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Solid-State Structures of *n*-Butyllithium–TMEDA, –THF, and –DME Complexes

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Abstract: Solid-state structures for a series of *n*-butyllithium (*n*-BuLi)–*N,N,N',N'*-tetramethylethylenediamine (TMEDA), *n*-butyllithium–THF, and *n*-butyllithium–dimethoxyethane (DME) complexes and their relevance to previous solution studies of related alkyllithium complexes and synthetic organic chemistry will be presented. X-ray crystal structures for the following complexes have been determined: $[(n\text{-BuLi})_4\cdot\text{TMEDA}]_\infty$ (**1**); $(n\text{-BuLi}\cdot\text{TMEDA})_2$ (**2**); $(n\text{-BuLi}\cdot\text{THF})_4\cdot n\text{-Hex}$ (**3**); and $[(n\text{-BuLi})\cdot\text{DME}]_\infty$ (**4**). An easy method of purification for *n*-butyllithium will also be discussed.

Introduction

Studies of the solid-state[1] and solution[2] structures of organoalkali compounds have been increasing in number over the last 30 years. Alkyllithium compounds are particularly important deprotonating reagents,[2,3] and polymerization catalysts.[4] *n*-Butyllithium (*n*-BuLi) is one of the most popular alkyllithium reagents in organic synthesis and polymerization chemistry, and it has been the focus of many solution structure studies in hydrocarbon,[5] tetrahydrofuran (THF),[6] diethyl ether,[7] and solutions containing *N,N,N',N'*-tetramethylethylenediamine (TMEDA).[6a,8]

n-BuLi forms hexameric aggregates in pure hydrocarbon solvents[5] and dimers in the presence of TMEDA[6a,8a] and exists in a tetramer–dimer equilibrium in pure THF solution.[6] Partially TMEDA-solvated alkyllithium aggregates, including tetramers, have been suggested by polymerization studies,[4c,9] calorimetric measurements,[4c] NMR,[2h] and colligative studies.[8b,10] Despite a wealth of structural and synthetic data regarding *n*-BuLi, only one X-ray crystal structure has been reported $(n\text{-BuLi}\cdot t\text{-Bu-O-Li})_4$.[11]

During the course of our solid-state structure studies involving mixed organoalkali reagents,[12] we obtained single crystals of an *n*-BuLi·TMEDA complex. Initially, these crystals were isolated from a pentane solution containing potassium bis(trimethylsilyl)amide (K-HMDS), TMEDA, and *n*-BuLi at –20 °C. Subsequently, we were able to isolate four more *n*-butyllithium complexes and determine their structures. Full crystallographic structures have been determined for $[(n\text{-BuLi})_4\cdot\text{TMEDA}]_\infty$ (**1**), $(n\text{-BuLi}\cdot\text{TMEDA})_2$ (**2**), $(n\text{-BuLi}\cdot\text{THF})_4\cdot n\text{-Hex}$ (*n*-Hex, *n*-hexane) (**3**), and $[(n\text{-BuLi})_4\cdot\text{DME}]_\infty$ (**4**) (DME, dimethoxyethane). Crystals of an $[(n\text{-BuLi})_4\cdot{}^3/_2\text{TMEDA}]_\infty$ complex (**5**) were also isolated, but only a partial refinement of this structure could be achieved.[13] In this paper, we will present these X-ray crystal structures and compare them with previous solution and theoretically calculated structures for a number of *n*-butyllithium aggregates.

Experimental Section

Sources and Purification. All compounds were available commercially, and all manipulations were carried out using inert atmosphere techniques[14] or in a Vacuum Atmospheres HE-43-2 drybox with a VAC HE-493 purification system. *n*-BuLi–hexanes solutions (2.5 M; Aldrich and Alfa) were used directly with the exact concentrations determined by direct titration with 3,5-dimethoxybenzyl alcohol in diethyl ether.[15] TMEDA (Aldrich) was purified by refluxing over CaH_2 and distilled under nitrogen. THF (Fisher) and DME (Aldrich) were distilled from the sodium–benzophenone ketyl under nitrogen. Toluene-d_8 was stirred over sodium metal for 24 h and distilled under nitrogen.

X-ray Crystallography. Suitable single crystals were selected and mounted under a cold stream of nitrogen gas. Intensity measurements were made using a Siemens P4 X-ray crystallographic system (Mo Kα radiation, λ = 0.710 73 Å, graphite monochromator, θ:2θ or ω scans) equipped with a Siemens LT-2 low-temperature device. The structures were solved by direct methods (SHELXS-86, UNIX version). Full-matrix least-squares adjustment (SHELXTL, version 4.2 large) of atomic position and thermal parameters (at first isotropic and then anisotropic) followed. Hydrogen atoms were placed in their calculated positions and

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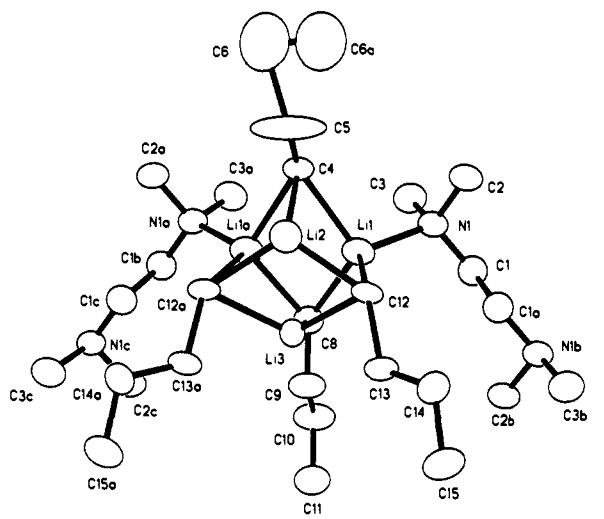

Figure 1. Computer-generated plot for the $[(n\text{-BuLi})_4\cdot\text{TMEDA}]_\infty$ complex (**1**). Hydrogen atoms have been omitted for clarity; 30% probability ellipsoids are shown.

allowed to ride with the atom to which they are attached. Crystallographic calculations were performed on IBM RS/6000 and Hewlett-Packard 9000 computer systems. X-ray crystallographic data for complexes **1**–**4** can be found in the supplementary material.

General Preparation of the *n*-BuLi Complexes. Four milliliters of a 2.5 M *n*-BuLi–hexanes solution was added to a septum-capped test tube and cooled to 0 or −78 °C. A known amount of a pure ligand was then added via syringe. The exact number of equivalents added and temperatures for crystal growth are listed below for each complex isolated.

Preparation of the $[(n\text{-BuLi})_4\cdot\text{TMEDA}]_\infty$ Complex (1).[16] This complex was originally prepared by the addition of ~1 mL of a 2.5 M *n*-BuLi–hexanes solution to a pentane solution containing K-HMDS and TMEDA. Crystals were isolated by cooling the solution to −20 °C overnight. However, this procedure for crystal preparation *could not* be replicated in later attempts. Complex **1** was also prepared by the general procedure with 0.25 equiv (0.30 mL) of pure TMEDA added. A white precipitate formed within a few seconds, and the solution was shaken for 1 min. Single crystals could be obtained by first heating the solution to 40 °C and slowly cooling it to −20 °C. Colorless, long rectangular crystals were isolated, and the X-ray crystal data were obtained at −80 °C.

Preparation of the $(n\text{-BuLi}\cdot\text{TMEDA})_2$ Complex (2).[17] This complex was prepared by the general procedure with 1.5 equiv (1.65 mL) of pure TMEDA added via syringe. The solution was frozen by immersing in liquid nitrogen, and the frozen solution was placed into a refrigerated bath at −92 °C overnight. Colorless, square crystals were isolated and mounted on the X-ray diffractometer at −110 °C. These crystals are extremely air- and temperature-sensitive.

Preparation of the $(n\text{-BuLi}\cdot\text{THF})_4\cdot\text{Hex}$ Complex (3).[18] This complex was prepared by the general procedure with 1 mL of pure THF added slowly at −78 °C. The solution was frozen in liquid nitrogen and placed at −92 °C overnight. Colorless, square crystals were isolated and mounted on the X-ray diffractometer at −78 °C. These crystals are also extremely air- and temperature-sensitive.

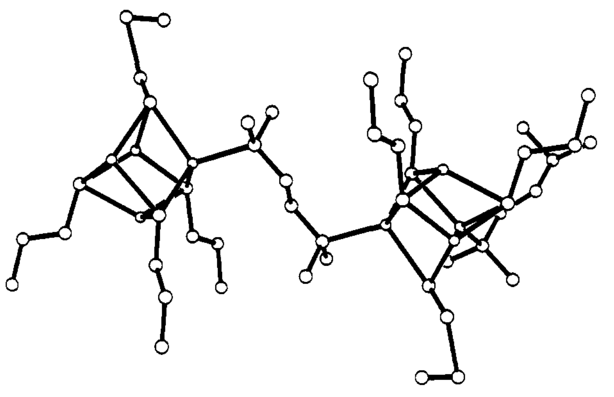

Figure 2. Computer-generated plot for the $[(n\text{-BuLi})_4\cdot\text{TMEDA}]_\infty$ complex (**1**) illustrating the polymeric nature of the complex. Hydrogen atoms have been omitted for clarity.

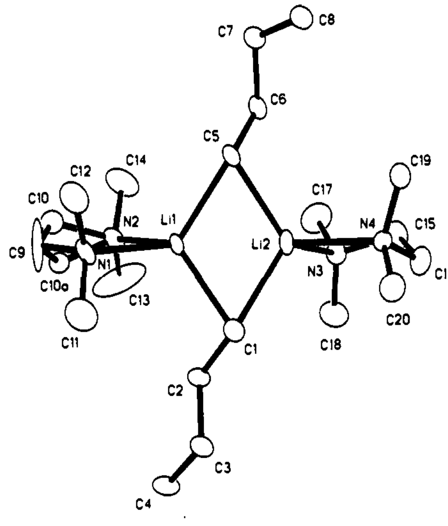

Figure 3. Computer-generated plot for the $(n\text{-BuLi}\cdot\text{TMEDA})_2$ complex (**2**). Hydrogen atoms have been omitted for clarity; 30% probability ellipsoids are shown.

Preparation of the $[(n\text{-BuLi}\cdot\text{DME})_4]_\infty$ Complex (4).[19] This complex was prepared using the general procedure with 1.2 equiv (1.0 mL) of TMEDA added. The solution was cooled to −40 °C, and colorless, square crystals were isolated. X-ray crystallographic data were collected at −35 °C.

Preparation of the $[(n\text{-BuLi})_4\cdot{}^3/_2\text{TMEDA}]_\infty$ Complex (5).[13,20] This complex was prepared using the general procedure with 1.0 equiv (1.0 mL) of TMEDA added. After a few seconds, a white precipitate formed and the solution was made homogeneous by heating to 40 °C. The solution was slowly cooled to room temperature, and colorless, hexagonal crystals were isolated. These crystals were also prepared by diluting the prepared solution to 1.0 M and cooling to −40 °C overnight. X-ray crystallographic data were collected at −35 °C, but unfortunately, despite many attempts, we have not been able to obtain crystals which yield a high-quality structure refinement.[13]

Purification of *n*-BuLi. *n*-BuLi can be purified by preparing and recrystallizing complex **5**. Attempts to remove the TMEDA solvate from the crystals of complex **5** in vacuo were unsuccessful and led to the decomposition of *n*-BuLi.[21] The TMEDA solvate can be removed by first adding more TMEDA to a hydrocarbon solution of **5** until the solution becomes homogeneous. The solution was then placed in a −20

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(16) Crystal data for $C_{22}H_{47}Li_4N_2$ (**1**): orthorhombic system; space group, *Pnma*; $a = 8.234(3)$ Å, $b = 16.158(7)$ Å, $c = 20.787(9)$ Å (from 25 orientation reflections, $24 < 2\theta < 26$); $V = 2769(2)$ Å^3; $Z = 4$; $d_{\text{calcd}} = 0.88$ g cm^{-3}; $\mu(\text{Mo K}\alpha) = 0.05$ mm^{-1}. Intensity data $h,k,\pm l$; 174 parameters refined using 1863 nonequivalent reflections ($2\theta_{\max} = 45°$); $R = 0.095$ ($R_w = 0.097$, GOF $= 3.37$) over 1032 reflections with $I > 4.0\sigma(I)$. Because of the severe disorder of the C6 methylene carbon in this structure, as well as the symmetry generation of the terminal methyl carbon (C6a) from this disordered methylene, five hydrogen atoms were not located.

(17) Crystal data for $C_{20}H_{50}Li_2N_4$ (**2**): monoclinic system; space group, $P2_1/n$; $a = 16.026(7)$ Å, $b = 10.327(5)$ Å; $c = 16.544(7)$ Å, $b = 111.54(3)°$ (from 18 orientation reflections, $22 < 2\theta < 26$); $V = 2562(2)$ Å^3; $Z = 4$; $d_{\text{calcd}} = 0.943$ g cm^{-3}; $\mu(\text{Mo K}\alpha) = 0.05$ mm^{-1}. Intensity data, $h,k,\pm l$; 256 parameters refined using 3738 nonequivalent reflections ($2\theta_{\max} = 45°$); $R = 0.082$ ($R_w = 0.078$, GOF $= 2.26$) over 1922 reflections with $I > 4.0\sigma(I)$.

(18) Crystal data for $C_{38}H_{82}Li_4O_4$ (**3**): monoclinic system; space group, $P2_1/n$; $a = 10.240(4)$ Å; $b = 16.075(15)$ Å; $c = 26.786(11)$ Å; $b = 99.97(3)°$ (from 26 orientation reflections, $22 < 2\theta < 28$); $V = 4342(5)$ Å^3; $Z = 4$; $d_{\text{calcd}} = 0.965$ g cm^{-3}; $\mu(\text{Mo K}\alpha) = 0.06$ mm^{-1}. Intensity data $h,k,\pm l$; 402 parameters refined using 5587 nonequivalent reflections ($2\theta_{\max} = 45°$); $R = 0.101$ ($R_w = 0.114$, GOF $= 3.91$) over 1408 reflections with $I > 10.0\sigma(I)$.

(19) Crystal data for $C_6H_{14}LiO$ (**4**): tetragonal system; space group, $P42_1c$; $a = b = 8.414(1)$ Å; $c = 21.071(6)$ Å; (from 25 orientation reflections, $22 < 2\theta < 28$); $V = 1492(1)$ Å^3; $Z = 8$; $d_{\text{calcd}} = 0.972$ g cm^{-3}; $\mu(\text{Mo K}\alpha) = 0.06$ mm^{-1}. Intensity data $h,k,\pm l$; 79 parameters refined using 733 nonequivalent reflections ($2\theta_{\max} = 45°$); $R = 0.078$ ($R_w = 0.084$, GOF $= 2.69$) over 584 reflections with $I > 3.0\sigma(I)$.

(20) Partial crystal data for $C_{8.33}H_{17.33}Li_{1.33}N_1$ (**5**): trigonal system; space group, $P3$; $a = b = 14.201(3)$ Å; $c = 11.397(4)$ Å; (from 25 orientation reflections, $22 < 2\theta < 28$); $V = 1991(1)$ Å^3; $Z = 6$; $d_{\text{calcd}} = 0.743$ g cm^{-3}; $\mu(\text{Mo K}\alpha) = 0.04$ mm^{-1}.

(21) The decomposition probably involves elimination of LiH to form butene.

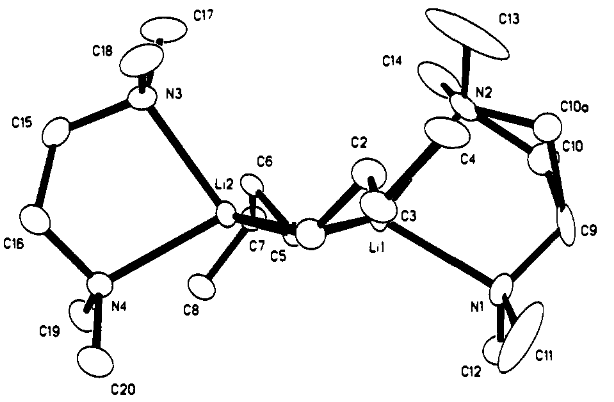

Figure 4. Computer-generated plot for the (n-BuLi·TMEDA)$_2$ complex (**2**). Noteworthy features include the cisoid conformation of the n-butyl groups and the 16(1)° bend in the Li–C–Li–C dimer ring.

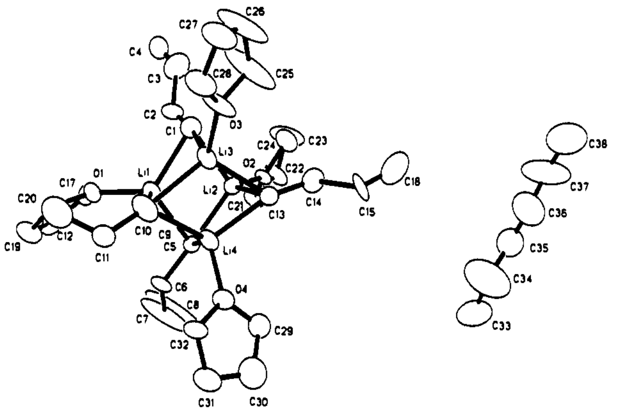

Figure 5. Computer-generated plot for the [(n-BuLi·THF)$_4$·Hex] complex (**3**). Hydrogen atoms have been omitted for clarity; 30% probability ellipsoids are shown.

to −40 °C bath under a ~50 mTorr vacuum until only the viscous n-BuLi oil remained.

Results and Discussion

The solid-state structure of the [(n-BuLi)$_4$·TMEDA]$_\infty$ complex (**1**) is shown in Figure 1. The alkyllithium is a distorted[22] tetramer, with two of the lithium cations η^1-solvated by TMEDA and two unsolvated in the structure. The TMEDA molecules link the tetramers together in an polymer network (see Figure 2). The conformations of three of the n-butyl groups are extended, which have been suggested as the predicted lowest energy conformations of the groups.[6e] The remaining n-butyl group is disordered.[22] The Li–C bond distances in the tetrameric core range from 2.105(11) to 2.334(13) Å, while the Li–N bond distances are 2.116(12) Å.

The X-ray structure for the fully saturated (n-BuLi·TMEDA)$_2$ complex (**2**) is shown in Figure 3. The complex is dimeric, with the lithium cations chelated by the nitrogen atoms of the TMEDA molecules. A very interesting feature of the structure is the nonplanar conformation of the dimer Li–C–Li–C ring. (See Figure 4.) Also, the conformations of the n-butyl groups are cisoid relative to the Li–C–Li–C dimer ring. Attempts are being made to analyze this structure using semiempirical calculations (MNDO, Gaussian 92[23]) to determine the most stable conformation of this dimeric aggregate and to understand why the dimer ring of complex **2** is bent. The Li–C bond distances for the dimer ring range from 2.215(11) to 2.227(9) Å, while the Li–N distances range from 2.209(12) to 2.223(10) Å. The dimer ring is bent by ~16(1)°, while the Li–C–Li and C–Li–C bond angles are 64.0(3) and 113.5(10)°, respectively.

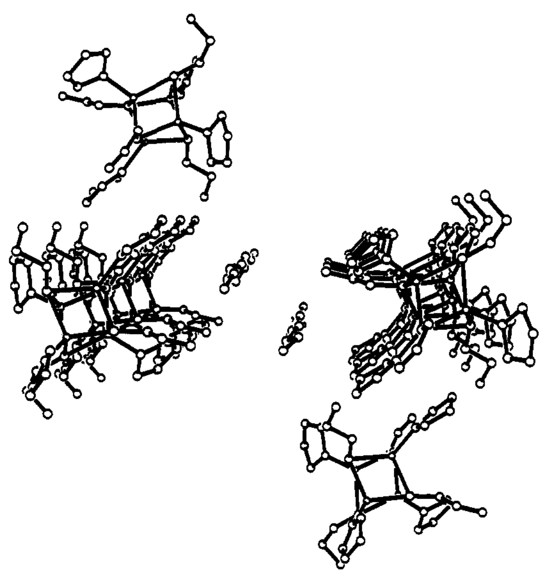

Figure 6. Computer-generated packing diagram for the [(n-BuLi·THF)$_4$·Hex] complex (**3**). Note that the hexane molecules lie in channels bounded by tetramers.

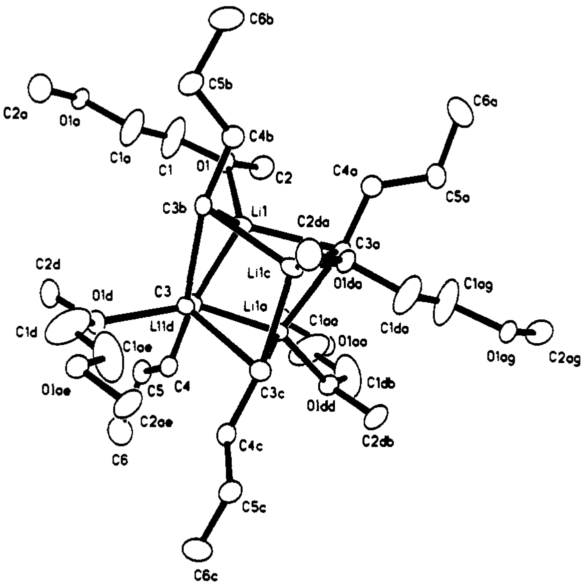

Figure 7. Computer-generated plot for the [(n-BuLi·DME)$_4$]$_\infty$ complex (**4**). Hydrogen atoms have been omitted for clarity; 30% probability ellipsoids are shown.

We also crystallized the (n-BuLi·THF)$_4$·Hex complex (**3**), and its X-ray structure is shown in Figure 5. The complex is a distorted[22] tetramer, similar to complex **1**, with each lithium cation solvated by one THF molecule. This crystal also contained hexane solvent molecules, which contribute to the temperature sensitivity of the crystals. These crystals melt above −80 °C. A packing diagram of the complex (Figure 6) shows that the hexane molecules reside in channels bounded by the alkyllithium tetramers. The Li–C bond distances in the tetrameric core are 2.181(3)–2.742(25) Å, while the Li–O distances are 1.952(23)–2.002(21) Å.

The X-ray structure of the [(n-BuLi·DME)$_4$]$_\infty$ (**4**) complex is shown in Figure 7. As in complex **1**, the distorted tetramer is observed, with each lithium cation solvated by one oxygen atom of a DME molecule. The DME molecules link tetramers together

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[22] The term distorted refers to the lack of perfect cubic symmetry of the tetrameric "cubic" Li–C core of complexes 1, 3, and 4 as compared to those Li–O cores of published X-ray structures of lithium alkoxides, enolates, and aldolates. (See ref 28.) For complexes 1, 3, and 4, this distortion is clearly seen as the nonplanarity of the six faces of the cube. The term disordered refers to noninteger site occupancy factors for the crystallographic model.

[23] Gaussian 92, Revision A: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1992.

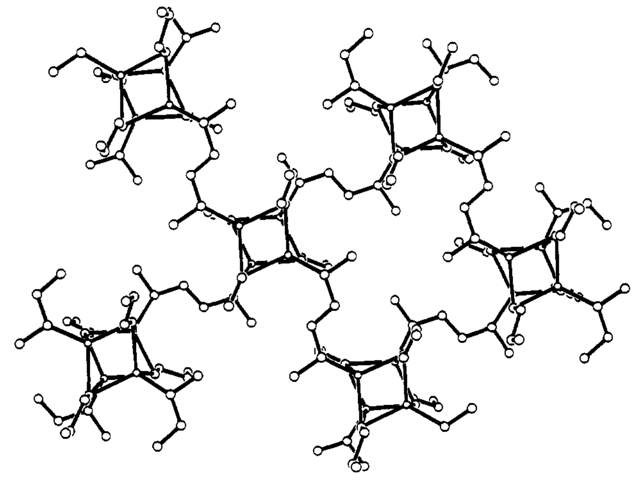

Figure 8. Computer-generated packing diagram for the $[(n\text{-BuLi}\cdot\text{DME})_4]_\infty$ complex (**4**) illustrating the polymeric nature of the complex.

in a polymer network. (See Figure 8.) This is similar to what is observed in **1**, except that each lithium is solvated by DME, whereas only two lithium cations were solvated by TMEDA in complex **1**. The Li–C distances range from 2.242(15) to 2.285(14) Å, while the Li–O distances are 2.005(14) Å.

As was stated earlier, we obtained crystalline material, complex **5**, when 0.75–1.0 equiv of TMEDA is added to a *n*-BuLi solution. Based upon the direct methods structure solution of the X-ray crystallographic data, the formula of the complex is $[(n\text{-BuLi})_4\cdot{}^3/_2\text{TMEDA}]_\infty$.[24] The structure of this complex appears to be similar to **1**, except that three of the four lithium cations of the distorted[22] tetramer are solvated by TMEDA molecules. While the structure of this complex became apparent after the direct methods structure solution technique was applied to the X-ray data collected, least-squares refinement was not totally successful (the agreement factors are R, $R_w = 0.25$). A problem is that the complex crystallizes as very thin plates, which diffract poorly. Because we cannot refine this structure satisfactorily, we do not feel comfortable reporting specific details of this structure at this time and are continuing our efforts to obtain a high-quality structure.

Many solution and theoretical structures of *n*-BuLi·TMEDA[6a,8] and *n*-BuLi·THF[6] complexes have been reported, but to date only one solid-state structure containing *n*-BuLi has been reported.[11] The four X-ray crystal structures reported here have direct relevance to previously reported solution structures and theoretical calculations. In the following discussion, the structural characteristics of complexes **1**–**4** will be compared to corresponding solution studies and their potential effects on the reactivity of *n*-BuLi will be outlined.

$[(n\text{-BuLi})_4\cdot\text{TMEDA}]_\infty$ (1). Three noteworthy features of this structure are as follows: (1) the distorted tetrameric aggregation state of *n*-BuLi (Figure 1) and the partial solvation of the tetramers by two TMEDA molecules; (2) the η^1-solvation by TMEDA and the polymeric nature of the crystalline material; and (3) the extended conformations of the *n*-butyl groups. To date *n*-BuLi tetramers in hydrocarbon solutions containing TMEDA have not been observed directly. However, NMR[2h] and colligative[8b] data suggest that tetrameric η^1-bound *n*-BuLi·TMEDA complexes could exist in equilibrium with the dimeric complex in the presence of low concentrations of TMEDA. Also, partially TMEDA-solvated *sec*-BuLi tetramers have been observed by colligative measurements.[10] Complex **1** provides a plausible structure for these proposed partially solvated tetramers, although the polymeric nature of the crystalline material makes *direct* extrapolations to possible solution structures nearly impossible and very risky.

$$\text{Li - C}^{\alpha}\text{H}_2\text{ - C}^{\beta}\text{H}_2\text{ - C}^{\gamma}\text{H}_2\text{ - C}^{\delta}\text{H}_3$$

Figure 9. Atom labeling scheme for *n*-BuLi.

Several X-ray structures[25] of η^1-bound TMEDA alkyl- and aryllithium compounds have been reported, including several polymeric materials. The tetramers of **1** are also very similar to those reported for methyllithium (MeLi),[26] ethyllithium,[27] and $(\text{MeLi}\cdot\text{TMEDA})_\infty$.[25d] While the origin of the distortions[22] in the tetrameric core structure relative to tetramers with cubic structures[2j,28] is not known at this time, it is clear that tetramer **1** could be pictured as being formed from nonplanar *n*-BuLi dimers (Figure 4).

The extended conformations of the *n*-BuLi groups are those predicted as the lowest energy conformations.[6e] In **1**, the protons attached to the α- and β-carbons (Figure 9) are in closest proximity (2.12–2.33 Å) to the lithium cations and are consistent with those determined using ^{6}Li–^{1}H NOE NMR for tetrameric *n*-BuLi in pure THF-d_8 at –96 °C,[6e] hexameric *n*-BuLi in cyclohexane-d_{12} at 12 °C,[5d] and dimeric *n*-BuLi in toluene-d_8 at –64 °C.[8a]

If the general structure of partially solvated tetramer **1** exists in solution, it may help explain many reported reactions where rate or product yield maxima are observed when less than 1 equiv of TMEDA is added, including polymerization rate maxima.[4c,9] Clearly, solution structure data for hydrocarbon solutions of *n*-BuLi containing less than 1 equiv of TMEDA are needed.

$(n\text{-BuLi}\cdot\text{TMEDA})_2$ (2). This dimeric aggregate has been observed in the presence of more than 1 equiv of TMEDA in both THF[6a] and toluene[8a] using NMR. Complex **2** is the solid-state representation of these solution structures. Notable features of **2** are the nonplanar Li–C–Li–C ring and the cisoid arrangement of the *n*-butyl groups relative to the ring. Recently, an X-ray structure of (sodium *N*-methylbenzylamide–TMEDA)$_2$ was reported, which also contains a nonplanar dimer ring, and the arrangement of the amido substituents was cis relative to the ring.[29] Several other organolithium complexes having nonplanar dimer structures have been determined by X-ray crystallography[30] and semiempirical MNDO calculations.[31] In complex **3**, the bend in the dimer ring is 16(1)°. It is interesting that all of the structures having nonplanar dimer rings contain either TMEDA or diglyme, both of which act as bidentate chelating ligands in these structures. We hope to address the issue of the bent dimer ring and the cisoid arrangement of the butyl groups relative to the dimer ring using semiempirical calculations. Schleyer et al. reported the MNDO-calculated structures for the *n*-BuLi$_2$–TMEDA–anisole dimer.[8a] However, this group did not report results for the *n*-BuLi·TMEDA dimer. Hence, it is not clear whether the *n*-BuLi·TMEDA dimer had been investigated at that time.

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[24] Integration of the TMEDA and *n*-BuLi resonances in the ^{1}H NMR spectrum of **5** in toluene-d_8 at room temperature yielded $(n\text{-BuLi})_4\cdot\text{TMEDA}_{2.6}$. Interestingly, complex **5** is soluble in toluene-d_8 at concentrations much higher than it is in pure pentane solution.

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[30] The X-ray structures of $(\text{LiBr}\cdot\text{TMEDA})_2$ and lithium pinacolonate $(\text{CH}_2{=}\text{C(OLi)C(CH}_3)_3)\cdot$diglyme $(\text{CH}_3\text{O(CH}_2)_2\text{O(CH}_2)_2\text{O(CH}_2)_2\text{OCH}_3)$ both contain planar and nonplanar dimer rings. In the case of the enolate, a cis arrangement between the *tert*-butyl groups relative to the dimer ring was observed in the nonplanar dimer: Williard, P. G.; Liu, Q.-Y., unpublished results.

[31] A nonplanar dimer ring and a cis arrangement between the *tert*-butyl groups relative to the dimer ring was determined as the most stable structure for (lithiopinacolonate–TMEDA)$_2$ using MNDO (Gaussian 86) calculations. See: Nichols, M. A. Ph.D. Dissertation, Duke University, Durham, NC, 1990.

Scheme I. Possible Mechanism for the Conversion of Hexameric *n*-Butyllithium to the Dimer upon Addition of One Equivalent of TMEDA in a Hydrocarbon Solution[a]

$$(n\mathrm{BuLi})_6 \underset{\text{TMEDA}}{\overset{\text{0.50 Equiv}}{\rightleftharpoons}} \underset{(\mathbf{6})}{(n\mathrm{BuLi})_4 \cdot \mathrm{TMEDA}_2} \underset{\text{TMEDA}}{\overset{\text{0.25 Equiv}}{\rightleftharpoons}} \underset{(\mathbf{7})}{(n\mathrm{BuLi})_4 \cdot \mathrm{TMEDA}_3} \underset{\text{TMEDA}}{\overset{\text{0.25 Equiv}}{\rightleftharpoons}} \underset{(\mathbf{2})}{(n\mathrm{BuLi} \cdot \mathrm{TMEDA})_2}$$

[a] If **6** and **7** are intermediates in this process, they could be the nonpolymeric analogues to complexes **1** and **5**, respectively.

Short Li–H contacts are observed for the α- (2.083–2.413 Å) and β-protons (2.724–3.576 Å) of *n*-BuLi, as well as for the TMEDA *N*-methylene protons (2.997–3.265 Å). These are in agreement with those observed using ^{6}Li–^{1}H NOE NMR in toluene-d_8 solutions containing *n*-BuLi, TMEDA, and anisole, where the (*n*-BuLi·TMEDA)$_2$ was proposed to exist.[8a]

Relevance to the Partially Solvated TMEDA Tetramers 1 and 5 to the Mechanism of Solvation of *n*-BuLi. Nonpolymeric partially solvated tetramers having structures similar to **1** and **5** could be proposed as intermediates in the conversion of hexameric *n*-BuLi to the dimeric form **2** upon addition of TMEDA to dilute (i.e., <1.0 M) hydrocarbon solutions of *n*-BuLi. (See Scheme I.) The validity of Scheme I and the exact intermediates that are formed in solution during the solvation of *n*-BuLi can be determined using NMR.[32,33]

(*n*-BuLi·THF)$_4$·Hex (3). Solid-state and solution structure studies of aryl- and alkyllithium compounds in THF are complicated by decomposition of THF over time at elevated temperatures.[34] Tetrameric *n*-BuLi has been observed in THF-d_8 using NMR,[6a,b,c,e] and the kinetics of THF addition have been studied using rapid-injection NMR.[6d] Complex **4** is the solid-state representation of this tetrameric aggregate observed in solution. Again, the tetrameric Li–C core is distorted with each lithium cation solvated by one THF molecule. Short Li–H contacts for the α- (1.837–2.510 Å) and β-protons (2.496–3.190 Å) of the *n*-butyl group are observed in the X-ray structure, which are consistent with the extended conformations of the butyl groups observed in the ^{6}Li–^{1}H NOE NMR studies.[6e] The presence of hexane molecules in the crystals is not of any significant importance, except that as a consequence, the crystalline material is extremely temperature-sensitive.

Purification of *n*-BuLi. Recrystallization of complexes **1** and **5** provides a very easy method to purify *n*-BuLi from alkoxide and halide impurities, which are common impurities in commercial and ^{6}Li isotopically labeled solutions.[35] An alternative method of purification involves the distillation of the oil at very low pressures.[36] For safety considerations, we feel that the recrystallization of complex **5** as a procedure to purify *n*-BuLi may prove very effective. Crystalline **1** and **5** can be recrystallized in Schlenk tubes.[14] For example, we have grown crystals up to 3 cm in diameter. Removal of TMEDA from the crystals of complexes **1** and **5** is not trivial. Placing **1** or **5** directly under a vacuum of 50–100 mTorr results in decomposition of *n*-BuLi. However, if extra TMEDA is added to a hydrocarbon solution of **1** or **5** and a homogeneous solution is formed, TMEDA and the solvent can be removed at reduced pressure (at −20 to −40 °C) to yield the viscous oil.[37] This procedure shows great promise as an easy, safe method to prepare very pure *n*-BuLi, particularly ^{6}Li-labeled, for mechanistic and solution structure studies.

Conclusions

The four X-ray crystal structures of *n*-BuLi complexes reported here are the solid-state representations of observed and proposed tetrameric and dimeric solution *n*-BuLi structures. However, the distortions in the tetrameric Li–C core structures relative to other tetramers and the nonplanar dimer Li–C–Li–C ring are novel and interesting. In particular, the partially TMEDA-solvated tetramers **1** and **5** support those suggested in many studies and may be intermediates in the conversion of hexameric *n*-BuLi to the dimeric form upon addition of TMEDA. The X-ray structure of the *n*-BuLi·TMEDA dimer contains a nonplanar dimer Li–C–Li–C ring and clearly warrants further examination using theoretical calculations. Finally, the purification procedure presented for *n*-BuLi has tremendous potential for use in preparing high-purity isotopically labeled *n*-BuLi for further mechanistic studies.

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Supplementary Material Available: Tables of crystallographic data, atomic numbering schemes, atomic positional and thermal parameters, bond lengths and angles, and selected torsion angles for complexes **1–4** (51 pages). Ordering information is given on any current masthead page.

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