Two Novel Lithium−15-Crown-5 Complexes: An Extended LiCl Chain Stabilized by Crown Ether and a Dimeric Complex Stabilized by Hydrogen Bonding with Water

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Two lithium chloride−15C5 (15C5 = 15-crown-5) complexes, [Li(15C5)(μ-Cl)$_2$Li]$_\infty$, **1**, and {[Li(15C5)(H$_2$O)]Cl}$_2$, **2**, were synthesized. Their structures, characterized by single-crystal X-ray diffraction analyses, are dictated by the absence of or presence of water. Complex **1**, prepared in an anhydrous environment, is the first example of an extended LiCl chain structure. It contains repeating units Li(μ-Cl)Li(15C5) that are connected by additional bridging Cl atoms. One Li has close contacts with one Cl and all five O atoms of 15C5 and the other Li with three Cl and one O of 15C5. However, the chain structure cannot form in the presence of water. Instead dimeric complex **2** was formed when LiCl·xH$_2$O (x = 1.14) was the starting material. In this case H$_2$O is coordinated to lithium through a Li−O linkage and is hydrogen bonded to Cl$^-$ (H···Cl). The Li$^+$ cation is coordinated to the five O atoms of 15C5 as well as the O atom from H$_2$O, and the Cl$^-$ counteranion is isolated from Li$^+$ by two hydrogen bonds with one H atom each from two H$_2$O molecules with H···Cl distances of 2.30(4) and 2.35(4) Å, respectively. A crystallographically imposed center of symmetry generates a dimer that resembles a 2:2 anion-paired encapsulate. Crystal data for **1**: space group $Pna2_1$ (no. 33), a = 14.974(1) Å, b = 13.553(1) Å, c = 7.160(1) Å, V = 1453.0(2) Å^3, Z = 4. Crystal data for **2**: space group $P2_1/n$ (no. 14), a = 10.353(1) Å, b = 7.9070(1) Å, c = 17.741 Å, β = 100.50(1)°, V = 1427.9(2) Å^3, Z = 4.

Introduction

Since the pioneering work of Pedersen,[1] crown ethers and their complexes with metal cations have attracted considerable attention. Their remarkable selectivity on metal cations, especially alkali and alkaline earth metal cations, is a topic of fundamental interest in both coordination chemistry and biological chemistry.[2−6]

Lithium complexes of crown ethers are of great interest due to their applications as anionic conductors in manufacturing lithium-based rechargeable batteries[6b−f] and electrolytes,[6] and as anion activators in organic synthesis.[2,4] Since the crown ether 15C5 (15-crown-5) and its derivatives are among the most frequently used in applications, knowledge of their structural features could help in understanding the underlying mechanisms of the processes and in designing new crown ether analogues with better properties. However, there is no report on the crystal structure of a LiCl−15C5 complex despite much work in this area. A search of the Cambridge Structural Database returned only four entries, with the structures of three Li$^+$−15C5 complexes: [Li−15C5][In(CH$_3$)$_3$Cl], **3**,[7a,8] and two polymorphs of 15C5−2LiOPh, **4a** and **4b**.[7b] All of them have large counteranions of low charge density. It was noted[2a,13] that it is difficult to synthesize the crown ether complexes when metal salts consist of cations with high charge density and small highly nucleophilic anions.

Given current interest in the electrochemical properties and molecular structures of inorganic arrays, we are studying solid-state structures of LiCl−15C5 complexes obtained from ethereal solutions. Reported are the syntheses and crystal structures of two novel LiCl−15C5 complexes: [Li(15C5)(μ-Cl)$_2$Li]$_\infty$, **1**, and {[Li(15C5)(H$_2$O)]Cl}$_2$, **2**. To the best of our knowledge, complex **1** is the first example of an extended chain structure consisting of alkali metal and bridging halogen. Complex **1** was the only product in water-free conditions, whereas complex **2** was the exclusive product in the presence of lithium chloride monohydrate. The effects of water ligand on the structures of the these two complexes will be discussed in connection with the frequently encountered ethereal LiCl aggregate phenomenon.[18]

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Table 1. Crystallographic Data for $[Li(15C5)(\mu\text{-}Cl)_2Li]_\infty$ (**1**) and $\{[Li(15C5)(H_2O)]Cl\}_2$ (**2**)

	1	**2**
empirical formula	$C_{10}H_{20}Cl_2Li_2O_5$	$C_{10}H_{22}ClLiO_6$
formula wt.	305.04	280.67
crystal system	orthorhombic	monoclinic
space group	$Pna2_1$	$P2_1/n$
a, Å	14.974(1)	10.353(1)
b, Å	13.553(1)	7.907(1)
c, Å	7.160(1)	17.741(1)
β, deg	90	100.50(1)
V, Å^3	1453.0(2)	1427.9(2)
Z	4	4
ρ(calcd), g·cm^{-3}	1.394	1.306
T, °C	−60	−60
radiation (λ, Å)	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)
μ, mm^{-1}	0.454	10.28
$R_1{}^a$	0.0313	0.0477
w$R_2{}^b$	0.0841	0.1186
R_{int}	0.0141	0.0298
GOF	1.139	1.059

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$. [c] $GOF = S = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/(n - p)\}^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Li(15C5)(\mu\text{-}Cl)_2Li]_\infty$ (1)[a]

Bond Distances (Å)			
Li(2)−Cl(2)	2.378(7)	Li(2)−Cl(2)#2	2.349(7)
Li(2)−Cl(1)	2.351(6)	Li(2)−O(5)	2.139(7)
Li(1)−Cl(1)	2.335(7)	Li(1)−O(1)	2.265(8)
Li(1)−O(2)	2.255(9)	Li(1)−O(3)	2.121(8)
Li(1)−O(4)	2.222(9)	Li(1)−O(5)	2.595(8)
Angles (deg)			
Li(2)#1−Cl(2)−Li(2)	145.35(11)	Li(1)−Cl(1)−Li(2)	91.7(2)
Li(2)−O(5)−Li(1)	90.0(3)	Cl(1)−Li(1)−O(5)	83.2(2)
O(5)−Li(2)−Cl(1)	93.8(3	O(5)−Li(2)−Cl(2)#2	113.0(3)
Cl(2)#2−Li(2)−Cl(1)	114.3(3)	O(5)−Li(2)−Cl(2)	101.5(3)
Cl(2)#2−Li(2)−Cl(2)	108.4(3)	Cl(1)−Li(2)−Cl(2)	124.0(3)
C(1)−O(1)−Li(1)	112.7(3)	C(10)−O(1)−Li(1)	115.3(3)
C(2)−O(2)−Li(1)	109.7(3	C(3)−O(2)−Li(1)	111.3(3)
C(4)−O(3)−Li(1)	120.6(4)	C(5)−O(3)−Li(1)	117.1(4)
C(6)−O(4)−Li(1)	105.9(3)	C(7)−O(4)−Li(1	113.5(3)
C(8)−O(5)−Li(1)	111.5(3)	C(9)−O(5)−Li(1)	108.0(3)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x$, $-y + 1$, $z + 1/2$; #2, $-x$, $-y + 1$, $z - 1/2$.

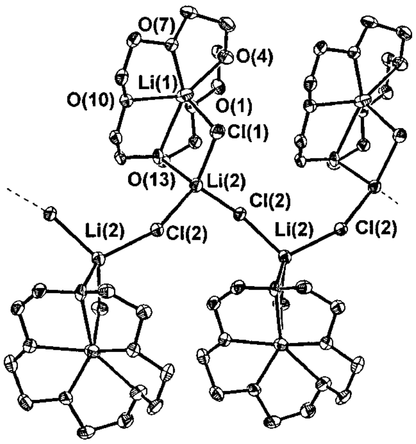

Figure 1. ORTEP drawing (50% thermal ellipsoids) of a portion of the extended chain structure of the extended chain complex $[Li(15C5)(\mu\text{-}Cl)_2Li]_\infty$, **1**.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $\{[Li(15C5)(H_2O)]Cl\}_2$ (2)

Bond Distances (Å)			
Li−O	1.899(5)	Li−O(1)	2.166(5)
Li−O(2)	2.267(6)	Li−O(3)	2.165(5)
Li−O(4)	2.174(6)	Li−O(5)	2.542(6)
O−H(21)	0.82(4)	O−H(22)	0.83(4)
Angles (deg)			
O−H(21)−Cl#	175 (3)	O−H(22)−Cl	171 (3)
C(1)−O(1)−Li	116.4(2)	C(10)−O(1)−Li	120.8(3)
C(2)−O(2)−Li	114.8(2)	C(3)−O(2)−Li	114.5(2)
C(4)−O(3)−Li	111.7(3)	C(5)−O(3)−Li	110.0(3)
C(7)−O(4)−Li	122.7(3)	C(6)−O(4)−Li	115.4(3)
C(9)−O(5)−Li	96.9(2)	C(8)−O(5)−Li	101.4(3)
Li−O−H(21)	118(3)	Li−O−H(22)	121(3)
H(21)−O−H(22)	117(4)		

Results

Complexes **1** and **2** were prepared in THF at room temperature according to the following reactions:

$$15C5 + 2LiCl \rightarrow {}^{1}/_{\infty}[Li(15C5)(\mu\text{-}Cl)_2Li]_\infty\ (\mathbf{1}) \qquad (1)$$

$$15C5 + LiCl{\cdot}H_2O \rightarrow {}^{1}/_{2}\{[Li(15C5)(H_2O)]Cl\}_2\ (\mathbf{2}) \qquad (2)$$

Compound **1** is obtained as colorless, needlelike crystals, and compound **2** is a white powder that produces colorless long needlelike crystals after recrystallization from THF/hexane. These compounds are stable at room temperature. However, both are very sensitive to moisture. The crystals of compound **1** turn into a white powder upon short exposure to the atmosphere. Compound **2** forms a colorless liquid after prolonged exposure to the atmosphere.

Molecular Structure of $[Li(15C5)(\mu\text{-}Cl)_2Li]_\infty$, 1. Compound **1** crystallizes in the orthorhombic space group $Pna2_1$. Crystallographic data and selected bond distances and angles are given in Tables 1 and 2, respectively. This complex possesses an extended LiCl chain structure which is shown in Figure 1. Units of composition $Li(\mu\text{-}Cl)Li(15C5)$ are connected by two additional bridging Cl atoms. There are two chemically and crystallographically different sites for Li atoms. Li(1) is coordinated to all five oxygen atoms from 15C5 (average[9a] bond distance of 2.290(18) Å) and one Cl atom (bond distance 2.335(7) Å) in a distorted pentagonal pyramidal geometry. The geometry around Li(2) can be best described as a distorted tetrahedron with three coordinated Cl atoms (average bond distance of 2.36(2) Å) and one oxygen atom (bond distance of 2.139(7) Å) from 15C5. Two of the three Cl atoms are also coordinated to Li(2) atoms of other monomeric units to form an infinite LiCl chain. The third Cl atom connects Li(1) and Li(2) atoms of the same monomeric unit. Li(1) lies 0.527(8) Å out of the least-squares plane defined by the five ethereal oxygen atoms, as compared to 0.45(2) Å for $[Li-15C5][In(CH_3)_3Cl]$, **3**[7a,9b] and 0.63 and 0.65(1) Å for the two 15C5−2LiOPh complexes **4a** and **4b**.[7b]

The Li−O bond distances are comparable (Table 4) to those reported[7a,b] for complexes **3** and **4** but are considerably longer than those observed for other Li^+−crown ether complexes (range from 1.90 to 2.16 Å).[2a] The Li−Cl−Li angles for the two different types of Cl bridges are 145.35(11)° for Li(2)−Cl(2)−Li(2)′ and 91.7(2)° for Li(1)−Cl(1)−Li(2). The Li(1)-Cl(1)Li(2)O(13) fragment is nearly rectangular with angles of 91.7(2)°, 93.8(3)°, 90.0(3)°, and 83.2 (2)°. The Li(1) atom is found to be at or near the C−O−C bisectors along the trigonal lone pair directions of the ethereal oxygen atoms. This is

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(9) (a) The standard deviations of the average values of the data obtained in this paper were calculated according to the following equation: $\sigma_l = [\sum_m(l_m - \langle l\rangle)^2/m(m - 1)]^{1/2}$, where l_m are the experimental data and l the average. (b) Calculated using the position parameters given in ref 7a.

Table 4. Average Li−O Distances in Complexes **1** and **2** and in Some Previously Reported Li−Crown Ether Complexes

complex	Li−O distances (Å) (range)	Li−O distances (Å)[9] (av)
$[Li(15C5)(\mu\text{-}Cl)_2Li]_\infty$ (**1**)	2.121(8)−2.595(8)	2.29(18)
$\{[Li(15C5)(H_2O)]Cl\}_2$ (**2**)	2.165(5)−2.542(6)	2.26(16)
LiCl(12C4)[14h]	2.128(2)	2.128(2)
LiNCS(12C4)[17a]	2.05(1)−2.14(1)	2.08(5)
LiNCS(B13C4)[19a]	2.012(8)−2.163(8)	2.07(8)
LiNCS(DB14C4)[19b]	2.033−2.054	2.044
LiNCS(16C4)[17b]	2.07(2)−2.09(1)	2.08(1)
$LiOPh)_2(18C6)$[20]	1.934(13)−2.416(15)	2.15(2)
$[LiOPh)_2(15C5)]_2$[7b]	2.210(4)−2.537(5)	2.38(2)
$[(LiOPh)_2(C15C5)]_2$[20]	2.586−2.083	2.290

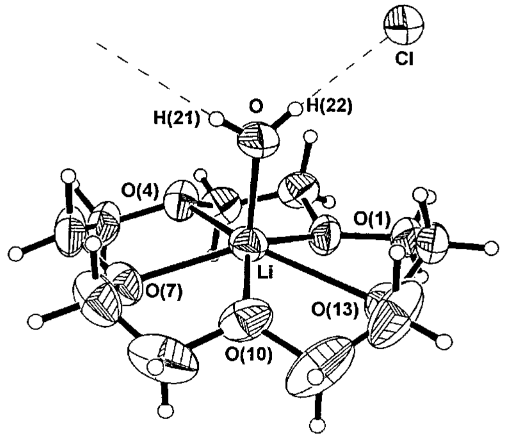

Figure 2. ORTEP drawing (50% thermal ellipsoids) of complex $\{Li(15C5)(H_2O)]Cl\}_2$, **2**.

consistent with the reported coordination pattern of other Li^+−crown ether complexes.[10] There is no major Li−Li interaction (Li−Li distance 3.362(9) Å) in contrast to complexes **4a** and **4b** with Li−Li distances of 2.55(1) and 2.58(1) Å.[7b]

Molecular Structure of $[Li(15C5)(H_2O)]Cl$, 2. Complex **2** crystallizes in the monoclinic space group $P2_1/n$. Crystallographic data and selected bond distances and angles are given in Tables 1 and 3, respectively. The molecular structure of complex **2** is shown in Figure 2. Lithium is coordinated to all five ethereal oxygen atoms as well as an additional oxygen atom from H_2O in a distorted pentagonal pyramidal geometry. The Li atom is 0.434(8) Å above the least-squares plane defined by the five ethereal oxygen atoms. As expected, the $Li-OH_2$ distance (1.899(5) Å) is significantly shorter than the average distance between the Li atom and the ethereal oxygen atoms (average bond distance of 2.26 (16) Å) and comparable (Table 4) to those of complexes **3** and **4**. Like **1**, the Li atom is found to be at or close to the C−O−C bisectors along the trigonal lone pair directions of the ethereal oxygen atoms. The geometry around the oxygen of the coordinated water molecule is nearly trigonal planar (the sum of three angles equal to 356.1°), and the H−O−H angle is 117(4)°.

The Cl^- counteranion is isolated from the Li^+ cation (average Li−Cl distance of 4.47(1) Å). The water molecule coordinated to Li^+ effectively expels Cl^- from the coordination sphere, which is rather common for anion-separated encapsulates.[2a] This Cl^- is connected to one of the hydrogen atoms of the coordinated water molecule, and to a second one from the H_2O molecule of a different monomer, generated by a center of symmetry in the crystal (Figure 3). Taken together this dimer resembles a 2:2 anion-paired encapsulate.[2a] The (O)H···Cl distances are 2.298(39) and 2.348(40) Å, the O···Cl distances are 3.123(5) and 3.161(5) Å, and the O−H···Cl angles are 171(3)° and 175(3)°, respectively. All of these values are typical for a hydrogen bond of this type.[11a,b] In particular, a similar pattern of H-bonds has been observed[11c] in the centrosymmetric dimer of $(CH_3)_4NCl{\cdot}H_2O$ with O···Cl distances of 3.204(4) and 3.247(4) Å. Four (C)H···Cl(2) contacts of less than 3.0 Å are found in complex **1**, varying from 2.79(4) to 2.95(4) Å with bending angles between 110(4)° and 138(4)°. Four (C)H···Cl contacts of less than 3.0 Å are also found in complex **2**, varying from 2.77(4) to 3.00(4) Å with bending angles between 143(4)° and 171(4)°. A study[11d] of such distances in structures determined by neutron diffraction has indicated that there may be weak hydrogen bonds of the (C)H···Cl type with as great as 2.95 Å separation. The shortening of the X-ray-measured values of the C−H bond lengths from the neutron value of 1.10 Å makes it seem likely that the short (C)H−Cl contacts should be considered weak hydrogen bonds. In both structures the torsion angles seem to follow the common pattern of these complexes,[12] with conformations that are approximately gauche for O−C−C−O and approximately anti for C−O−C−C but with one major exception in **1**, C2−O2−C3−C4 = 86.2(5)°. The various bond distances and bond angles of the 15C5 rings appear to be normal (Supporting Information).

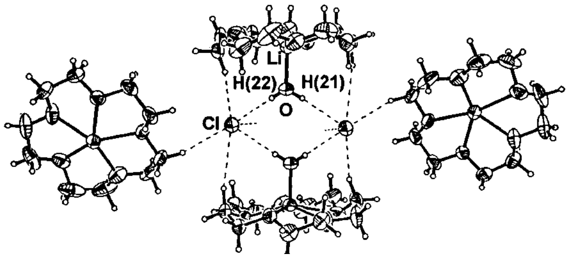

Figure 3. ORTEP drawing (50% thermal ellipsoids) of complex **2** showing the O−H···Cl hydrogen bonds and the 2:2 anion-paired encapsulate generated by a center of symmetry.

NMR and IR Results. NMR data of the complexes are similar to those of pure 15C5.[8] ^1H NMR of **1** gives a sharp singlet at 3.57 ppm, comparable with the 3.58 ppm singlet reported for 15C5. ^{13}C NMR of complex **1** has a singlet at 71.78 ppm as compared with 70.62 ppm for 15C5. Besides a sharp singlet at 3.53 ppm from methylene groups of 15C5, ^1H NMR of **2** also shows a broad peak at 1.68 ppm from the protons of its water ligand. ^{13}C NMR of **2** is identical with that of **1**, with a singlet at 71.78 ppm.

The two medium-intensity IR bands of 15C5 crown ether at 975 and 925 cm^{-1} that are attributed to either the wag or twist mode of vibration of the methylene groups[1] are shifted toward each other upon formation of lithium−15C5 crown complexes **1** and **2**. For complex **1** these bands occur at 953 and 939 cm^{-1}, and for complex **2** they occur at 969 and 959 cm^{-1}. In both cases the bands are more intense than in the uncomplexed crown ether. These results are in accord with earlier observations of crown ether−metal complexes, and they indicate that there is less restriction on the coupling of these vibrational modes because the ethereal oxygen atoms in the complexes have less effect when they are bonded to lithium atoms.[1]

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Discussion

While dimeric alkali metal halides have been observed,[2] complex **1** appears to be the only example of any alkali and/or alkaline earth metal halides we know of that possess an extended chain structure. The relatively high charge density of the Li$^+$ cation compared to other alkali metal cations favors ion-pairing or partial covalent bonding with the chloride ion in the formation of the LiCl chain.[13] The 15C5 crown ether inhibits branching of the chains by serving as a pentadentate ligand to lithium. It also serves as a monodentate ligand to the lithium in the chain.

In both complexes **1** and **2**, the 15C5-complexed Li atoms are displaced from the geometrical centers of the cavities, with one Li−O bond being significantly longer than the others. The cavity size of 15C5 is too large[13] to provide effective Li−O contact without some distortion in its conformation. A partially wrapped-around model was suggested for the conformational change of the crown ether in the metal cation−crown ether complex when cavity size exceeds cation size,[2a] and the effect has been observed in complexes of large crown ethers. The best description for the present small ring systems seems to be that of a distorted pentagonal pyramid, based especially on the conformation of complex **2**, where there is little change from an ideal planar arrangement of the oxygen atoms of 15C5 (mean deviation from planarity 0.16 Å). The larger deviation in complex **1** (0.31 Å) may be attributable to the additional metal−ligand interaction between a second Li$^+$ center and the O(13) of the crown ether ring, which serves as a bidentate ligand in this case.

In complex **1** the coordination around Li is complicated since it includes both oxygen and chlorine atoms. The Li(1)−Cl(1) distance is 2.335(7) Å, and the average of three Li(2)−Cl distances is 2.36(1) Å. Some previously reported Li−Cl bond lengths are given in Table 5. These vary from 2.02 Å for gaseous LiCl monomer[14a] to 2.566 Å for crystalline LiCl.[15b] The Li−Cl separation is a function of coordination number: in gaseous Li_2Cl_2, Li−Cl = 2.23 Å, and the sum of ionic radii for 4-fold coordination in the solid state gives Li−Cl = 2.40 Å.[15] The sum of covalent radii for Li and Cl is 2.33 Å.[15] Since oxygen is also coordinated to Li(1) and Li(2), some provision must be made for its influence on the observed Li−Cl distances. An alternative description, the bond valence method,[16] has been used to correlate bond distances in solids. In this method, each lithium, with a variety of oxygen and chlorine close contacts, has a total valence, V_i, given by $V_i = \sum v_{ij}$ with v_{ij} the contribution to the total valence of Li from each atom, j, coordinated to it. When this calculation is carried out using formulas and atom size parameters given in ref 13, the total valence for Li(1) is 0.92 and for Li(2) is 0.98, both values reasonably close to the ideal valence for Li of 1.00. In **2**, a similar calculation involving only the oxygen atoms of 15C5 and H_2O yields a valence for Li of 1.01. However, similar calculations that were carried out on other alkali metal−crown ether complexes gave a much wider variation of such values, between 0.9 and 1.4.

Table 5. Comparison of the Li−Cl Distances in Some Known Compounds

compound	type of Cl[a]	bond distance(s), (Å)
$[Li(15C5)(\mu\text{-}Cl)_2Li]_\infty$ (**1**): Cl(1)	μ_2	2.349(7), 2.378(7)
Cl(2)	μ_2	2.335(7), 2.351(6)
$LiCl_{mon}$[14a]	t	2.02[b]
$(LiCl)_2$[14a]	μ_2	2.23(3)[b]
$LiCl_{cryst}$[15b]		2.566
LiCl(12C4)[14h]	t	2.290
$[LiCl(dioxane)]_2$[14b]	μ_2	2.39, 2.42
$LiCl(C_4H_8SO_2)$[14c]	μ_2	2.375(8), 2.309(7)
$[LiCl(THF)_2]_2$[14d]	μ_2	2.342(3), 2.308(8)
$(Pr_2{}^iNLi)_2LiCl(TMEDA)_2$[14e]	μ_3	2.478(3), 2.364(3), 2.384(3)[c]
$[ClLi\{OP(NMe_2)_3\}]_4$[14f]	μ_3	2.357(10)−2.441(12)
$[(2\text{-Me-py})_2LiCl]_2$[14g]	μ_2	2.378(8), 2.383(9)

[a] t, terminal; μ_2, bridging; μ_3, triply bridged. [b] Determined by electron diffraction in vapor. [c] TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.

Lithium chloride is an aggregate in ethereal solutions.[18] Little information is available on the compositions and structures of such aggregates. $MW_{appar}/MW_{empirical}$ obtained using vapor pressure osmometry gives value of 1.83 for 0.04−0.4 M LiCl solutions in THF,[18a] suggesting substantial dimerization. Recent studies of similar systems using the FT-IR techneque[18b] and HMPA (hexamethylphosphoramide) titration[18c] monitored by low-temperature ^7Li and ^{31}P NMR led to a similar conclusion. Also, $Li(\mu\text{-}Cl)_2Li$ is a recurring structural motif in several complexes (Table 5).[14a,b,d,g]

The cavity size of 15C5 is best suited for Na$^+$ while 12C4 matches well with Li$^+$.[2,13] Indeed, Li salts form monomeric complexes with 12C4 and its analogues.[2,14h] On the other hand, structural data are rare for Li$^+$−C15C complexes, while numerous examples are reported for Na$^+$−15C5 complexes.[2] So far, there are only three reported structures for two Li salt complexes of 15C5: one ion-paired monomeric [Li−15C5]-$[In(CH_3)_3Cl]$, **3**,[7a] and two polymorphs of the tetrameric 15C5−2LiOPh, **4a** and **4b**.[7b] Watson et al. argued[7c] that complexation of Li salts by 15C5 itself is not sufficient enough to induce a separation of the lithium salt aggregates. The complexing ability of 15C5 toward Li$^+$ is weaker than that of 12C4. This is supported by the longer Li−O bond distances observed in 15C5 systems than those in 14C4 complexes.[2,7] However, the de-aggregation process can be facilitated with a bulky counteranion such as $[In(CH_3)_3Cl]^-$ in the case of complex **3**,[7a] or the existence of a more polar solvent such as H_2O in the case of complex **2**. In the latter case, the counteranion was replaced by an H_2O molecule. In the case of complexes **4a** and **4b**,[7b] however, the strong interaction between Li$^+$ and the oxygen of the phenoxide keeps the tetrameric structure intact even in the

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presence of a polar solvent. Complex **1** may be the result of a delicate balance of the solvent−ligand−counteranion interactions, as implicated by comparing the distances of the Li atoms to the least-squares planes defined by the ethereal oxygen atoms. The Li atoms are 0.63(1) and 0.65(1) Å out of the plane for complexes **4a** and **4b**,[7b] and the Li atom is 0.527(8) Å out of the plane for **1**, 0.45(2) Å for **3**,[9b] and 0.434(5) Å for **2**. The presence of water (of the hydrate of LiCl) prevents this delicate balance between the LiCl chain and the ethereal solvent from happening, which is critical in the formation of complex **1**. As a result, the more stable monomeric hydrogen-bonded complex **2** is formed.

The fact that hydrated LiCl is sufficient to prevent complex **1** from forming provides insight into the formation and stability of gel-like aggregates of lithium chloride etherates in general, which often present a difficult task for the removal of LiCl (a side product from reactions between organolithium compounds and chlorides) through filtration. Considering the fact that there is no water present in those systems, it is expected that lithium chloride etherate aggregates should be the preferred product under such circumstances since ethereal solvents are similar to crown ethers in some aspects. Nonprotic solvents help to stabilize the polymeric forms of LiCl, with the Li−Cl bond remaining intact. It should be possible however to overcome the aforementioned LiCl filtration problem by introducing a trace amount of protic substances to break down the strong interaction between lithium cation (of high charge density) and the nucleophilic Cl anion, as demonstrated by the formation of **2**.

It is noteworthy that the ion-paired complex **2** is not the expected[13] product in the absence of water because the Li^+ cation is encapsulated by 15-crown-5. While it destabilizes complex **1**, the coordinated water molecule actually stabilizes the unusual complex **2** by stabilizing the Li^+ cation through filling the lithium coordination sphere. It also stabilizes the Cl^- anion by providing hydrogen bonding, thereby diminishing the nucleophilic power of the Cl^- anion.[2] Interestingly, NaOPh also forms a dimer with 15C5 from THF solutions, presumably as a result of strong interaction between Na^+ and the oxygen atom of the phenoxide.[7c]

Experimental Section

General Data. THF and hexane were dried over Na/benzophenone and distilled under N_2 prior to use. 15C5 (Aldrich) was used as purchased without further purification. Anhydrous LiCl (Aldrich) was heated at 200 °C under dynamic vacuum overnight. Lithium chloride monohydrate (Aldrich) was assayed in this laboratory as $LiCl{\cdot}1.14H_2O$. All manipulations were performed on a standard high-vacuum line or in a drybox under an atmosphere of dry, pure N_2. Proton and ^{13}C NMR (δ(TMS) = 0.00 ppm) spectra were recorded on a Bruker AM-250 NMR spectrometer operating at 250.134 and 62.896 MHz at 303 K, respectively. Infrared spectra were recorded on a Mattson Polaris Fourier transform spectrometer with 2 cm^{-1} resolution.

Preparation of $[Li(15C5)(\mu\text{-}Cl)_2Li]_\infty$, 1. About 50 mg (1.18 mmol) of anhydrous LiCl was stirred overnight in dry THF (20 mL) at room temperature. After LiCl was dissolved, 260 mg (1.18 mmol) of 15C5 was added. The solution was stirred for another 30 min. It was then layered with dry hexane. Colorless needlelike single crystals of **1** suitable for single-crystal X-ray diffraction study were obtained. FT-IR (CCl_4, 0.1 mm NaCl cell): 2898(vs), 1507(m), 1377(m), 1276(w), 1244(m), 1124(s), 1092(s), 953(m), 939(m), 838(s) cm^{-1}. ^1H NMR (d_8-THF, TMS): 3.57 (s) ppm. ^{13}C NMR (d_8-THF, TMS): 71.778 (s) ppm.

Preparation of $[Li(15C5)(H_2O)]Cl$, 2. In a typical synthesis, ca. 121 mg (2 mmol) of $LiCl{\cdot}1.14H_2O$ was dissolved in 20 mL of dry THF. A 440 mg (2 mmol) quantity of 15C5 in 10 mL of dry THF was added. A white precipitate immediately appeared. The mixture was stirred for several hours at room temperature. The precipitate was filtered and dried to give 550 mg (ca. 561 mg, yield 98%) of white powder. FT- IR (CCl_4, 0.1 mm NaCl cell): 2877(vs), 1476(m), 1350(m), 1296(w), 1250(m), 1124(s), 1104(s), 969(m), 959(m), 831(s) cm^{-1}. ^1H NMR (d_8-THF, TMS): 3.53 (20 H, s), 1.68 (2 H, br) ppm. ^{13}C NMR (d_8-THF, TMS): 71.779 (s) ppm. It was then recrystallized from THF/hexane (1:1). Colorless long needlelike single crystals of **2** suitable for single-crystal X-ray diffraction studies were obtained.

X-ray Crystal Structure Determination. Crystals of suitable size were placed in 0.5 mm capillaries. All crystallographic data were collected at −60 °C on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. Unit cell parameters were obtained by a least-squares refinement of the angular settings from 25 reflections, well distributed in reciprocal space and lying in a 2θ range of 24−30°. All reflections were corrected for Lorentz and polarization effects. No empirical absorption correction was applied.

The structures were solved by direct methods and refined by Fourier and least-squares procedures using SHELXTL programs (Version 5, Siemens Energy & Automation, Inc., 1994). After all non-hydrogen atoms were located and refined anistropically, all hydrogen atoms were located and refined isotropically.

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Supporting Information Available: Tables listing additional X-ray experimental details and anisotropic parameters for complexes **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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