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The Many Guises of Lithium Chloride: Crystal Structure of the Single-Strand Polymer $\{\mathrm{LiCl{\cdot}2MeCN}\}_\infty$

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The fate of lithium halide molecules extruded during metathetical reactions can be difficult to predict. For example, we have noted previously that LiX (X = Cl, Br, I, OH)[1] and Li_2O[2] can be trapped by lithium amidinates to generate isolable laddered aggregates. Indeed, numerous cases are known where LiX fragments interact with reaction products, reactants, intermediates, or solvents in various ways.[3] Additional interest is often conferred upon these clusters by virtue of their relevance to laddering chemistry,[4] as well as by the realization that they represent interrupted $\{\mathrm{LiX}\}_\infty$ lattice growth.[5] Potential industrial uses for complexes of inorganic lithium salts center on their solubility in organic solvents, which can be great compared to that of the uncomplexed salts. Proposed applications include the deposition of alkali metals via electrolysis, lithium-ion battery materials, and a wide range of functions in organic syntheses.[3,5]

Here we present a remarkable addition to the family of known LiCl-solvent adducts: the single-strand, unladdered polymer $\{\mathrm{LiCl{\cdot}2MeCN}\}_\infty$ (**1**, Figure 1). This compound was initially obtained as a minor byproduct in several different metathetical reactions between CuCl and lithium salts of various anionic ligands in acetonitrile.[6] Although we were unable to generate **1** by dissolving LiCl in acetonitrile, it can be conveniently synthesized via the addition of freshly distilled $SiMe_3Cl$ to an equimolar amount of MeLi in Et_2O/acetonitrile. This route gives mostly unsolvated LiCl as a white precipitate (ca. 95%), with a minute yield of colorless, crystalline **1** (ca. 3%).

Previously characterized complexes of LiCl with neutral Lewis bases (e.g., solvents) include monomers, dimers, tetramers, polymers, extended three-dimensional arrays, and separated ion-pairs (Table 1). Excepting the first and last of these categories, all the aggregated examples contain portions where LiCl laterally associates with other LiX fragments. The novel adduct **1** is unique in that it contains no laddered sections, consisting solely of a single-strand LiCl polymer in which each lithium cation is solvated by two acetonitrile molecules. The solvent protrudes from the polymer backbone in four directions, imposing separations between the chains of 6−8 Å (Figure 2).

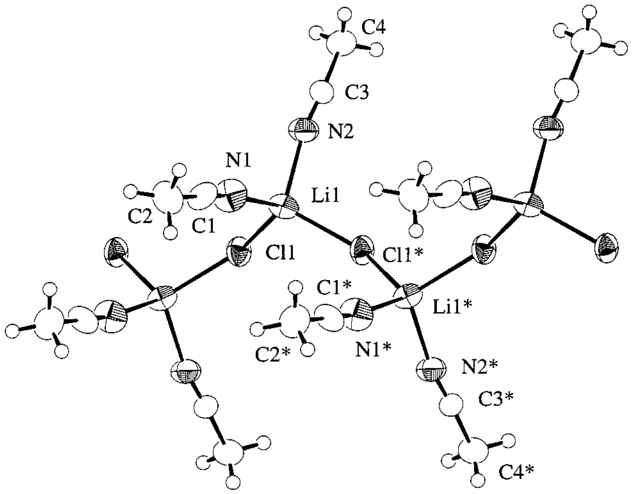

Figure 1. ORTEP of $\{\mathrm{LiCl{\cdot}2MeCN}\}_\infty$ (**1**) showing the atom-labeling scheme. Thermal ellipsoids are depicted at 50% probability. Symmetry transformations used to generate equivalent atoms: *, $-x + {}^1/_2, y, z - {}^1/_2$. Selected bond distances [Å]: Cl1−Li1 = 2.312(16); Cl1−Li1* = 2.291(17); N1−C1 = 1.128(4); N2−C3 = 1.128(4); N1−Li1 = 2.084(5); N2−Li1 = 2.065(5). Selected bond angles [deg]: Li1*−Cl1−Li1 = 146.9(2); Cl1*−Li1−Cl1 = 111.14(18); N2−Li1−N1 = 106.4(2).

The ^{1}H NMR spectrum of **1** in benzene-d_6 consists of a singlet at 0.59 ppm. However, when the same spectrum is run in THF-d_8, the singlet appears at 1.94 ppm, characteristic of free MeCN. Thus THF evidently displaces acetonitrile as a ligand in solutions of **1**, probably giving $\{\mathrm{LiCl{\cdot}THF}\}_\infty$ or $\{\mathrm{LiCl{\cdot}2THF}\}_2$. Free acetonitrile is also observed in solutions of **1** in benzene-d_6 after 1−2 h, presumably due to formation of $\{\mathrm{LiCl}\}_\infty$. The ^{7}Li NMR spectrum of **1** evinces a singlet at 1.28 ppm (versus LiCl in D_2O); the only other reported value for a similar compound is 4.27 ppm for the azetidine adduct$\{\mathrm{LiCl}\}_4{\cdot}(\mathrm{C_3H_6NH})_2(\mathrm{C_3H_6N}\text{-}[\mathrm{C_3H_6NH_2}])_2$ (versus LiBr in D_2O).[7] Although the NMR data for **1** in benzene solution are consistent with the solid structure, the breakdown of the polymer into smaller units (with the requisite symmetry) cannot be ruled out. The C≡N stretch of **1** appears at 2249 cm^{-1} in the infrared spectrum, very close to the corresponding value for free acetonitrile.

Examples of single-strand polymers containing only lithium and one other element in the backbone are rare. We recently reported the lithium thioamidate $\{[\mathrm{MeCS(N}t\mathrm{Bu)]Li{\cdot}THF}\}_\infty$,[8] and Banister et al. have described the structure of $\{\mathrm{PhSLi{\cdot}(NC_5H_5)_2}\}_\infty$,[9] both of which have a $\{\mathrm{LiS}\}_\infty$ backbone. However, both of these compounds also have substituents on lithium *and* sulfur and thus are not strictly analogous to **1**. From the point of view of sterics, a better comparison is to lithium diisopropylamide: a single-strand $\{\mathrm{LiN}\}_\infty$ polymer with four-coordinate nitrogen centers bridged by μ_2-lithium cations in a helical arrangement.[10]

The first example of an extended chain of alkali metal cations bridged by halogens was reported only recently: $\{[\mathrm{LiCl}]_2{\cdot}$

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Table 1. Complexes of LiCl with Neutral Lewis Bases[a]

adduct	donor ligands	structural type	ref
$[\mathrm{LiCl}]_4 \cdot \mathrm{L}_2\mathrm{L}'_2$	$\mathrm{L} = \mathrm{C_3H_6NH}^b$ $\mathrm{L}' = \mathrm{C_3H_6N\{C_3H_6NH_2\}}^c$	unfolded $[\mathrm{LiCl}]_4$ cube (cf. **C**-type polymer)	7
$\{\mathrm{LiCl}\cdot\mathrm{L}\}_\infty$	L = THF	**C**-type polymer	13
$\{\mathrm{LiCl}\cdot\mathrm{L}_2\}_2$	L = THF	**A**-type dimer	15
$\{[\mathrm{LiCl}]_2\cdot\mathrm{L}\}_\infty$	L = 15C5	**B**-type polymer "solvated" by LiCl•15C5 units	11
$\{\mathrm{LiCl}\cdot\mathrm{L}\cdot\mathrm{L}'\}_2$	L = 15C5 $\mathrm{L}' = \mathrm{H_2O}$	solvent-separated ion-pairs	11
$[\mathrm{LiCl}]\cdot\mathrm{L}$	L = 12C4	monomer	20
$\{([\mathrm{Li}]^+[\mathrm{Cl}]^-)_3\cdot\mathrm{L}_2\}_\infty$	L = TMEDA	solvent-separated ion-pairs	21
$\{[\mathrm{LiCl}]_4\cdot\mathrm{L}_{3.5}\}_2$	L = TMEDA	$[\mathrm{LiCl}]_4$ subunits linked by solvent; each subunit consists of fused $[\mathrm{LiCl}]_3$ and $[\mathrm{LiCl}]_2$ rings	22
$[\{[\mathrm{LiCl}]_2\cdot\mathrm{L}\cdot\mathrm{L}'\}_2\mathrm{L}_2]_\infty$	L = TMEDA $\mathrm{L}' = \mathrm{H_2O}$	**A**-type dimers linked by solvent molecules	23
$\{\mathrm{LiCl}\cdot\mathrm{L}\}_4$	L = HMPT	$[\mathrm{LiCl}]_4$ cube	24
$\{[\mathrm{LiCl}]_2\cdot\mathrm{L}_2\}_\infty$	$\mathrm{L} = \mathrm{O_2SC_4H_8}^d$	**A**-type dimers linked by solvent molecules	25
$\{[\mathrm{LiCl}]_2\cdot\mathrm{L}_2\}_\infty$	$\mathrm{L} = 1,4\text{-}\mathrm{C_4H_8O_2}^e$	**A**-type dimers linked by solvent molecules	26
$\{\mathrm{LiCl}\cdot\mathrm{L}\cdot\mathrm{L}'_{0.5}\}_\infty$	L = DMF $\mathrm{L}' = \mathrm{H_2O}$	$[\mathrm{LiCl}]_2$ and LiCl units linked by solvent molecules	27
$[\mathrm{LiCl}]_4\cdot\mathrm{L}_3$	L = PMDIEN	two $[\mathrm{LiCl}]_2$•PMDIEN units linked by a Li−Cl contact and one solvent molecule	28
$\mathrm{LiCl}\cdot\mathrm{L}_3$	L = 3,5-DMP	monomer	29
$\{\mathrm{LiCl}\cdot\mathrm{L}'\}_2$	L′ = 2-MP	**A**-type dimer	29
$\{[\mathrm{Li}]^+[\mathrm{Cl}]^-\cdot\mathrm{L}_2\}_\infty$	L = EN	solvent-separated ion-pairs	30
$\{\mathrm{LiCl}\cdot\mathrm{L}_2\}_\infty$	L = MeCN	**B**-type polymer	this work

[a] Abbreviations: THF = tetrahydrofuran; *x*C*y* = *x*-crown-*y*; TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine; HMPT = hexamethylphosphoric triamide; DMF = dimethylformamide; PMDIEN = *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine; DMP = dimethylpyridine; MP = methylpyridine; EN = ethylenediamine. [b] Azetidine. [c] *N*-(3-Aminopropyl)azetidine. [d] Sulfolane. [e] *p*-Dioxane.

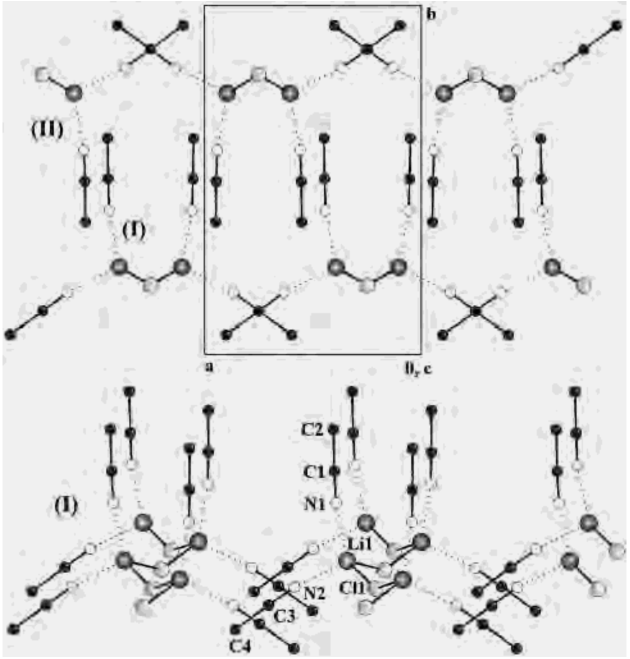
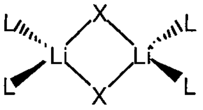


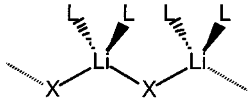
Figure 2. Unit cell of LiCl•2MeCN (packing range: *a*, −0.5 to 1.5; *b*, 0 to 1; *c*, −0.5 to 1.5) showing the two polymeric strands (I and II) viewed down the *c*-axis (top). Packing sequence inside one polymeric strand (I, bottom).

(15C5)}$_\infty$ (**2**) comprises a $\{\mathrm{LiCl}\}_\infty$ strand in which each lithium cation is "solvated" by a LiCl•(15C5) unit.[11] The metrical parameters in the two compounds are similar, although the mean Li−Cl distance within the chain of **2** [2.364(7) Å] is slightly longer than that in **1** [2.302(17) Å], probably due to the larger steric profile of the LiCl•(15C5) unit compared to that of acetonitrile. The bond angles at lithium [∠(Cl1*−Li1−Cl1) = 111.14(18)°] and chlorine [∠(Li1*−Cl1−Li1) = 146.9(2)°] in **1** are also close to the corresponding angles in **2** [108.4(3)° and 145.35(11)°, respectively].

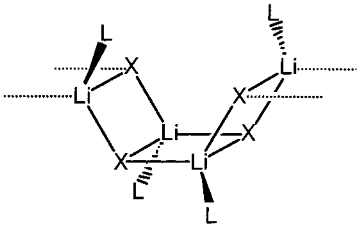
Acetonitrile adducts of LiBr and LiI are known, the former being a laddered dimer $\{\mathrm{LiBr}\cdot 2\mathrm{MeCN}\}_2$ (**3**) (i.e., **A**, where L = MeCN and X = Br) and the latter a solvent-separated ion-pair $\{[(\mathrm{MeCN})_4\mathrm{Li}]^+[\mathrm{I}]^-\}$.[12] For comparison, the 1:1 THF adducts of LiCl[13] and LiBr[14] are isostructural (i.e., **C**, where L = THF and X = Cl, Br), and the 2:1 adduct $\{\mathrm{LiCl}\cdot 2\mathrm{THF}\}_2$ (**4**) is isostructural with **3** (i.e., **A**, where L = THF and X = Cl).[15] Given these observations, it is not immediately clear why **1** should adopt an unladdered **B**-type structure rather than a dimeric structure **A**.



A



B



C

In rationalizing the formation of **1**, consideration of the behavior of an incipient monomeric unit of the polymer (a disolvated LiCl fragment in this case) is key. To disperse

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electronic charge, these fragments can associate laterally to give **A**-type dimers, or end-on to give **B**-type architecture. Where steric constraints are not preclusive (e.g., if only one solvent molecule is present per monomer unit), **A**-type dimers can further associate to give **C**-type laddered polymers. In the case of **1**, generation of LiCl in a large excess of coordinating solvent probably prevents formation of **C** due to disolvation at lithium.

The balance between structures **A** and **B** is likely influenced both by steric and electronic factors and evidently is quite delicate. Both architectures comprise disolvated, four-coordinate lithium centers linked by μ_2-halogens; however **A** requires severe restriction of the internal angle at the halogen [cf. $\angle$(Li−Br−Li) = 78.2(3)° in **3**] compared to **B** [cf. $\angle$(Li−Cl−Li) = 146.9(2)° in **1**]. Thus **A** is favored for the larger halogen and **B** for the smaller. Furthermore, **B**-type architecture causes increased steric congestion relative to **A** because solvent molecules must bend toward one another as the Li−X−Li angle opens. Hence **A** will also be favored in cases where the attached solvent molecules are bulkier. To wit, **4**, which has THF ligands, adopts **A**-type architecture, whereas the rodlike steric profile of MeCN allows **1** to adopt a **B**-type conformation.

Complexes of alkali metal halides with organic ligands are of significant interest, in both academia and industry. The observation that LiCl adopts an unladdered, polymeric structure in acetonitrile can be rationalized through consideration of steric and electronic influences on LiCl fragments generated in situ in metathetical reactions. The molecular architecture of **1** is unique among Lewis base adducts of LiX salts, and we anticipate that it may serve as a useful building block for extended arrays. Multifunctional donor molecules capable of bridging Li-centers have been used to link **A**-type dimers previously (i.e., sulfolane[25] and *p*-dioxane[26−30] adducts of LiCl), and we anticipate that a similar strategy could be useful in forming linked **B**-type $\{\mathrm{LiCl}\}_\infty$ chains. This approach may offer a path to novel organo-alkali-metal supramolecular frameworks and is certainly a topic worthy of future investigation.

Experimental Section

All manipulations were performed using standard glovebox and Schlenk techniques under an atmosphere of high-purity, dried argon. Acetonitrile and $\mathrm{SiMe_3Cl}$ were obtained from Aldrich and distilled immediately prior to use; MeLi (1.4 M solution in $\mathrm{Et_2O}$) was obtained from Aldrich and used as received. Deuterated solvents were purchased from Cambridge Isotope Laboratories in predried ampules and degassed by using three freeze/thaw cycles prior to use.

Preparation of $\{\mathrm{LiCl{\cdot}2MeCN}\}_\infty$ (1). Addition of MeLi in $\mathrm{Et_2O}$ (1.4 M, 1.5 mL, 2.1 mmol) to acetonitrile (4 mL) at room temperature produced a cloudy, white solution. A syringe was used to add neat $\mathrm{SiMe_3Cl}$ (0.3 mL, 2.4 mmol) to this solution, producing a white precipitate below a clear, colorless mother liquor. This was allowed to stir for 1 h. After reducing the solution in volume by ca. 25% under vacuum, the liquid was decanted and the remaining solid pumped down to yield a dry white precipitate. The total yield of unsolvated LiCl was 95% (84 mg, 2.0 mmol). Storage of the decanted mother liquor at −7 °C for 4 days yielded a few crystals of **1** (9 mg, 0.07 mmol, 3%).

Satisfactory melting point and elemental analysis determinations could not be completed due to the tendency of **1** to lose solvent on standing, leaving $\{\mathrm{LiCl}\}_\infty$. IR (KBr, Nujol mull), ν [cm^{-1}]: 2725, 2669, 2249, 1296, 1256, 1158, 1071, 1025, 805, 497. ^{1}H NMR [200 MHz, δ (TMS in $\mathrm{CDCl_3}$)] in $\mathrm{C_6D_6}$ at 25 °C: δ 0.59 (s). ^{13}C NMR [50.288 MHz, δ (TMS in $\mathrm{CDCl_3}$)] in $\mathrm{C_6D_6}$ at 25 °C: δ 91.14 (s, Me*C*N), 18.87 (s, *Me*CN). ^{7}Li NMR [155.508 MHz, δ (1M LiCl in $\mathrm{D_2O}$)] in $\mathrm{C_6D_6}$ at 25 °C: δ 1.28. LRMS (EI, 70 eV): *m/z* 167, $\{[\mathrm{LiCl}]_2{\cdot}2\mathrm{MeCN}\}^+$, 5%; 42, $\{\mathrm{LiCl}\}^+$, 52%.

X-ray Measurements. A crystal of **1** (0.6 × 0.5 × 0.4 mm), grown from the reaction mixture, was coated with oil (Paratone 8277, Exxon) and mounted on a glass fiber. Crystal data for **1**: $\mathrm{C_4H_6N_2ClLi}$, M = 124.50 g/mol; orthorhombic, space group $Pca2_1$ (#29); a = 7.752(3) Å, b = 12.568(4) Å, c = 7.593(3) Å; V = 739.8(5) Å^3; Z = 4; D_{calc} = 1.118 g/cm^3; μ(Mo Kα) = 0.42 mm^{-1}; λ(Mo Kα) = 0.71069 Å, T = 170(2) K, F_{000} = 256. All data were measured on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation in the range $5.0° \leq 2\theta \leq 50.0°$ (711 reflections collected, 711 independent reflections, R_{int} = 0.00). The structure was solved by direct methods[16] and expanded using Fourier techniques.[17] The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement using F^2 [18] was based on 507 observed reflections [$I > 2\sigma(I)$] and 75 variable parameters and converged with R_1 = 0.029 [$I > 2\sigma(I)$], wR_2 = 0.086 [all data]. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.12 and −0.31 e$^-$/Å^3, respectively. All calculations for data reduction were performed using teXsan.[19]

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Supporting Information Available: X-ray diffraction data including tables of atomic coordinates, thermal parameters, crystallographic data, and bond distances and angles for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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