1.36$ and -1.08 ppm (in methanol- d_4) or at 1.21 and -1.56 ppm (in DMSO- d_6). In methanol- d_4 the ratio of signal intensities is 3:1. This corresponds to the dimeric complex $\text{Li}[\text{Li}_3\text{2e}_6\text{Ti}_2]$. In DMSO- d_6 the observed ratio is 3:2.26. The latter integral represents the “free” lithium cation of the dimer $\text{Li}[\text{Li}_3\text{2e}_6\text{Ti}_2]$ (integral 1.0) and of the monomeric complex $\text{Li}_2\text{2e}_3\text{Ti}$ (integral 1.26). From this ratio, a dimerization constant of $K_{\text{dim}} = 1602 \pm 441 \text{ M}^{-1}$ is calculated for the monomer-dimer equilibrium of $\text{Li}_2\text{2e}_3\text{Ti}/\text{Li}[\text{Li}_3\text{2e}_6\text{Ti}_2]$ in DMSO- d_6 .

In methanol- d_4 or acetone- d_6 , the dimer is the dominating species. ^7Li NMR spectroscopy does not show significant amounts of monomer.

$$K_{\text{dim}} = \frac{3 \cdot I_{\text{solvated}} \cdot I_{\text{bound}} + 3 \cdot I_{\text{bound}}^2}{36 \cdot c_0 \cdot \left(\frac{I_{\text{solvated}} - \frac{I_{\text{bound}}}{3}}{2} \right)^2}$$

K_{dim}	dimerization constant
I_{solvated}	integral of the solvated Li^+ in the ^7Li -NMR spectrum
I_{bound}	integral of the bound Li^+ in the ^7Li -NMR spectrum

Scheme 2. Calculation of K_{dim} from the integral of the ^7Li -signals.

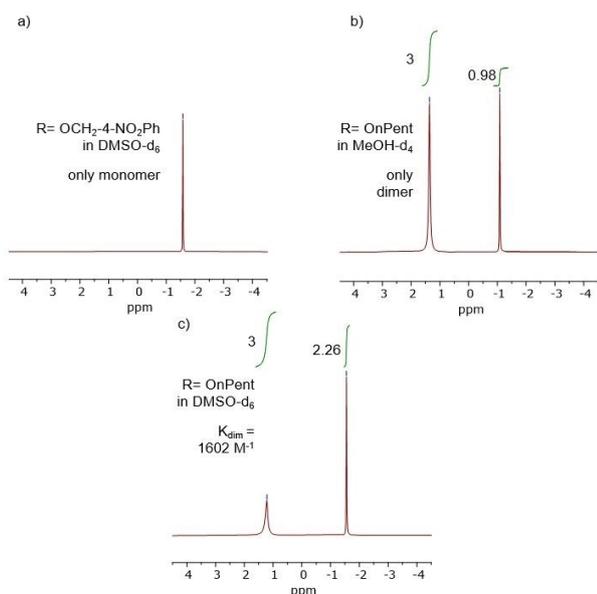


Figure 5. Representative ^7Li NMR spectra of $\text{Li}[\text{Li}_3\mathbf{2d}_6\text{Ti}_2]$ (in DMSO-d_6) (a) and of $\text{Li}[\text{Li}_3\mathbf{2e}_6\text{Ti}_2]$ in methanol- d_4 (b) as well as in DMSO-d_6 (c).

In DMSO-d_6 both monomer and dimer are easily observable for the ester-based systems. Therefore, a series of dimerization constants was determined in this solvent using ^1H as well as ^7Li NMR.

Table 1 reveals the dimerization constants of the helicates $\text{Li}[\text{Li}_3\mathbf{2}/\mathbf{3}_6\text{Ti}_2]$ in DMSO-d_6 showing similar values obtained by NMR of the two different nuclei (^1H or ^7Li). For comparison, the

Table 1. Dimerization constants K_{dim} of the ester-based helicates $\text{Li}[\text{Li}_3\mathbf{2}/\mathbf{3}_6\text{Ti}_2]$ determined by ^1H and ^7Li NMR in DMSO-d_6 at room temperature and 2 mmol/L of dimer concentration.			
R=	K_{dim} ^7Li NMR, M^{-1}	K_{dim} ^1H NMR, M^{-1}	
$\text{Li}[\text{Li}_3\mathbf{2a}_6\text{Ti}_2]$	OMe	120 ± 34	134 ± 19
$\text{Li}[\text{Li}_3\mathbf{2b}_6\text{Ti}_2]$	OEt	855 ± 216	930 ± 158
$\text{Li}[\text{Li}_3\mathbf{2c}_6\text{Ti}_2]$	OnPr	1236 ± 327	1142 ± 190
$\text{Li}[\text{Li}_3\mathbf{2d}_6\text{Ti}_2]$	OnBu	1431 ± 386	1217 ± 210
$\text{Li}[\text{Li}_3\mathbf{2e}_6\text{Ti}_2]$	OnPent	1602 ± 441	1900 ± 337
$\text{Li}[\text{Li}_3\mathbf{2f}_6\text{Ti}_2]$	OnOct	1539 ± 421	1806 ± 319
$\text{Li}[\text{Li}_3\mathbf{2g}_6\text{Ti}_2]$	OiPr	904 ± 230	949 ± 161
$\text{Li}[\text{Li}_3\mathbf{2h}_6\text{Ti}_2]$	OcyBu	147 ± 40	183 ± 27
$\text{Li}[\text{Li}_3\mathbf{2i}_6\text{Ti}_2]$	OcyPent	456 ± 112	481 ± 77
$\text{Li}[\text{Li}_3\mathbf{3a}_6\text{Ti}_2]$	OCH ₂ Ph	123 ± 34	146 ± 21
$\text{Li}[\text{Li}_3\mathbf{3b}_6\text{Ti}_2]$	OCH ₂ -2-MePh	62 ± 21	59 ± 7
$\text{Li}[\text{Li}_3\mathbf{3c}_6\text{Ti}_2]$	OCH ₂ -4-MeOPh	94 ± 28	104 ± 14
$\text{Li}[\text{Li}_3\mathbf{3d}_6\text{Ti}_2]$	OCH ₂ -4-NO ₂ Ph	monomer	monomer
$\text{Li}[\text{Li}_3\mathbf{3e}_6\text{Ti}_2]$	OCH ₂ -3,5-Me ₂ Ph	302 ± 75	378 ± 59
$\text{Li}[\text{Li}_3\mathbf{3f}_6\text{Ti}_2]$	OCH ₂ -3,5-F ₂ Ph	66 ± 22	70 ± 9
$\text{Li}[\text{Li}_3\mathbf{3g}_6\text{Ti}_2]$	OCH ₂ -3,5-Cl ₃ Ph	127 ± 35	122 ± 17
$\text{Li}[\text{Li}_3\mathbf{3h}_6\text{Ti}_2]$	OCH ₂ -3,5-Br ₂ Ph	108 ± 31	124 ± 17

data shown in Table 1 are represented as a graph in Figure 6. Within the error limit ^1H as well as ^7Li NMR spectroscopy show similar K_{dim} for the monomer-dimer equilibrium.

^7Li Solid-State NMR Spectroscopy of Hierarchical Helicates

In the solid state, the differentiation of encapsulated (bound) and free Li cations (coordinated by solvent molecules in the crystal) in the hierarchical helicates is achieved from the ^7Li chemical-shift values deduced from magic-angle spinning (MAS) solid-state NMR spectra. Figure 7a and b shows the ^7Li MAS spectra of $\text{Li}[\text{Li}_3\mathbf{2d}_6\text{Ti}_2]$ and $\text{Li}[\text{Li}_3\mathbf{3a}_6\text{Ti}_2]$ recorded at 16.4 T with 17.0 kHz MAS. For $\text{Li}[\text{Li}_3\mathbf{2d}_6\text{Ti}_2]$, two ^7Li resonances with isotropic chemical-shift values of 1.8 and 0.6 ppm assigned to the three crystallographically-identical encapsulated and the single free Li cations, respectively, were detected, which is in agreement with the observation of two resonances in the solution-state NMR spectra. In case of $\text{Li}[\text{Li}_3\mathbf{3a}_6\text{Ti}_2]$, three resonances with ^7Li chemical-shift values of 2.0, 0.7 and 0.1 ppm are observed. Those are assigned again to encapsulated and free Li cations. The two resonances for the free Li cations at lower frequencies are attributed to different Li coordination sites (*vide infra*). To determine the quadrupolar coupling information of the quadrupolar ^7Li nuclei ($I=3/2$), satellite-transition spectroscopy experiments (SATRAS)^[23] were performed. The quadrupolar coupling parameters determined from such spectra (the ^7Li quadrupolar coupling constant C_Q , as well as the asymmetry parameter η_Q) serve as sensitive probes for the electronic environments of the Li nuclei as well as for local dynamics. Figure 7c and 7d show the comparison of the

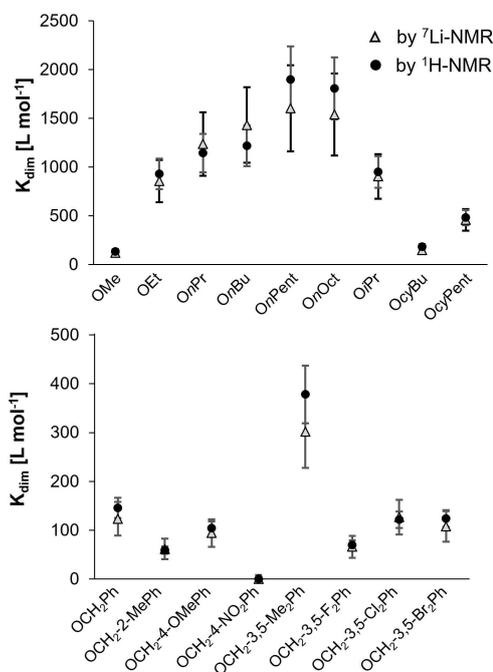


Figure 6. Comparison of dimerization constants K_{dim} of the alkyl $\text{Li}[\text{Li}_3\mathbf{2}_6\text{Ti}_2]$ (a) and benzyl ester complexes $\text{Li}[\text{Li}_3\mathbf{3}_6\text{Ti}_2]$ (b) obtained by ^7Li (square) and ^1H NMR (circle) in DMSO-d_6 .

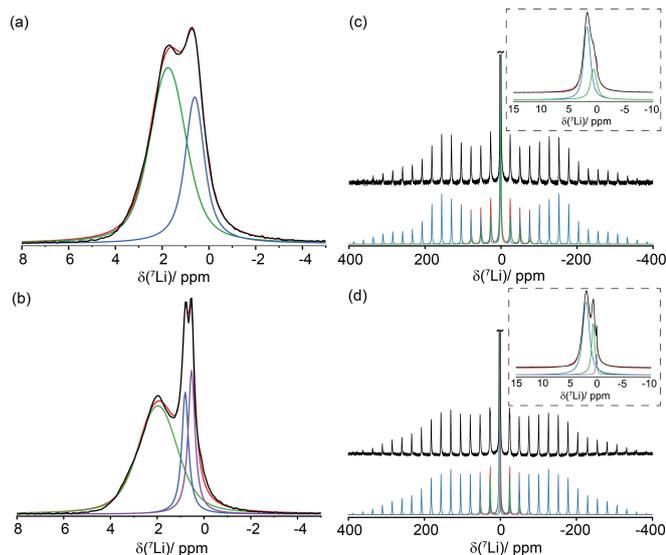


Figure 7. ^7Li solid-state NMR spectra of samples $\text{Li}[\text{Li}_3 2 \mathbf{d}_6 \text{Ti}_2]$ (a) and $\text{Li}[\text{Li}_3 3 \mathbf{a}_6 \text{Ti}_2]$ (b) recorded at 17.0 kHz MAS and 16.4 T magnetic-field strength with their respective numerical deconvolutions (coloured lines). (c) and (d) show the ^7Li SATRAS NMR spectra of samples $\text{Li}[\text{Li}_3 2 \mathbf{d}_6 \text{Ti}_2]$ (c) and $\text{Li}[\text{Li}_3 3 \mathbf{a}_6 \text{Ti}_2]$ (d) recorded at 5.0 kHz MAS and 11.7 T magnetic-field strength with their respective numerical deconvolutions (coloured lines). Zooms into the central transition are given in addition. The simulations only take the first-order quadrupolar interaction into account, which explains small deviations compared to the experimental spectrum, e.g. for the first MAS sideband.

experimental spectra with the simulated ones. For $\text{Li}[\text{Li}_3 2 \mathbf{d}_6 \text{Ti}_2]$, the ^7Li resonance at 1.8 ppm possesses a C_Q -value of 145 kHz ($\eta_Q=0.2$), whereas the C_Q -value for the second resonance at 0.6 ppm is much smaller ($C_Q=30$ kHz). The first resonance corresponds to encapsulated Li species and the latter to free species, in which the Li nuclei possess different electronic environments and thus C_Q -values. Similar conclusions can be drawn for $\text{Li}[\text{Li}_3 3 \mathbf{a}_6 \text{Ti}_2]$ (Figure 7d). The resonance at 2.00 ppm with the largest C_Q -value of 140 kHz and η_Q of 0.35 is again assigned to the encapsulated Li species, while the resonances at 0.7 ppm ($C_Q=20$ kHz) and at 0.1 ppm ($C_Q=40$ kHz) are assigned to free Li species. The two resonances for the free species are attributed to Li^+ atoms bound to terminal catechol oxygen atoms as well as solvent molecules and to “solvated” Li^+ species only. Binding of Li^+ to the terminus of the hierarchical helicates was frequently observed in crystal structures of the complexes.^[19]

Expandable/Compressible Helicates

Besides the simple monocatechol-ester ligands the alkyl (4- H_4) bridged dicatechol has been used to obtain an expandable/compressible helicate $\text{Li}[\text{Li}_3 4_3 \text{Ti}_2]$ which in its compressed state bears three internal bridging lithium cations.

Hereby we observed that alkyl bridged dicatechol esters with alkyl bridges with 8–12 CH_2 units only form the compressed helicates. Those expand by decomplexation of the lithium cations using [2.1.1] cryptand.^[16]

Now the hexadecyl-bridged ligand 4- H_4 has been prepared. In the ^1H NMR spectrum of the complex $\text{Li}[\text{Li}_3 4_3 \text{Ti}_2]$ in DMSO-d_6 the typical signals of the compressed helicate are observed as it is shown in Figure 8b for the catechol protons marked with a. In addition, a minor second set of signals (denoted with b) appears.

Due to the characteristic chemical shift,^[11] set b of the signals is assigned to the expanded species $\text{Li}_4[4_3 \text{Ti}_2]$ which is in equilibrium with the compressed one (set a). Integration of the ^1H NMR spectrum shows a ratio of 1:0.3 for compressed to expanded helicate. This finding is supported by the ^7Li NMR spectrum in which a ratio of bound to free lithium cations of 3:2.31 is observed corresponding to a ratio of 1:0.3 of $\text{Li}[\text{Li}_3 4_3 \text{Ti}_2] : \text{Li}_4[4_3 \text{Ti}_2]$.

Averaged Dimerization Constants of Hierarchical Helicates Obtained from Ligand Mixtures

The formation of heteroleptic hierarchical helicates possessing two (or more) different catechol ligands leads to statistical mixtures of complexes. Such mixtures having distinct kinds of ligands in the complexes are of interest for reaction control or catalysis.^[22]

Figure 9 shows as an example the negative ESI MS spectra of three different mixtures of $\text{Li}[\text{Li}_3 3 \mathbf{c}_n 3 \mathbf{d}_m \text{Ti}_2]$ ($n+m=6$) obtained with the ligand ratios $3 \mathbf{c} : 3 \mathbf{d} = 5:1$, $3:3$; and $1:5$; The change of the maximum of the distribution of complexes $\text{Li}[\text{Li}_3 3 \mathbf{c}_n 3 \mathbf{d}_m \text{Ti}_2]$ in the mixture depending on the used ratio of the ligands is nicely observed.

Nevertheless, in solution the monomer-dimer equilibrium still is found for the mixture of heteroleptic hierarchical helicates $\text{Li}[\text{Li}_3 \mathbf{L}_1 \mathbf{L}_2 \text{Ti}_2]$. The ^1H NMR spectrum of the mixture is extremely complicated and cannot be interpreted. On the other hand, ^7Li NMR does allow to estimate the ratio between monomeric and dimeric species (Figure 8c) and even an

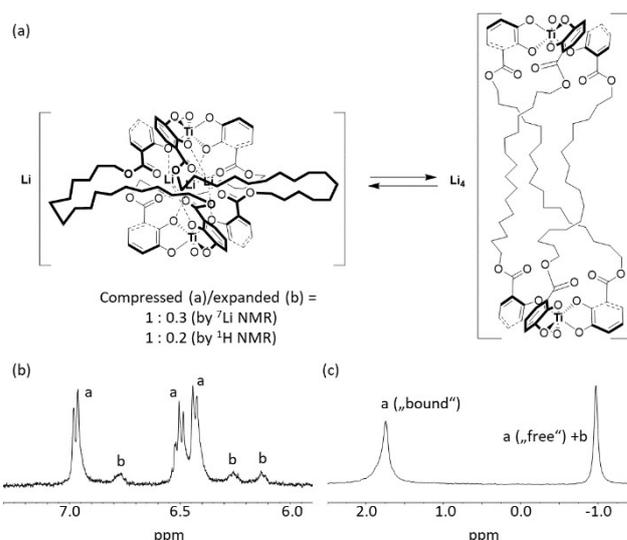


Figure 8. Equilibrium of the compressed and expanded form of $\text{Li}[\text{Li}_3 4_3 \text{Ti}_2]$ (a) which can be observed by ^1H (b, only aromatic region is shown) and ^7Li NMR (c). Solvent: DMSO-d_6 .

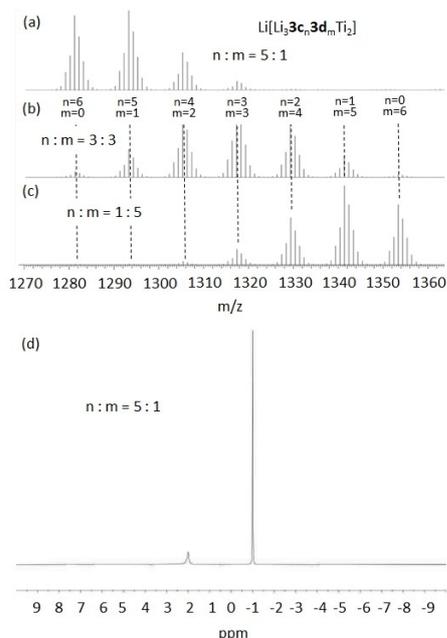


Figure 9. Negative ESI MS (MeOH) of mixtures of complexes $\text{Li}[\text{Li}_3\text{c}_n\text{3d}_m\text{Ti}_2]$ ($n+m=6$) obtained with the ligand ratios $3\text{c}:3\text{d}=5:1$ (a), $3:3$ (b) and $1:5$ (c) as well as the ^7Li NMR spectrum of $\text{Li}[\text{Li}_3\text{c}_5\text{3d}_1\text{Ti}_2]$ ($n:m=5:1$) in DMSO-d_6 (d).

averaged dimerization constant is calculated for the dimerization of the triscatecholates by ignoring the difference at the substituents.

Figure 9d shows as an example the ^7Li NMR spectrum of $\text{Li}[\text{Li}_3\text{c}_5\text{3d}_1\text{Ti}_2]$ ($n:m=5:1$) in DMSO-d_6 . It reveals only one averaged signal for internally bound lithium cations at $\delta = 2.0$ ppm, although a mixture of dimeric helicates is present (see ESI MS). Besides this signal the resonance of the solvated lithium cations appears around $\delta = -1$ ppm. From the ratio of the signal intensities an averaged dimerization constant of $K_{\text{dim}}(\text{av}) = 95 \text{ M}^{-1}$ is estimated.

Figure 10 shows the dependence of the averaged dimerization constant on the ratio between the two ligands 3c and 3d . The homoleptic complex $\text{Li}[\text{Li}_3\text{3c}_6\text{Ti}_2]$ reveals a dimerization constant of $K_{\text{dim}} = 94 \text{ M}^{-1}$ similar to the one of the $5:1$ complex $\text{Li}[\text{Li}_3\text{c}_5\text{3d}_1\text{Ti}_2]$ ($n:m=5:1$). However, starting with Li -

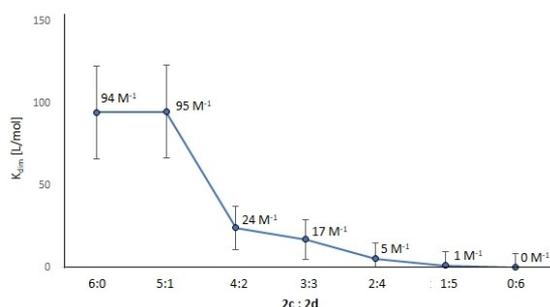


Figure 10. Averaged dimerization constants of complex mixtures $\text{Li}[\text{Li}_3\text{c}_n\text{3d}_m\text{Ti}_2]$ ($n+m=6$) with two different ligands 3c and 3d depending on the ratio of the ligands.

$[\text{Li}_3\text{c}_n\text{3d}_m\text{Ti}_2]$ ($n:m=4:2$) K_{dim} drops dramatically to 24 M^{-1} . Further change of the ligand ratio in favour of 3d results in further minor reduction of K_{dim} and finally the homoleptic complex of 3d forms exclusively as the monomer $\text{Li}_2\text{3d}_3\text{Ti}$. Thus, the least stabilizing ligand 3d seems to have the highest impact on the dimerization constants in the heteroleptic (mixed) complexes.

A similar behaviour as observed for $\text{Li}[\text{Li}_3\text{c}_n\text{3d}_m\text{Ti}_2]$ ($n+m=6$) is found by mixing the ligands 3a and 3d .

In case of the ligands 3a and 3c the homoleptic complexes $\text{Li}[\text{Li}_3\text{3a}_6\text{Ti}_2]$ and $\text{Li}[\text{Li}_3\text{3c}_6\text{Ti}_2]$ show - within the error - similar dimerization constants of 123 or 94 M^{-1} , respectively. Consequently, the mixed complexes show a similar dimer stability.

The destabilization of the dimeric complexes by the least stabilizing ligand also takes place for the alkyl substituted ester complexes with the ligand pairs $2\text{g}/2\text{h}$, $2\text{i}/2\text{e}$ and $2\text{i}/2\text{f}$ (Figure 11).

In conclusion it can be stated that ^7Li NMR is a simple, but very effective tool to study the monomer/dimer equilibrium of catechol based hierarchical helicates and of related lithium dependent molecular switches in solution. The ^7Li NMR signals of the internally bound (encapsulated) and the external (free) lithium cations are well separated. Their chemical-shift differences report on the shielding of the internally bound lithium cations and allow distinguishing between alkyl and benzyl ester substituted catechol ligands. From the integration of the ^7Li NMR signals, dimerization constants are estimated. This is even possible for mixtures of complexes resulting in averaged dimerization constants. Solid-state ^7Li MAS NMR is also sufficiently sensitive to reveal the difference in the chemical shift of internal and external lithium cations complementing crystallographic studies.

Furthermore, expendable/compressible switches based on a tethered "hierarchical helicate" can be well investigated showing the ratio between expanded and compressed species.

In summary, here we present an analytical tool which makes it easy to study lithium bridged hierarchical helicates even if ^1H NMR spectroscopy does not give useful information. Thus, it is expected that this technique will be able to help solving some mysteries which up to now can be tentatively explained but are not fully

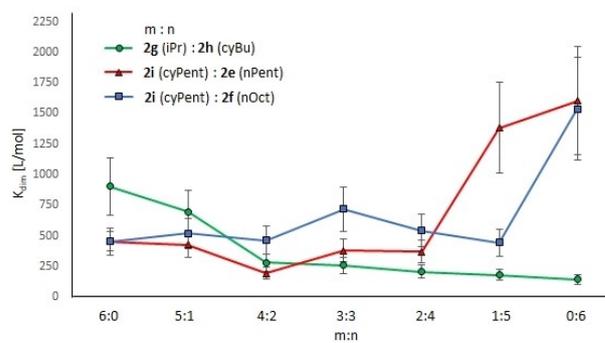


Figure 11. Averaged dimerization constants of complex mixtures $\text{Li}[\text{Li}_3\text{L}_1\text{nL}_2\text{mTi}_2]$ with two different ligands (circle: $2\text{g}/2\text{h}$, triangle: $2\text{i}/2\text{e}$ and square: $2\text{i}/2\text{f}$) depending on the ratio of the two ligands $m:n$.

understood.^[24] ⁷Li NMR is a valuable tool to investigate supramolecular systems containing lithium cations as components.

Conclusion

In conclusion it can be stated that ⁷Li NMR is a simple, but very effective tool to study the monomer/dimer equilibrium of catechol based hierarchical helicates and of related lithium dependent molecular switches in solution. The ⁷Li NMR signals of the internally bound (encapsulated) and the external (free) lithium cations are well separated. Their chemical-shift differences report on the shielding of the internally bound lithium cations and allow distinguishing between alkyl and benzyl ester substituted catechol ligands. From the integration of the ⁷Li NMR signals, dimerization constants are estimated. This is even possible for mixtures of complexes resulting in averaged dimerization constants. Solid-state ⁷Li MAS NMR is also sufficiently sensitive to reveal the difference in the chemical shift of internal and external lithium cations complementing crystallographic studies.

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In summary, here we present an analytical tool which makes it easy to study lithium bridged hierarchical helicates even if ¹H NMR spectroscopy does not give useful information. Thus, it is expected that this technique will be able to help solving some mysteries which up to now can be tentatively explained but are not fully understood.^[24] ⁷Li NMR is a valuable tool to investigate supramolecular systems containing lithium cations as components.

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Conflict of Interest

The authors declare no conflict of interest.

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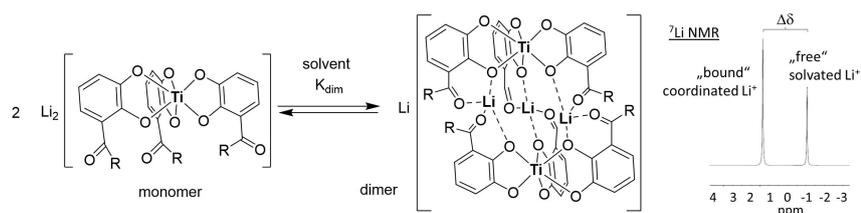
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RESEARCH ARTICLE



⁷Li NMR is a perfect tool for the evaluation of supramolecular aggregates. In case of titanium(IV) based hierarchical helicites dimerization as well as averaged dimerization constants are determined and the expansion and

compression of molecular switches is followed. Thus, ⁷Li NMR helps to understand phenomena far beyond the simple observation of a heteroatom resonance in solution or in the solid.

*T. Krüchel, S. Schauerte, J. Ke, Dr. M. Schlottmann, S. Bausch, Dr. X. Chen, Dr. C. Räuber, Dr. I. d'A. Almeida Silva, Prof. Dr. T. Wiegand, Prof. M. Albrecht**

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⁷Li NMR Spectroscopy: a Tool for Determining Dimerization Constants and Averaged Dimerization Constants of the Monomer/Dimer Equilibrium of Hierarchical Helicites

