

[[$(\text{MeLi})_4(\text{dem})_{1.5}\}_{\infty}$] and [$(\text{thf})_3\text{Li}_3\text{Me}\{(\text{N}t\text{Bu})_3\text{S}\}$]]— How to Reduce Aggregation of Parent Methylithium

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In memory of Professor Ron Snaith

Abstract: Organolithium compounds play the leading role among the organometallic reagents in synthesis and in industrial processes. Up to date industrial application of methylithium is limited because it is only soluble in diethyl ether, which amplifies various hazards in large-scale processes. However, most reactions require polar solvents like diethyl ether or THF to disassemble parent organolithium oligomers. If classical bidentate donor solvents like TMEDA (TMEDA = *N,N,N',N'*-tetramethyl-1,2-ethanediamine) or DME (DME = 1,2-dimethoxyethane) are added to methylithium, tetrameric units are linked to form polymeric arrays that suffer from reduced reactivity and/or solubility. In this

paper we present two different approaches to tune methylithium aggregation. In [[$(\text{MeLi})_4(\text{dem})_{1.5}\}_{\infty}$] (**1**; DEM = EtOCH₂OEt, diethoxymethane) a polymeric architecture is maintained that forms microporous soluble aggregates as a result of the rigid bite of the methylene-bridged bidentate donor base DEM. Wide channels of 720 pm in diameter in the structure maintain full solubility as they are coated with lipophilic ethyl groups and filled with solvent. In compound **1** the long-range Li₃CH₃⋯Li interactions found in solid [[$(\text{MeLi})_4$]_∞] are maintained. A different

Keywords: carbanions • lithium • metalation • solvent effects • sulfur

approach was successful in the disassembly of the tetrameric architecture of [[$(\text{MeLi})_4$]_∞]. In the reaction of dilithium triazasulfite both the parent [$(\text{MeLi})_4$] tetramer and the [[Li₂{(N*t*Bu)₃S}]]₂ dimer disintegrate and recombine to give an MeLi monomer stabilized in the adduct complex [(*thf*)₃Li₃Me{(N*t*Bu)₃S}] (**2**). One side of the Li₃ triangle, often found in organolithium chemistry, is shielded by the tripod-like triazasulfite, while the other face is μ₃-capped by the methanide anion. This Li₃ structural motif is also present in organolithium tetramers and hexamers. All single-crystal structures have been confirmed through solid-state NMR experiments to be the same as in the bulk powder material.

Introduction

Unequivocally organolithium compounds play the leading role among the organometallic reagents in synthesis^[1] and industrial processes.^[1b] Industrial production of *n*-butyllithi-

um, the most applied organolithium compound, is 2000–3000 tons of parent *n*BuLi per year. However, demand for others like methylithium is increasing.^[2] Up to date industrial application of methylithium is limited because it is only soluble in diethyl ether (ca. 5%), which amplifies various hazards in large-scale processes. In general, the reactivity, basicity, and regio- and stereoselectivity of organolithium compounds can easily be modified by additives (transition metals, halides, alkoxides, amides, etc.) or donor bases (monodentate/chelating ethers/amines, cryptands, etc.) and make them immaculate reagents in metalations. It is one of the paradigms in organolithium chemistry that neutral donor bases lower the aggregation in solution and enhance the reactivity, because in general the rate-determining species seems to be the monomer.^[3] Hence, most reactions require polar solvents like diethyl ether or THF to disassemble parent organolithium oligomers. This is always a borderline approach between solvent attack (e.g., ether cleavage leads to lithium alkoxides) and sufficient solubility.

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The dominant aggregation polyhedron in parent organolithium solid-state structures^[4] is the tetrahedron in [(MeLi)₄],^[5] [(EtLi)₄],^[6] and [(tBuLi)₄],^[7] and the octahedron in [(nBuLi)₆],^[7] [(iPrLi)₆],^[8] [(CyLi)₆]^[9] (Cy = cyclohexyl), [(Me₂C)₂CHCH₂Li]₆,^[10] and [(Me₃SiCH₂Li)₆]^[11] made up of four or six lithium atoms, respectively, with the α -carbon capping an Li₃ face of the deltahedron. As the [(MeLi)₄] tetramer persists in the known solvated MeLi structures, the tetrahedron seems to be the favorite aggregate of solvated lithium organics like [(MeLi(thf))₄],^[12] [(nBuLi(thf))₄],^[13] [(tBuCH₂CH₂Li(thf))₄],^[14] and [(tBuC≡CLi(thf))₄].^[15] This structural motif is maintained when the donating group is intramolecular provided in a side arm donation like in [(MeO(CH₂)₂(Me)CHLi)₄],^[16] [(MeO(CH₂)₂CH₂Li)₄],^[17] and [(H₁₀C₅NCH₂Li)₄(thf)₂].^[18] Only two dimeric structures, [(tBuLi(OEt₂))₂]^[7] and [(nBuLi(tmeda))₂]^[13] (TMEDA = *N,N,N',N'*-tetramethyl-1,2-ethanediamine, Me₂NCH₂CH₂NMe₂) are known. If bidentate donor solvents are added tetrameric units

are linked to form polymeric arrays as in [(MeLi)₄(tmeda)₂]_∞,^[19] [(nBuLi)₄(tmeda)]_∞,^[13, 20] and [(nBuLi)₄(dme)]_∞,^[13] (DME = 1,2-dimethoxyethane, MeOCH₂CH₂O-Me). From a synthetic point of view the most striking disadvantages of this solvated aggregates are their reduced reactivity (e.g., [(MeLi(thf))₄]^[12]) and/or solubility (e.g., [(MeLi)₄(tmeda)₂]_∞,^[19] [(nBuLi)₄(tmeda)]_∞,^[13, 20]).

Results and Discussion

In this paper we present the polymeric aggregate [(MeLi)₄(dem)_{1.5}]_∞ (**1**; DEM = diethoxymethane, EtO-CH₂OEt), which does not suffer from the drawbacks of reduced reactivity or solubility. Apart from the low flame and boiling point of diethyl ether, commercially available solutions of MeLi in diethyl ether turn milky white and precipitate a white solid in medium- to long-term storage. This decreases the concentration of the solution. Hence repeated titration is required prior to stoichiometric reactions. Addition of the frequently used TMEDA or DME lowers the solubility even further. The answer to the challenge was the employment of DEM.^[21] DEM provides higher solubility (8% in commercially available solution) and requires lower explosion protection than diethyl ether (T3 instead of T4).

In the solid-state structure of [(MeLi)₄(dem)_{1.5}]_∞ (**1**) straight polymeric rods of Li₄ tetrahedra are formed by face-to-vertex-bridging methyl groups along a threefold axis. This basic polymeric arrangement emulates the solid-state structure of parent [(MeLi)₄]_∞ along the body diagonal of the cubic body centered cell (Figure 1, top).

In contrast to [(MeLi)₄]_∞ only one methyl group in [(MeLi)₄(dem)_{1.5}]_∞ is exposed to intertetrameric long-range Li...C interactions. The remaining three methyl groups cap a single Li₃ face each without further coordination (Figure 1, bottom). Each of the three lithium atoms of the Li₃ face orthogonal to the threefold axis are coordinated to a single oxygen atom of the DEM donor. The second oxygen atom of the DEM donor provides a link to another [(MeLi)₄]_∞ rod (Figure 1, bottom).

An hexagonal channel, made up from six rods, with an inner diameter greater than 700 pm is generated from the space-group symmetry. These channels can easily accommodate various solvents as the lipophilic ethyl groups of the DEM molecules coat the inner walls. In the presented structure the channels are filled with cyclopentane molecules (ca. 370 pm in diameter). The oxygen donor atoms are so close to each other in diethoxymethane that the bite is not suitable to coordinate the same lithium atom (like TMEDA in [(nBuLi(tmeda))₂]^[13]). It is also inappropriate to achieve closest sphere packing of [(RLi)₄] by linking two units as in [(MeLi)₄(tmeda)₂]_∞,^[19] [(nBuLi)₄(tmeda)]_∞,^[13, 20] and [(nBuLi)₄(dme)]_∞.^[13] The donor bases in these structures are so flexible that they tolerate the most dense arrangement of the organolithium units in the lattice without any space for additional solvent; this encourages precipitation. DEM yields the microporous structure of [(MeLi)₄(dem)_{1.5}]_∞ with solvent-filled channels, reminiscent of the structure of ice, that improves solubility (Figure 2).

Abstract in German: *Lithiumorganische Verbindungen spielen sowohl in der Laborsynthese als auch in industriellen Prozessen unter den metallorganischen Verbindungen die Hauptrolle. Jedoch ist bis heute die Anwendung von Methyl-lithium beschränkt, da es nur in Diethylether löslich ist. Gerade dieses leicht entzündliche Lösungsmittel vergrößert die Gefahren des ohnehin schon pyrophoren Methyl-lithiums. Dennoch sind in den meisten Reaktionen polare Lösungsmittel wie Diethylether oder Tetrahydrofuran notwendig, um die Organolithium-Oligomere aufzubrechen. Klassische chelatisierende Donorbasen wie TMEDA oder DME helfen hier nicht, da sie zur Aggregation von tetrameren [(MeLi)₄]-Einheiten führen und die Reaktivität und/oder Löslichkeit herabsetzen. In dieser Arbeit stellen wir zwei Strategien vor, um die Aggregation von Methyl-lithium zu steuern. In [(MeLi)₄(dem)_{1.5}]_∞ (**1**; DEM = EtOCH₂OEt, Diethoxymethan) wird eine polymere Architektur aus löslichen mikroporösen Kanälen aufgebaut. Die starre Verankerung der Methylenbrücke in Diethoxymethan führt zu einer weitmaschigen Verknüpfung von [(MeLi)₄]-Stäbchen. Die gebildeten Kanäle mit einem lichten Durchmesser von 720 pm gewährleisten die volle Löslichkeit, da sie mit lipophilen Ethylgruppen ausgekleidet sind und Lösungsmittelmoleküle aufnehmen können. Die weitreichenden Li₃CH₃...Li Wechselwirkungen, wie man sie aus der Festkörperstruktur von [(MeLi)₄]_∞ bereits kennt, bleiben in [(MeLi)₄(dem)_{1.5}]_∞ (**1**) erhalten. Ein anderer Ansatz war bei der Deaggregation von [(MeLi)₄]-Tetrameren erfolgreich. In der Reaktion von Dilithiumtriazasulfid mit Methyl-lithium wird sowohl die dimere Struktur des [(Li₂(NtBu)₃S)]₂ als auch die tetramere des [(MeLi)₄] aufgegeben. Durch Adduktbildung wird monomeres MeLi in [(thf)₃Li₃Me(NtBu)₃S] (**2**) stabilisiert. In der Struktur ist die eine Seite des in der lithiumorganischen Chemie weit verbreiteten Li₃-Dreiecks vom tripodalen S(NtBu)₃²⁻-Dianion besetzt, während die andere μ_3 von der Methanid-Gruppe überdacht wird. Dieses Strukturmotiv findet man auch in lithiumorganischen Tetrameren oder Hexameren. Durch Festkörper-NMR-Spektroskopie haben wir gezeigt, dass die Einkristallstrukturen auch die Bauprinzipien des mikrokristallinen Pulvers wiedergeben.*

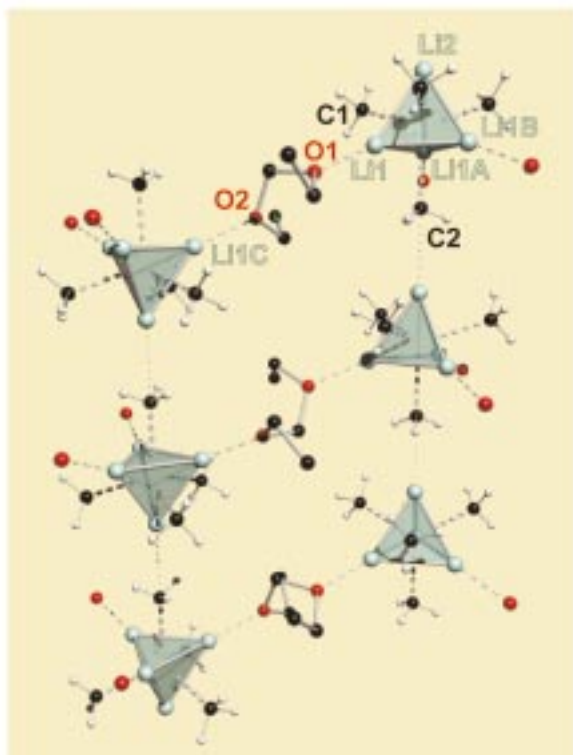
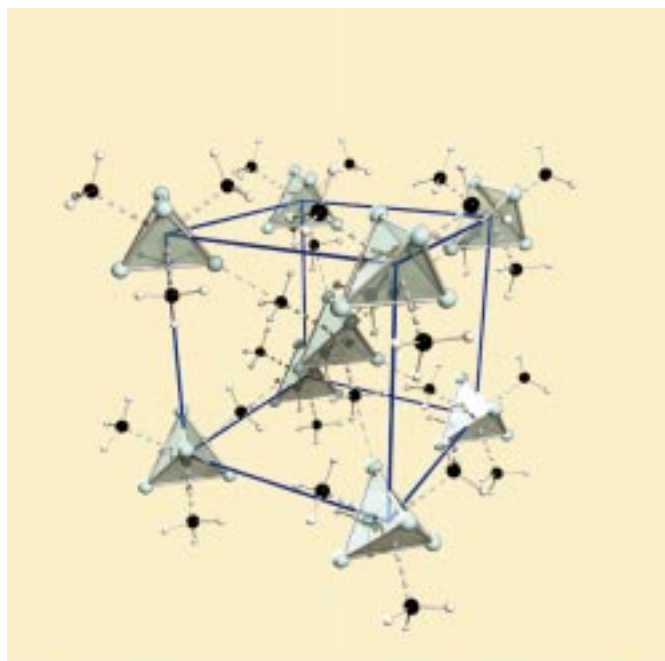


Figure 1. Top: Solid-state structure of $[(D_3CLi)_4]_\infty$ at 1.5 K.^[5c] Li–C 225.6(6), Li \cdots C 235.6(6), Li \cdots Li 259.1(9) pm. Bottom: Section of the solid-state structure of $[(MeLi)_4(dem)_{1.5}]_\infty$. The $(MeLi)_4$ units are located at a crystallographic threefold axis, emulating the body diagonal arrangement of parent $[(MeLi)_4]_\infty$. Three lithium atoms of the Li_4 tetrahedra are coordinated to one oxygen atom of the diethoxymethane donor base. The second oxygen atom provides the link to a second Li_4 unit each. The fourth lithium atom supplies long-range $Li_3CH_3\cdots Li$ interaction of 243.5(8) pm. Selected bond lengths [pm]: C1–Li1 224.0(6), C1–Li2 227.1(4), C2–Li1 227.3(5), Li1 \cdots Li2 252.0(8), Li1 \cdots Li3 255.1(8), Li1–O1 197.8(16), O2–Li1C 199.5(15).

As far as the activation of the methanide group is concerned the long-range $Li_3-CH_3\cdots Li$ interactions seem to be vital. In the $R_3C_\alpha Li_3$ moiety in organolithium deltahedra

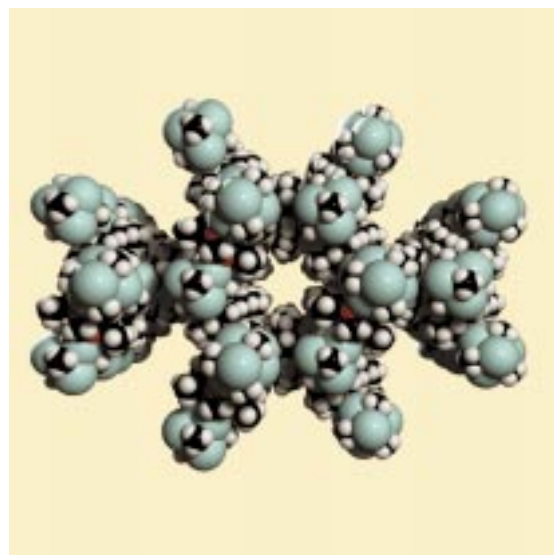


Figure 2. Space-filling diagram depicting the channels orthogonal to the paper plane, which can accommodate solvent. The inner diameter of the channels is 720 pm.

the α -carbon atom is hexacoordinate. In the base-free structures C_β –Li contacts are vital to provide electron density to the metal core. They range from the same distance as the long C_α –Li bonds to the Li_3 triangle ($[iPrLi]_6$,^[8] $[nBuLi]_6$ ^[7]) to about 18 pm longer ($[CyLi]_6$,^[9] $[(Me_2C)_2CHCH_2Li]_6$ ^[10]). If no β -carbon atoms are available, long-range Li \cdots C interactions between tetrameric units are employed ($Li_3CD_3\cdots Li$ in $[(D_3CLi)_4]_\infty$ ^[5c] 235.6(6) in comparison to 225.6(6) pm for Li– C_α , 250.1 and 228.1 pm in $[(EtLi)_4]_4$ ^[6b] and 227.1(4) and 243.5(4) pm in $[(MeLi)_4(dem)_{1.5}]_\infty$). These long-range interactions increase the basicity of the C_α atom as the related lithium atom coordinates the methyl group from the H_3 face. In contrast to other known monomeric or polymeric donor-stabilized organolithium compounds, in $[(MeLi)_4(dem)_{1.5}]_\infty$ the additional Li \cdots C long-range interactions are maintained.

In the triple quantum 7Li MAS NMR spectroscopic experiment,^[22] we observed two signals in the ratio 3:1 of which the first ($\delta_{iso}=2.1$) is assigned to the three lithium atoms orthogonal to the threefold axis along the rods of the Li_4 tetrahedra and the second ($\delta_{iso}=1.0$) to the lithium atom on the crystallographic threefold axis (Figure 3). The signal at $\delta_{iso}=1.2$ is due to some lithium halide impurities. In the ^{13}C CP MAS NMR spectrum the magnetically different methyl groups could not be resolved and gave rise to a broad singlet at $\delta = -14.2$ relative to external TMS. In DEM four different sites could be resolved in the 7Li NMR experiment upon cooling the sample. At room temperature the singlet at $\delta = 3.5$ broadens and gives signals at $\delta = 3.8, 3.1, 2.8,$ and 2.3 at $-80^\circ C$ (relative to external 1M LiCl in D_2O). This indicates a monomer/oligomer/polymer equilibrium in DEM.

The next challenge was to break up the tetrameric aggregation of $[(MeLi)_4]$. An obvious choice was to employ the cap-shaped triazasulfite dianion.^[23] The lone pair at the sulfur atom in the tripodal ligand $S(NtBu)_3^{2-}$ in $[(Li_2-(NtBu)_3S)]_2$ ^[24] is stereochemically active, and the negative charge is delocalized over the three nitrogen atoms. Formally

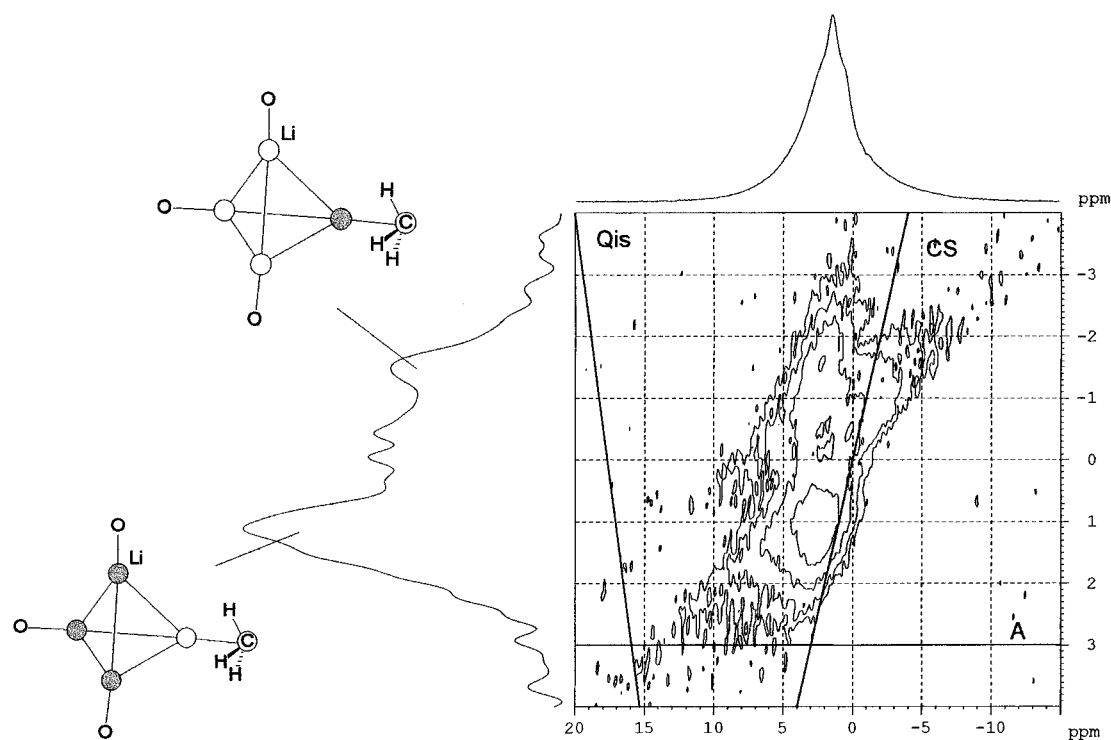


Figure 3. Sheared, t_1 -rotor-synchronized and z -filtered 3Q MQMAS ^7Li NMR spectrum of $[(\text{MeLi})_4(\text{dem})_{1.5}]_\infty$ (**1**) showing three sites for ^7Li . On the left is the projection onto F_1 along F_2 as obtained after shearing FT. Top spectrum is the standard single pulse ^7Li MAS spectrum. Additional axes are included for interpretation: **A** is the anisotropic axis lying parallel to the F_2 axis, **Qis** is the quadrupolar induced shift axis, and **CS** is the chemical shift axis.

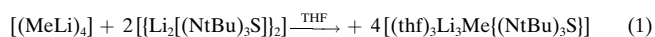
coordination of three lithium atoms to the dianionic cap converts it to a monocationic cap, which can be regarded as an inverted crown ether or cryptand. The three lithium atoms prearrange to form an Li_3 triangle, often found in organolithium structures. Hence, coordination of a single methanide anion seems feasible (Scheme 1).

From our work we know that the dilithium triazasulfite is capable of co-ordination of various salts like LiX ($\text{X} = \text{halide}$) in $[(\text{thf})_3\text{Li}_3\text{I}[(\text{NtBu})_3\text{S}]_2]^{[25]}$ and $[(\text{thf})_3\text{Li}_3\text{Br}[(\text{NtBu})_3\text{S}]_2]^{[25]}$ LiN_3 in $[(\text{thf})_3\text{Li}_3\text{N}_3[(\text{NtBu})_3\text{S}]_\infty]^{[26]}$ or KOtBu in $[(\text{thf})_2\text{Li}_2\text{K}(\text{OtBu})[(\text{NtBu})_3\text{S}]_2]^{[27]}$. The $\text{Li}\cdots\text{Li}$ distances in this cap-shaped $\text{Li}_3(\text{NtBu})_3\text{S}^+$ cation (Scheme 1, middle) are quite variable and depend on the radius of the coordinated anion (275 (S^{2-}),^[28] 285 (N^{3-}),^[26] 293 (Br^-),^[25] and 300 pm (I^-)^[25]). Similarly, the dilithium triazaselenite $[\text{Li}_2[(\text{NtBu})_3\text{Se}]_2]^{[29]}$ also co-ordinates to lithium halides.^[30] In general the $\text{Li}\cdots\text{Li}$ distances are larger than those found in parent tetrameric organolithium complexes (241 $[(\text{tBuLi})_4]$,^[7] 253 $[(\text{EtLi})_4]$,^[6] 259 pm $[(\text{MeLi})_4]$,^[5]), but similar distances can be found in the

Scheme 1. Conversion of the cap-shaped $\text{S}(\text{NtBu})_3^{2-}$ dianion to a cationic $\text{Li}_3(\text{NtBu})_3\text{S}^+$ ligand capable of anion solvation.

hexameric aggregates (294 in $[(\text{nBuLi})_6]$ ^[7] or 296 pm in $[(\text{iPrLi})_6]$,^[8]).

With this in mind the dilithium triazasulfite $[\text{Li}_2[(\text{NtBu})_3\text{S}]_2]$ should be a suitable synthon to achieve disintegration of the parent $[(\text{MeLi})_4]$ tetramer and stabilization of a MeLi monomer in a $[(\text{thf})_3\text{Li}_3\text{Me}\{(\text{NtBu})_3\text{S}\}]$ complex, similar to the species mentioned above. $[(\text{MeLi})_4]$ reacts smoothly with a triazasulfite solution when warmed to slightly above room temperature for a couple of minutes. Both the $[(\text{MeLi})_4]$ tetramer and the $[\text{Li}_2[(\text{NtBu})_3\text{S}]_2]$ dimer disintegrate and recombine to give $[(\text{thf})_3\text{Li}_3\text{Me}\{(\text{NtBu})_3\text{S}\}]$ (**2**), [Eq. (1)].



Compound **2** is a white solid which instantaneously turns blue when it is air exposed. It is as pyrophoric as parent $[(\text{MeLi})_4]_\infty$. The compound is readily soluble in THF and also in hexane once THF is coordinated. Equation (1) shows that recombination of one tetrameric methyllithium and two dimeric triazasulfites gives four methanidetrilithium triazasulfite monomers. Compound **2** was crystallized from hexane solution at -36°C . The colorless crystals were of sufficient quality for X-ray crystallographic studies.

The crystal structure of **2** (Figure 4) shows a triazasulfite coordinated to three lithium atoms in a μ_2 arrangement at every SN_2 bisection so that a Li_3 triangle, known from organolithium compounds, is formed. The upper triangle face is shielded by the triazasulfite, while the lower face is capped by the methanide anion.^[31] The $\text{Li}-\text{C}$ bond lengths in **2** range from 224.0(7) to 232.5(8) pm and match those found in organolithium compounds (224.6(14) in $[(\text{tBuLi})_4]$,^[7] 225.6(6)

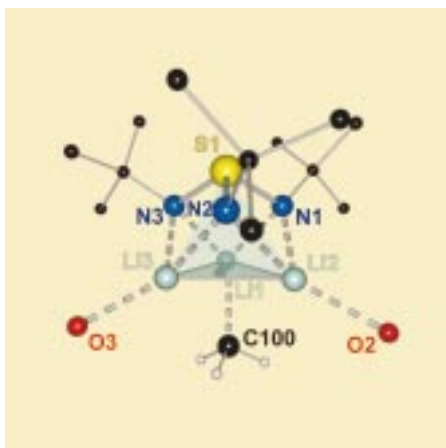
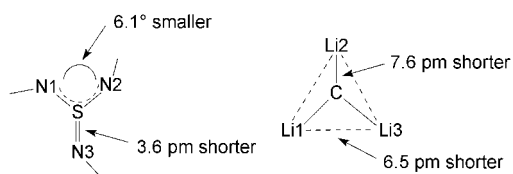


Figure 4. Solid-state structure of $[(\text{thf})_3\text{Li}_3\text{Me}\{(\text{NtBu})_3\text{S}\}]$ (**2**); selected bond lengths [pm] and angles [$^\circ$]: S1–N1 166.7(3), S1–N2 167.1(3), S1–N3 163.2(3), N1–Li1 205.9(7), N1–Li2 202.8(7), N2–Li2 212.4(7), N2–Li3 197.5(7), N3–Li3 215.4(7), N3–Li1 199.2(7), Li1 \cdots Li2 263.5(8), Li2 \cdots Li3 267.0(9), Li3 \cdots Li1 257.4(8), C100–Li1 232.5(8), C100–Li2 224.0(7), C100–Li3 230.6(8), N1–S1–N2 96.84(15), N2–S1–N3 101.03(14), N3–S1–N1 104.26(15).

in $[(\text{MeLi})_4]$,^[5] 228.1 pm in $[(\text{EtLi})_4]$ ^[6]. The Li \cdots Li distances in **2** range from 257.4(8) to 267.0(9) pm and the shortest is almost identical to the related distance in $[(\text{MeLi})_4]$. The three THF molecules coordinated to the lithium atoms form a suitable cavity and provide sufficient shielding to the methanide anion. At first sight one anticipates a C_3 axis in the molecule along the S1 \cdots C100 vector, but besides the non-isosceles Li_3 triangle, the S–N bonds of the triazasulfite are not equal. The S1–N3 bond (163.2(3) pm) is 3.6 pm shorter than the other two (av. 166.8(3) pm). N3 is coordinated to the shorter Li1 \cdots Li3 side of the Li_3 triangle (257.4(8) pm; 6.5 pm shorter than the two others). To counterbalance this N3 shift the methanide C100 is more shifted towards Li2. The C100–Li2 bond length (224.0(7) pm) is 7.6 pm shorter than the C100–Li1,3 bond lengths (av. 231.6(8) pm) (Scheme 2).



Scheme 2. Bonding in the triazasulfite moiety: N3 is coordinated to the shorter Li1 \cdots Li3 side of the Li_3 triangle, while the methanide C is more shifted towards Li2.

The unsheared two-dimensional ^7Li MQMAS NMR spectrum of **2** has a sharp and a broad signal at isotropic shifts of $\delta_{\text{iso}} = 2.75$ and 1.55, respectively, with the area ratio 2:1.^[32] The shape of the contour plot in Figure 5 indicates that the site at of $\delta_{\text{iso}} = 2.75$ is well defined because the signal shows neither a distribution of chemical shifts nor of quadrupolar couplings. This peak can be assigned to the two sites Li1 and Li3, because they have the same distance to the methanide anion. Hence the broad signal of the two-dimensional MQMAS has to be assigned to the Li2 site and shows a small distribution of

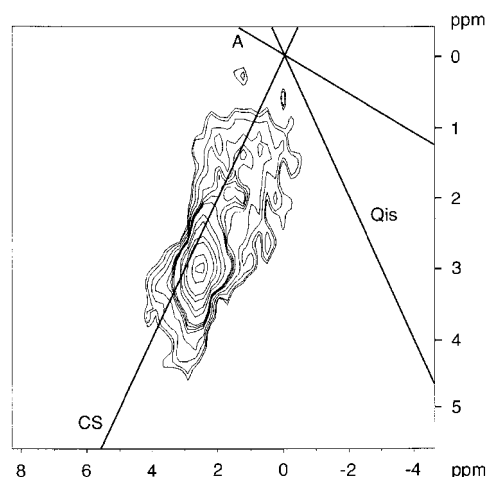


Figure 5. The unsheared 3Q MQMAS ^7Li solid-state NMR spectrum of **2** shows two ^7Li sites with an intensity ratio of the two signals nearly 2:1. Additional axes are included for interpretation: **A** is the anisotropic axis with the slope of $-7/27$, **Qis** is the quadrupolar induced shift axis, and **CS** is the chemical shift axis.

chemical shifts. The result of the ^7Li MQMAS is consistent with the single-pulse high-power decoupled ^6Li MAS NMR experiment, which also exhibits two sites for **2** in the ratio 2:1.

Conclusion

The rigid bite of the methylene-bridged bidentate donor base DEM in $[(\text{MeLi})_4(\text{dem})_{1.5}]_\infty$ (**1**) generates soluble microporous aggregates, while the more flexible ethylene-bridged donor bases like DME and TMEDA create insoluble polymers. In compound **1** the long-range $\text{Li}_3\text{CH}_3 \cdots \text{Li}$ interactions found in solid $[(\text{MeLi})_4]_\infty$ are maintained. All solid-state structural features of $[(\text{thf})_3\text{Li}_3\text{Me}\{(\text{NtBu})_3\text{S}\}]$ (**2**) indicate that the molecule can be interpreted as a $[\text{Li}_2\{(\text{NtBu})_3\text{S}\}]$ moiety that stabilizes a monomeric unit of MeLi by forming a Li_3 triangle, which has one face shielded by the tripodal $\text{S}(\text{NtBu})_3^{2-}$ dianion. We currently investigating the reactivity of this species. The planned experiments will elucidate whether the reactivity of $[(\text{MeLi})_4(\text{dem})_{1.5}]_\infty$ is enhanced relative to that of MeLi in diethyl ether and whether it is possible to transfer methanide groups with $[(\text{thf})_3\text{Li}_3\text{Me}\{(\text{NtBu})_3\text{S}\}]$ without participation of the triazasulfite in the reaction.

Experimental Section

General: All experiments were performed under a nitrogen atmosphere either by using modified Schlenk techniques or in a drybox. Solvents were freshly distilled from sodium-potassium alloy prior to use. ^1H , ^7Li , and ^{13}C NMR spectra were recorded in C_6D_6 (^1H C_6HD_5 : $\delta = 7.15$; ^{13}C C_6D_6 : $\delta = 128.0$) with a JEOL Lambda 300 and a Bruker AMX 400 spectrometer. The solid-state ^6Li MAS and ^{13}C CP/MAS NMR experiments were performed by using a Bruker DSX 400 spectrometer, while the two-dimensional ^7Li MQMAS was recorded on a Bruker MSL 400 spectrometer. Melting (decomposition) points were determined by using a MEL TEMP II melting point apparatus. Elemental analysis were performed by the analytical laboratory of the Department of Inorganic Chemistry at Würzburg.

Crystallization of $[(\text{MeLi})_4(\text{dem})_{1.5}]_{\infty}$ (1**):** A clear commercially available solution of methyl lithium in diethoxy methane (8%, CHEMETALL, Frankfurt) in a Schlenk flask under argon atmosphere was connected to a second Schlenk flask containing cyclopentane. The pressure in both flasks was reduced to 0.1 bar and the cyclopentane is allowed to diffuse into the MeLi/DEM solution. Overnight colorless crystals started to grow, which could be enlarged to about $5 \times 5 \times 5$ mm in size within a week. They should be handled with care as the material is as pyrophoric as parent MeLi.

Syntheses of $[(\text{thf})_3\text{Li}_3\text{Me}(\text{NtBu})_3\text{S}]$ (2**):** $[(\text{thf})\text{Li}_2[(\text{NtBu})_3\text{S}]]_2$ was obtained as described previously in ref. [24]. Methyl lithium (3M, 3.4 mL, 10.14 mmol) were slowly added to a solution of $[(\text{thf})\text{Li}_2[(\text{NtBu})_3\text{S}]]_2$ (3.0 g, 5.07 mmol) in THF (20 mL) at -78°C and stirred for 1 h. The solution was stirred for two hours at room temperature. THF was removed in vacuum and the white precipitate was redissolved in warm hexane. Storage of the solution at -36°C for three days affords colorless crystals which were suitable for X-ray structure determination, (2.6 g, 78%). ^1H NMR (300.4 MHz, C_6D_6): $\delta = -1.41$ (s, 3H, CH_3), 1.34 (m, 12H, THF), 1.55 (s, 27H, $\text{C}(\text{CH}_3)_3$), 3.70 (m, 12H, THF); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 25.54$, 68.46 (THF), 34.61 ($\text{C}(\text{CH}_3)_3$), 53.24 ($\text{C}(\text{CH}_3)_3$); ^7Li NMR (155.5 MHz, external saturated LiCl solution) $\delta = 2.16$, (brs, 2Li), 2.67 (brs, 1Li); ^6Li MAS NMR (58.9 MHz, external solid LiCl): $\delta = 2.1$ (brs, 1Li), 2.8 (brs, 2Li); ^{13}C CP/MAS NMR (100.6 MHz, external TMS): $\delta = -13.9$ (Li_3CH_3), 25.8, 26.0, 26.2, 68.6, 69.0 (THF), 34.4, 34.8 ($\text{C}(\text{CH}_3)_3$), 52.5, 52.8, 53.0 ($\text{C}(\text{CH}_3)_3$); elemental analysis calcd (%) for $\text{C}_{25}\text{H}_{54}\text{Li}_3\text{N}_3\text{O}_3\text{S}$: C 60.34, H 10.94, N 8.45, S 6.44; found C 59.67, H 9.89, N 9.04, S 6.08.

X-ray crystal structure determinations of **1 and **2**:** Relevant crystallographic data are presented in Table 1. Data of both structures were collected on a Stoe IPDS diffractometer at 153(2) K on a shock-cooled pyrophoric crystal

Table 1. Crystal data and structure refinement for **1** and **2**.

	1	2
formula	$\text{C}_{14}\text{H}_{35}\text{Li}_4\text{O}_3$	$\text{C}_{25}\text{H}_{54}\text{Li}_3\text{N}_3\text{O}_3\text{S}$
M_r	279.18	497.59
crystal size [mm]	$0.6 \times 0.5 \times 0.5$	$0.2 \times 0.2 \times 0.1$
space group	$P3c1$	$P2_1/c$
a [pm]	1386.47(11)	1574.7(3)
b [pm]	1386.47(11)	1376.1(3)
c [pm]	1242.25(12)	1449.9(3)
β [$^\circ$]	90	92.40(3)
V [nm 3]	2068.0(3)	3139.1(11)
Z	4	4
ρ_{calcd} [Mg m $^{-3}$]	0.897	1.053
μ [mm $^{-1}$]	0.056	0.130
$F(000)$	620	1096
θ range [$^\circ$]	2.94–20.81	2.39–26.46
reflections measured	9137	4520
unique reflections	733	4523
data/restraints/parameters	733/51/107	4520/369/384
goodness-of-fit on F^2	1.069	1.079
$R1$ [$I > 2\sigma(I)$]	0.0620	0.0621
$wR2$ [all data]	0.1752	0.1888
largest difference peak/hole [e nm $^{-3}$]	405/–167	315/–272

$$[a] R1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, [b] wR2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}}{w} = \frac{1}{\sigma(F_o^2) + (g_1 P)^2 + g_2 P}; P = [\max(F_o^2) + 2F_c^2]/3.$$

in an oil drop.^[33] The structures were solved by direct methods (SHELXS-97)^[34] and refined on F^2 .^[35] A single uncoordinated disordered cyclopentane molecule in **1** was located in the threefold channel. The DME molecules suffered from disorder, which was successfully modeled by employment of 51 ADP and distance restraints. Both disorders caused the intensities only to reach up to slightly higher than 20° in θ .

All non-hydrogen atoms in **2** were refined with anisotropic displacement parameters. Hydrogen atoms bonded to the methanide atom were located by difference Fourier syntheses and refined freely. All other hydrogen atoms of the molecule were refined by using a riding model. One THF molecule (O3T–C34T) was disordered and refined to a split occupancy of 0.48/0.52 by using distance and similarity restraints. The structure was

successfully refined as a twin by assigning the data to two different orientation matrices.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-153452 (**1**) and CCDC-153453 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft, the Deutsche Akademische Austauschdienst (INIDA grant) and the Fonds der Chemischen Industrie. D.S. kindly acknowledges support of BRUKER axs Systems, Karlsruhe.

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Received: August 21, 2000 [F2907]