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Steric and Solvation Effects on the Aggregation of Lithium Thioamidates: Single-Strand Polymers with $(LiS)_n$ and $(LiNCS)_n$ Backbones

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The addition of methyllithium or *n*-butyllithium to alkyl isothiocyanates produces lithium thioamidates $\{Li[RCS(NR')]\}_n$. Three such compounds were structurally characterized after recrystallization from THF. When R = *n*-Bu and R′ = *t*-Bu, an unsolvated hexamer $\{Li[n\text{-}BuCS(N\text{-}t\text{-}Bu)]\}_6$ (**1**) is obtained. By contrast, the solvated derivatives $\{Li\cdot THF[MeCS(N\text{-}t\text{-}Bu)]\}_\infty$ (**2**·THF) and $\{Li\cdot 2THF[MeCS(NMe)]\}_\infty$ (**3**·2THF) form single-strand polymers. The monosolvated complex **2**·THF involves four-membered $\overline{\text{LiNCS}}$ rings with an $(LiS)_n$ backbone whereas the disolvate **3**·2THF is comprised of LiNCS repeating units. The structures of all three aggregates can be generated via sterically directed solvation of a common dimeric precursor. Crystal data for **2**·THF: $C_{10}H_{20}NLiOS$, monoclinic, $P2_1/a$ (#14), $a = 9.129(2)$ Å, $b = 11.099(2)$ Å, $c = 12.537(2)$ Å, $\beta = 94.14(2)°$, $V = 1267.0(4)$ Å^3, $Z = 4$. Crystal data for **3**·2THF: $C_{11}H_{22}NLiSO_2$, monoclinic, $P2_1/a$ (#14), $a = 10.974(3)$ Å, $b = 8.575(5)$ Å, $c = 14.898(5)$ Å, $\beta = 91.33(3)°$, $V = 1401.6(10)$ Å^3, $Z = 4$.

Introduction

Recently we have been interested in preparing lithium salts of various main-group carboxylate analogues such as amidinates $Li[RC(NR')_2]$ and heteroamidates $Li[RCE(NR')]$ (E = O, S, etc.) in order to elucidate modes of aggregation in the solid state and to observe ligand behavior. Amidinates have attracted considerable attention as controllable ligands in transition-metal[1] and main-group chemistry.[2] Among the various carboxylate analogues, thioamidates $[RCS(NR')]^-$ are of particular interest due to their ambidentate combination of hard (N) and soft (S) centers. The determination of the structural features of alkali-metal derivatives of thioamidates is an important prelude to investigations of their coordination complexes.[3] In addition, these ligands are germane for studies of peptides wherein carbonyl oxygen atoms are replaced by sulfur; the resulting "thiopeptides" contain thioamidate groups which can alter conformation and bioactivity in larger molecules.[4]

Aggregation via lateral association, or "laddering," of Li−X (X = pnicogen, halogen, halide, etc.) fragments is a well-known structural motif in organolithium chemistry.[5] This unit is unique in its structural versatility, allowing the generation of frameworks ranging from monomers (generally only when highly solvated) to a great variety of aggregated rings and cages involving any number of Li−X fragments. Aggregation can even occur infinitely, as illustrated by organolithium polymers such as $\{Li[N(i\text{-}Pr)_2]\}_\infty$,[6] and other examples.[5,7] Similar phenomena have been observed in the field of lithium−sulfur chemistry, where aggregation about $[LiS]_n$ fragments has been noted in a number of cases,[8] e.g., $\{PhSLi(NC_5H_5)_2\}_\infty$.[8c]

Lithiated carboxylate analogues have been shown to aggregate in the solid state in most cases; typically dimers, and occasionally monomers, are observed in the presence of coordinating solvent.[9−12] A common conformation is the step-shaped dimer (**A**) (Scheme 1), formed by association of two monomer units

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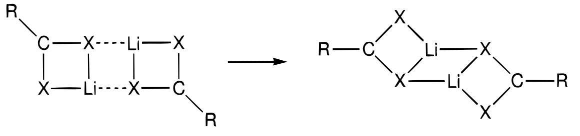
Scheme 1

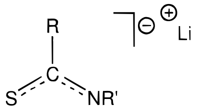


A

via LiX edges (formally a transoid Li$_2$X$_2$ ring). Except for lithiated *N*,*N*′-dialkylbenzamidinates,[1] investigation of the solid-state structures of main-group carboxylate analogues has been relatively limited.

An exception to this paucity of information is provided by the lithium oxoamidate Li[(C$_6$H$_5$)CO(N-*i*-Pr)], which was structurally characterized in both the presence and absence of THF as a hexamer and an octamer, respectively.[12] The core of the hexamer consists of a Li$_3$O$_3$ hexagonal prism, while that of the octamer comprises four stacked Li$_2$O$_2$ rings.

Our general route to amidinates and heteroamidates is derived from a well-known synthesis of carboxylic acids.[13] It involves the addition of organolithium reagents to heteroallenes,[2b−f,14] many combinations of which are commercially available. In a preliminary communication we reported the use of this method to synthesize {Li[(*n*-Bu)CS(N-*t*-Bu)]}$_6$ (**1**), which aggregates in the solid state to form an unsolvated Li$_6$S$_6$ hexagonal prismatic core.[15] To our knowledge, **1** was hitherto the only example of a structurally characterized alkali-metal thioamidate.



1, R = *n*-Bu, R′ = *t*-Bu
2, R = Me, R′ = *t*-Bu
3, R = Me, R′ = Me

Our interest in these species led us to consider the effect of changing the size of the R and R′ substituents. We reasoned that replacing bulky *n*- and *tert*-butyl groups in **1** by more svelte methyl groups (**2**, R = Me, R′ = *t*-Bu; **3**, R = Me, R′ = Me) might afford alternative aggregation pathways resulting in higher oligomers. Herein we report that the choice of R and R′ groups in lithium thioamidates significantly affects not only the aggregation pathway for such species, but also the degree of solvation in a coordinating solvent (THF). Control over aggregation is apparently dominated by steric factors, which in turn direct solvation to produce various oligomers (**1**) and polymers (**2**·THF, **3**·2THF) in the solid state.

Experimental Section

Reagents and General Procedures. All reactions and manipulations of air- or moisture-sensitive compounds were carried out using standard glovebox and Schlenk techniques under an atmosphere of high-purity, dried argon. The reagents *t*-BuNCS, MeNCS, MeLi (1.4 M in diethyl ether), and *n*-BuLi (2.5 M in hexanes) were obtained from Aldrich and used as received. Solvents (toluene, tetrahydrofuran, hexane, and diethyl ether) were purchased commercially and distilled twice over a mixture of sodium metal and benzophenone prior to use. Deuterated solvents (C$_6$D$_6$ and *d*$_8$-THF) were purchased in predried ampules and degassed by using three freeze/thaw cycles prior to use. All solvents were stored over molecular sieves in glass flasks equipped with Teflon needle valves and hose-joint side arms.

^{1}H, ^{7}Li, and ^{13}C NMR spectra were obtained using either a Bruker ACE200 (200 MHz) or AM400 (400 MHz) instrument. Measurements of carbon, nitrogen, and hydrogen content (by percent) were performed on a Control Equipment Corporation (CEC) 440 Elemental Analyzer by the Analytical Services Laboratory, Department of Chemistry, University of Calgary. Fourier transform infrared (FTIR) spectra were obtained on a Mattson Genesis Series instrument.

Preparation of {Li[(*n*-Bu)CS(N-*t*-Bu)]}$_6$ (1). A yellow, 2.5 M solution of ^{n}BuLi in hexanes (4.45 mL, 11.13 mmol) cooled to 0 °C was added dropwise via a stainless steel transfer needle to a clear, colorless solution of *tert*-butyl isothiocyanate (1.442 g, 12.52 mmol) in hexane (∼10 mL), also at 0 °C. This produced an opaque white reaction mixture which was allowed to warm to 23 °C and stirred for 2 h. Removal of volatiles in vacuo yielded a fine white powder; this was washed twice with hexane (2 × 5 mL) and pumped to dryness under dynamic vacuum. Total yield of white solid identified as **1** was 1.934 g (1.80 mmol, 97%). mp: 155−156 °C (dec). Crystals were obtained as colorless blocks from a saturated toluene solution cooled to −20 °C overnight.

Anal. Calcd for C$_9$H$_{18}$NSLi [%]: C, 60.30; H, 10.12; N, 7.81. Found: C, 59.69; H, 10.67; N, 7.86. IR (KBr, Nujol mull), ν [cm^{-1}]: 1584, 1362, 1232, 1202, 1141, 1042, 805, 738, 719, 622, 451. ^{1}H NMR [200 MHz, δ(TMS in CDCl$_3$)] in C$_6$D$_6$ at 25 °C: δ = 2.72 (m, $-\mathrm{C}H_2\mathrm{CH_2CH_2CH_3}$, 2H), 2.07 (m, $-\mathrm{CH_2C}H_2\mathrm{CH_2CH_3}$, 2H), 1.40 (m, $-\mathrm{CH_2CH_2C}H_2\mathrm{CH_3}$, 2H), 1.33 (s, $-\mathrm{C(C}H_3)_3$, 9H), 0.941 (t, $-\mathrm{CH_2CH_2CH_2C}H_3$, 3H). ^{13}C NMR [50.288 MHz, δ(TMS in CDCl$_3$)] in C$_6$D$_6$ at 25 °C: δ = 185.9 (s) [(^{n}Bu)*C*S(N^{t}Bu)], 56.0 (s) [$-C(\mathrm{CH_3})_3$], 31.7 (s) [$-\mathrm{C}(C\mathrm{H_3})_3$], 43.1 (s) [$-C\mathrm{H_2CH_2CH_2CH_3}$], 32.5 (s) [$-\mathrm{CH_2}C\mathrm{H_2CH_2CH_3}$], 24.0 (s) [$-\mathrm{CH_2CH_2}C\mathrm{H_2CH_3}$], and 14.6 (s) [$-\mathrm{CH_2CH_2CH_2}C\mathrm{H_3}$]. ^{7}Li NMR [155.508 MHz, δ(1M LiCl in D$_2$O)] in C$_6$D$_6$ at 25 °C: δ = −0.31 (s).

Preparation of {Li·THF[MeCS(N-*t*-Bu)]}$_\infty$ (2·THF). A solution of methyllithium in diethyl ether (1.4 M, 8.0 mL, 11.20 mmol) was added dropwise to a clear, colorless solution of *tert*-butyl isothiocyanate (1.290 g, 11.20 mmol) in diethyl ether (10 mL) via a stainless steel transfer needle. After ca. 50% of the alkyllithium reagent had been added, a white solid was observed, and after complete addition, the reaction mixture became white and opaque. After 2 h removal of volatiles under dynamic vacuum yielded a white powder identified as **2** (1.441 g, 10.51 mmol, 94%). mp: 111−113 °C (dec). Crystals suitable for X-ray diffraction studies were obtained from a saturated, 1:1 mixture of hexane and THF stored at −20 °C for several days.

Anal. Calcd for C$_6$H$_{12}$NSLi [%]: C, 52.53; H, 8.82; N, 10.21. Found: C, 51.84; H, 9.14; N, 10.64. IR (KBr, Nujol mull), ν [cm^{-1}]: 2702, 2617, 2071, 1983, 1584, 1564, 1461, 1367, 1232, 1209, 1125, 1032, 1005, 991, 889, 806, 771, 727, 580, 525. ^{1}H NMR [200 MHz, δ(TMS in CDCl$_3$)] in C$_4$D$_8$O at 298 K: δ = 3.58 (broad s, THF), 2.33, 2.11 (both s, [*Me*CS(N^{t}Bu)], 3H), 1.73 (broad s, THF), 1.35, 1.18 (both s, [MeCS(N^t*Bu*)], 9H). The relative intensities of the pairs of resonances at δ 2.33 and 1.18 compared to those at δ 2.11 and 1.35 are 1.15:1. ^{13}C NMR [50.288 MHz, δ(TMS in CDCl$_3$)] in C$_4$D$_8$O at 298 K: δ = 189.24 and 172.17 (both s, [Me*C*S(N^{t}Bu)]), 67.49 (q, THF), 55.12 and 54.51 (both s, $C(\mathrm{CH_3})_3$), 40.16, 30.80 (both s, [*Me*CS(N^{t}Bu)], 3H), 31.45 and 29.40 (both s, $\mathrm{C}(C\mathrm{H_3})_3$), 25.35 (q, THF). ^{7}Li NMR [155.508 MHz, δ(1M LiCl in D$_2$O)] in C$_4$D$_8$O at 298 K: δ = −1.22 (s).

Preparation of {Li·2THF[MeCS(NMe)]}$_\infty$ (3·2THF). A 1.4 M solution of methyllithium in diethyl ether (9.8 mL, 13.7 mmol) was

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Table 1. Crystallographic Data for **2**·THF and **3**·2THF

	2·THF	**3**·2THF
empirical formula	$C_{10}H_{20}NliOS$	$C_{11}H_{22}NLiSO_2$
fw (g mol^{-1})	209.28	239.30
temp (°C)	−103(1)	−103(1)
cryst syst	monoclinic	monoclinic
space group	$P2_1/a$ (#14)	$P2_1/a$ (#14)
a (Å)	9.129(2)	10.974(3)
b (Å)	11.099(2)	8.575(5)
c (Å)	12.537(2)	14.898(5)
β (deg)	94.14(2)	91.33(3)
V (Å^3)	1267.0(4)	1401.6(10)
Z	4	4
ρ_{calcd} (g cm^{-3})	1.097	1.134
μ (cm^{-1})	2.16	2.16
F_{000}	456	520
cryst size (mm)	0.50 × 0.50 × 0.30	0.42 × 0.38 × 0.222
θ_{max} (deg)	50.1	50.1
reflns colld	2516	2814
indep reflns	2364	2669
R_{int}	0.041	0.062
data [$I > 3\sigma(I)$]/params	1021/127	695/145
max shift/error in final cycle	0.01	0.01
GOF	1.87	1.78
R,[a] R_w[b]	$R = 0.049$, $R_w{}^c = 0.047$	$R = 0.053$, $R_w{}^d = 0.043$

[a] $R = \sum||Fo| - |Fc||/\sum|Fo|$. [b] $R_w = [\sum w(|Fo| - |Fc|)^2/\sum wFo^2]^{1/2}$, where $w = [\sigma^2(Fo)]^{-1} = [\sigma_c{}^2(Fo) + 0.25p^2Fo^2]^{-1}$. [c] $p = 0.018$. [d] $p = 0.011$.

added dropwise via a stainless steel transfer needle to a clear, yellow solution of methyl isothiocyanate (0.947 g, 12.95 mmol) in diethyl ether (10 mL) at −80 °C. This produced a cloudy, yellow solution that, on warming to 23 °C, became bright yellow and completely opaque. After 1 h a yellow precipitate settled out below a clear, pale yellow solution. The precipitate was isolated by decantation, and subsequent removal of solvent under dynamic vacuum produced **3** as a fine, yellow powder (1.023 g, 10.77 mmol, 83%). mp: 185−187 °C (dec). The compound produces a sulfurous stench on exposure to air. Crystals suitable for X-ray diffraction were obtained from a highly concentrated THF solution stored at −14 °C for 4 days.

Characterization of **3**: mp: 221−223 °C (dec). Anal. Calcd for C_3H_6NLiS [%]: C, 37.89; H, 6.36; N, 14.73. Found: C, 37.92; H, 6.11; N, 13.97. Characterization of **3**·2THF: mp: 494−497 K (dec). Anal. Calcd for $C_3H_6NLiS\cdot(C_4H_8O)_2$ ($C_{11}H_{22}NLiSO_2$) [%]: C, 55.21; H, 9.27; N, 5.85. Anal. Calcd for $C_3H_6NLiS\cdot(C_4H_8O)$ ($C_7H_{14}NLiSO$) [%]: C, 50.29; H, 8.43; N, 8.38. Found (for example): C, 50.10; H, 7.72; N, 8.18. Elemental analyses for **3**·xTHF gave values of x ranging from 0.5 to 1.5 (four samples) depending on the age of the sample. IR (KBr, Nujol mull), ν [cm^{-1}]: 2727, 1910, 1582, 1304, 1172, 1115, 940, 801, 640, 587. ^{1}H NMR [200 MHz, δ(TMS in $CDCl_3$)] in C_4D_8O at 298 K (one drop of C_6D_6 was added as a reference): $\delta = 3.53$ (m, THF), 3.30 and 3.29 (s, [MeCS(N*Me*)], 3H), 2.54 and 2.53 (s, [*Me*CS(NMe)], 3H), 1.49 (m, THF). ^{13}C NMR [50.288 MHz, δ(TMS in $CDCl_3$)] in C_4D_8O at 300 K: $\delta = 189.03$ and 188.98 (s, [Me*C*S(NMe)]), 67.40 (q, THF), 41.18 and 41.10 (s, [MeCS(N*Me*)]), 36.46 and 36.26 (s, [*Me*CS(NMe)]), 25.31 (q, THF). ^{7}Li NMR [155.508 MHz, δ(1M LiCl in D_2O)] in C_4D_8O at 300 K: $\delta = 1.48$ (s). NMR data for the conformational isomer: ^{1}H NMR [200 MHz, δ(TMS in $CDCl_3$)] in C_4D_8O at 298 K: $\delta = 3.53$ (m, THF), 2.84 and 2.83 (s, [MeCS(N*Me*)], 3H), 2.33 and 2.32 (s, [*Me*CS(NMe)], 3H), 1.49 (m, THF). ^{13}C NMR [50.288 MHz, δ(TMS in $CDCl_3$)] in C_4D_8O at 300 K: $\delta = 191.71$ (s, [Me*C*S(NMe)]), 67.40 (q, THF), 38.44 and 38.26 (s, [MeCS(N*Me*)], 3H), 27.04 (s, [*Me*CS-(NMe)], 3H), 25.31 (q, THF).

X-ray Measurements. All data were collected at low temperature using oil or epoxy coated crystals mounted on glass fibers. Measurements for **1** were collected on a Smart CCD diffractometer. Details of the structure solution and refinement for this compound have been communicated previously.[15]

Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) in **2**·THF and **3**·2THF

	2·THF		**3**·2THF
Li(1)−S(1)	2.562(8)	Li(1)−S(1*)	2.497(12)
Li(1*)−S(1)	2.463(8)	Li(1)−O(1)	1.985(16)
Li(1)−O(1)	1.907(9)	Li(1)−O(2)	1.951(14)
Li(1)−N(1)	2.043(9)	Li(1)−N(1)	2.047(16)
C(1)−N(1)	1.482(6)	C(3)−N(1)	1.470(9)
C(5)−N(1)	1.271(5)	C(1)−N(1)	1.279(8)
C(5)−S(1)	1.750(5)	C(1)−S(1)	1.716(8)
C(5)−C(6)	1.517(6)	C(1)−C(2)	1.510(10)
S(1)−Li(1)−S(1*)	164.6(3)	N(1)−Li(1)−S(1*)	119.0(7)
Li(1)−S(1)−Li(1*)	131.6(4)		
Li(1*)−(S1)−C(5)	109.5(3)	Li(1)−S(1*)−C(1*)	112.3(3)
Li(1)−S(1)−C(5)	72.4(2)		
Li(1)−N(1)−C(1)	131.8(4)	Li(1)−N(1)−C(1)	130.6(7)
C(1)−N(1)−C(5)	125.4(4)	C(1)−N(1)−C(3)	116.1(7)
Li(1)−N(1)−C(5)	102.5(4)	Li(1)−N(1)−C(3)	108.0(6)
N(1)−C(5)−C(6)	128.4(5)	N(1)−C(1)−C(2)	115.7(8)
N(1)−C(5)−S(1)	117.3(3)	N(1)−C(1)−S(1)	127.3(7)
S(1)−C(5)−C(6)	114.3(3)	S(1)−C(1)−C(2)	117.0(6)
Li(1)−N(1)−Li(1*)−N(1*)	−5.7(5)	C(2)−C(1)−N(1)−C(3)	−178.6(7)
N(1)−Li(1)−S(1)−C(5)	−2.8(2)		

Measurements for **2**·THF and **3**·2THF were made on a Rigaku AFC6S diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å). Empirical absorption corrections were applied in each case.[16] Both structures were solved by direct methods[17] and expanded using Fourier techniques.[18] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not refined. Full-matrix least-squares refinement was performed using the teXsan[19] crystallographic software package of Molecular Structure Corporation. Relevant crystallographic data are presented in Table 1, and pertinent metrical parameters for both structures are given in Table 2.

Results

Preparation of Lithium Thioamidates. Convenient synthetic access to thioamidates is available via eq 1, whereby addition

$$x\mathrm{LiR} + x\mathrm{R'N{=}C{=}S} \rightarrow (1/x)\{\mathrm{Li[RCS(NR')]}\}_x \qquad (1)$$

1, R = *n*-Bu, R′ = *t*-Bu

2, R = Me, R′ = *t*-Bu

3, R = Me, R′ = Me

of an alkyllithium reagent to an isothiocyanate yields the desired anion as its lithium derivative. This route is attractive not only because it is fast and relatively easy, but also because the starting materials are available cheaply and in wide variety from a number of commercial sources.

Structure of 1. Production of the previously reported unsolvated hexamer **1**[15] can be visualized as a trimerization of cisoid or "tub-shaped" dimers linked via Li_2S_2 rings as illustrated in Scheme 2.

During formation of **1** the emergent inter-dimer Li···S contacts cause the bridged Li−S bonds of the dimeric units to become rungs connecting two Li_3S_3 rings in a "paddle-wheel" arrangement with D_{3d} symmetry. The metrical data support this view, with a shorter mean Li−S bond distance [2.405(7) Å]

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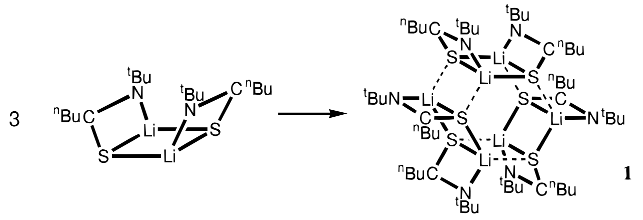
Scheme 2



within the Li_3S_3 rings than that observed for the bridged Li−S bonds [2.638(7) Å]. By contrast, the lithium oxoamidate $\{Li[(n\text{-}Bu)CO(N\text{-}t\text{-}Bu)]\}_6$ (**4**) adopts a D_3, “trilobate” structure[15] resulting from interaction of the circumannular Li−O bonds of three cisoid dimers; in this case the inter-dimer Li−O contacts are oriented such that the bridged Li−O bonds form alternating edges of two stacked Li_3O_3 rings. As a result, the Li−O distances alternate within the Li_3O_3 rings, with mean values of 2.085(5) Å and 1.869(5) Å for the bridged and unbridged bonds, respectively. We speculate that **4** is unable to adopt a paddle-wheel conformation due to steric constraints arising from the shorter Li−O distances as compared to the Li−S distances in **1**.

X-ray Structure and Spectroscopic Characterization of 2·THF. The reaction of *tert*-butyl isothiocyanate with methyllithium in diethyl ether produced **2** as a moisture-sensitive white solid in essentially quantitative yield (eq 1). Unlike **1**, the new thioamidate **2** is only sparingly soluble in noncoordinating organic solvents. Both species are highly soluble in coordinating solvents, however, and the polymer $\{\mathbf{2}\cdot THF\}_\infty$ was isolated on recrystallization of **2** from THF. An X-ray structural determination revealed a single-strand polymer with a backbone consisting of alternating bridged and unbridged Li−S bonds (Figure 1), the former being longer than the latter by ~0.1 Å [d(Li(1)−S(1)) = 2.562(8) Å, d(Li(1*)−S(1)) = 2.463(8) Å]. These distances are similar to the alternating values [d(Li−S) = 2.513(6), 2.459(7) Å] observed in the $[LiS]_\infty$ polymer backbone of $[PhSLi\cdot(NC_5H_5)_2]_\infty$,[8c] in which the sulfur atoms are also three-coordinate, but none of the Li−S bonds are bridged.

The geometry about the C−N bonds in each thioamidate molecule is cis. This facilitates bidentate chelation of a single lithium ion by N and S within the same monomer unit and allows the formation of four-membered $\overline{\text{LiNCS}}$ rings. A distorted tetrahedral coordination sphere about lithium is completed by interaction with the oxygen atom of a single THF molecule [d(Li(1)−O(1)) = 1.907(9) Å] and by contact with the S atom of an adjacent monomer unit to form the polymer chain. The geometry at sulfur is three-coordinate and lies between a planar T-shape and trigonal pyramidal, with the largest angle being subtended by the Li−S−Li unit of the polymer backbone [∠(Li(1)−S(1)−Li(1*) = 131.6(4)°] (Figure 1a).

Each of the four-membered rings in **2**·THF is approximately planar [τ = −5.7(5)° and −2.8(2)° in adjacent rings], as are the geometries about N(1) [Σ∠N(1) = 359.7°] and C(5) [Σ∠C(1) = 360.0°]. All four-membered rings and associated organic groups lie in the same hemisphere with respect to the polymer backbone, but neighboring units are oriented in opposite directions to minimize steric crowding; the THF molecules exhibit a similar arrangement in the opposite hemisphere (Figure 1b). The ^{1}H and ^{13}C NMR spectra of **2**·THF in d_8-THF at 298 K exhibit two Me and two *t*-Bu resonances. Since the two sets of resonances do not have equal intensities (ca. 1.15:1), they cannot be attributed to different chemical environments for neighboring four-membered rings in the polymer chain. We speculate that a second species, possibly a different aggregate of **2**, may be present in solution. However, the ^{7}Li NMR spectrum exhibits only a singlet, suggesting that the environment around lithium is similar in both cases.

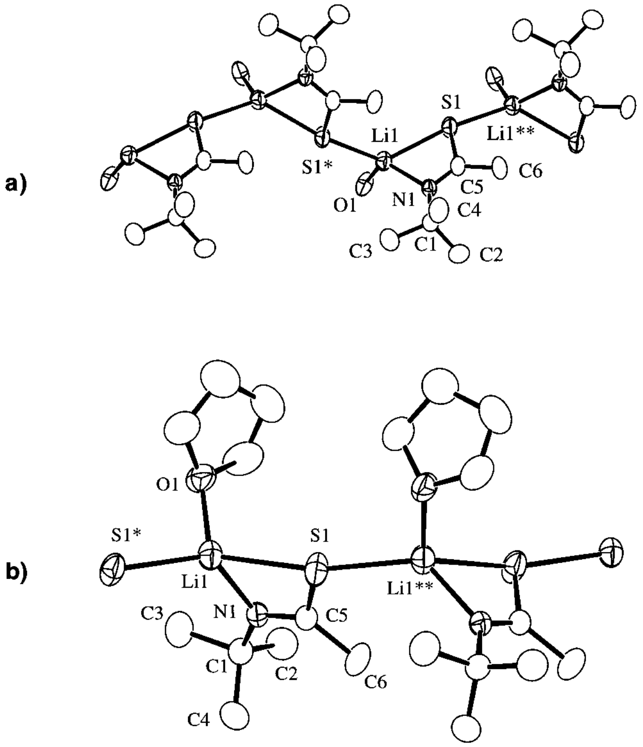


Figure 1. (a) ORTEP of $\{Li\cdot THF[MeCS(N\text{-}t\text{-}Bu)]\}_\infty$ (**2**·THF) showing the atom labeling scheme. Thermal ellipsoids are depicted at 50% probability; for clarity, hydrogen atoms have been omitted and only the oxygen atoms of the THF molecules are shown. Symmetry operation for the starred atoms: *, $x - (^1/_2)$, $(^1/_2) - y$, z; **, $^1/_2 + x$, $^1/_2 - y$, z. (b) A second view of **2**·THF showing the orientation of the THF molecules.

X-ray Structure and Spectroscopic Characterization of 3·2THF. To further probe the effects of steric hindrance on solvation and aggregation of lithium thioamidates, the R′ group attached to N in Li[RCS(NR′)] was changed from *t*-Bu to Me. The addition of a slight excess of MeLi to methylisothiocyanate in diethyl ether at −78 °C precipitated **3** as a moisture-sensitive yellow solid in 84% yield eq 1. Like **2**, the lithium thioamidate **3** is insoluble in noncoordinating organic solvents, but very soluble in THF. Recrystallization from THF provided crystals of **3**·2THF, which readily lost solvent molecules on standing. An X-ray structural determination revealed a single-strand polymer with LiNCS repeat units and trans geometry about the C−N bond (Figure 2). Unlike **2**·THF, each lithium ion in **3**·2THF is solvated by *two* THF molecules [|d(Li−O)| = 1.968 Å] and the sulfur atoms are two-coordinate. A related arrangement has been observed for the 1:1 complex $[LiSCN\cdot TMEDA]_\infty$, although this species contains *linear* LiNCS repeat units.[5e,7e] The novel single-strand polymer **3**·2THF provides the first example of a thioamidate in a bridging, rather than a chelating, mode with trans geometry at the C−N bond.

In the case of **2**·THF, orientation of similar organic groups toward one another causes interstrand separations on the order of 11−12 Å, effectively preventing any interaction between neighboring strands. A similar arrangement is observed in **3**·2THF; the two solvent molecules coordinated to each lithium ion protrude in four directions from the polymer backbone and impose separations of 8−10 Å between polymer chains.

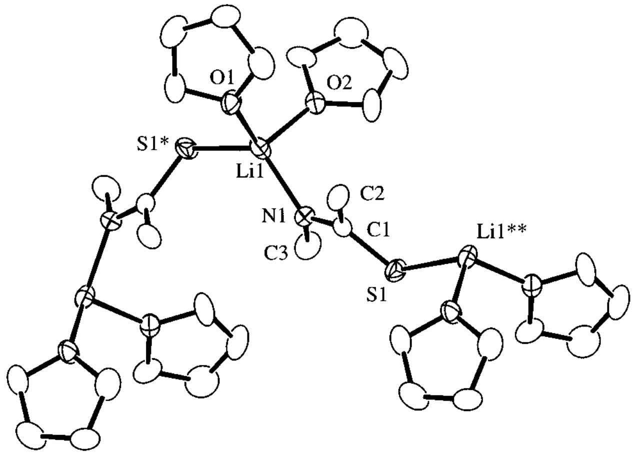


Figure 2. ORTEP of $\{Li{\cdot}2THF[MeCS(NMe)]\}_\infty$ (**3**·2THF) showing the atom labeling scheme. Thermal ellipsoids are depicted at 50% probability; hydrogen atoms have been omitted for clarity. Symmetry operation for the starred atoms: *, $x - (^1/_2)$, $(^3/_2) - y$, z; **, $x + (^1/_2)$, $1 - y$, z.

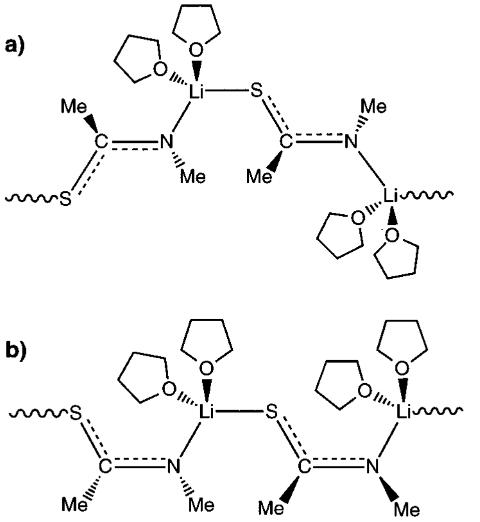


Figure 3. Structural drawings of (a) trans and (b) cis isomers of **3**·2THF.

The geometry at the three-coordinate carbon atoms in **3**·2THF is planar [$\Sigma\angle(C1) = 360.0°$] and that at the nitrogen atoms is almost planar [$\Sigma\angle N(1) = 354.7°$]. The C−N and C−S bond distances are 1.279(8) and 1.716(8) Å, indicating delocalized multiple bonding in the NCS units. For comparison the corresponding mean bond distances in the chelated complex $NbCl_3[MeC(S)(NMe)]_2$ are 1.30(2) and 1.73(2) Å, respectively.[3f] The Li−N and Li−O distances in **3**·2THF are unremarkable and similar to those observed in **1** and **2**·THF. The Li−S distance of 2.497(12) Å is close to the mean value of 2.405 Å found for the Li−S bonds in the Li_3S_3 ring of **1**, and lies between the values found for bridged and unbridged Li−S bonds in **2**·THF. The torsion angles for neighboring LiNCS units are 166.0(8)° and −150.5(7)°.

The orientation of substituents about the $[LiNCS]_\infty$ backbone of **3**·2THF provides two symmetrically distinct environments for adjacent monomer units in the polymer chain. Consistently, two very closely spaced pairs of resonances are observed for NCH_3 and CCH_3 groups in both the ^1H and ^{13}C NMR spectra of the recrystallized complex **3**·2THF, and two resonances may also be resolved for the carbon atoms in the polymer backbone. Although other explanations are possible, these data suggest that the polymeric structure of **3**·2THF may be retained in solution. The NMR spectra of **3**·2THF in d_8-THF prior to recrystallization revealed the presence of a second species, which exhibits a similar pattern of very closely spaced resonances for the NCH_3 and CCH_3 groups and the chain C atoms. Variable temperature NMR spectra showed that *trans*-**3**·2THF and the second species interconvert reversibly, although the effects of temperature changes in the range 200−320 K were small. In view of this facile interconversion, we tentatively suggest that the second species is another conformational isomer, possibly the cis isomer (Figure 3), of **3**·2THF in which adjacent monomer units are in slightly different environments as a result of twisting about the Li−S bond.

Discussion

It is noteworthy that the structures of **1**, **2**·THF, and **3**·2THF can all be generated from a common dimeric precursor. Thus, trimerization of dimeric cisoid units produces the hexameric "paddle-wheel" conformation adopted by **1** (Scheme 2). The polymeric arrangement seen in **2**·THF can be produced from an analogous precursor by envisioning solvation of both lithium centers leading to the rupture of one Li−S bond (Figure 4). Similarly, the orientation adopted by **3**·2THF can be generated either from further solvation of **2**·THF leading to disruption of the endocyclic Li−S bonds, or directly from the common dimeric unit through solvation of each lithium ion by two THF molecules (Figure 4).

Recent work in the field of lithium amide chemistry has shown that organolithium ladder polymers are generally broken down into chains of finite length by solvation,[7b,c] and that cyclic ladder structures can be unraveled through similar means.[20] Indeed, seminal work in this area showed that the helical polymer structure of $\{Li[N(i\text{-}Pr)_2]\}_\infty$[6] is disrupted by coordinating solvents, e.g., $\{Li{\cdot}THF[N(i\text{-}Pr)_2]\}_2$.[21] However, solvation does not always lead to limitation of the laddering framework. For example, lithium benzylamide[7d] and sodium *tert*-butylamide[22] both form infinite ladders despite solvation by their parent amines. In addition, we have recently demonstrated that solvation and laddering can both function simultaneously as mechanisms for the dispersal of electronic charge in mixed lithium amidinate/lithium halide systems.[23]

Given the observed dependence of structure on solvation for lithium thioamidates and other organolithium species, the fact that **1** remains unsolvated in the solid state, even when recrystallized from THF, is of significance. We suggest that this occurs for two reasons: (1) the steric bulk of the substituents in **1** hinders solvent molecules from entering the coordination sphere of lithium and (2) aggregation via laddering competes with solvation as a route to dispersal of electronic charge at *both* termini of the [Li−S] bond in **1**. Hence, when R and R′ are large in Li[RCS(NR′)], solvation is impeded and unsolvated, laddered oligomers are favored. As the size of the substituents employed is decreased, solvation becomes more facile and the dimeric unit opens up to give the polymeric structure seen in **2**·THF.

Likewise, it appears that the preference for a solvated, single-strand polymeric arrangement in **3**·2THF (rather than unsolvated, oligomeric alternatives) reflects the minimal steric requirements of the methyl substituents attached to C and N in

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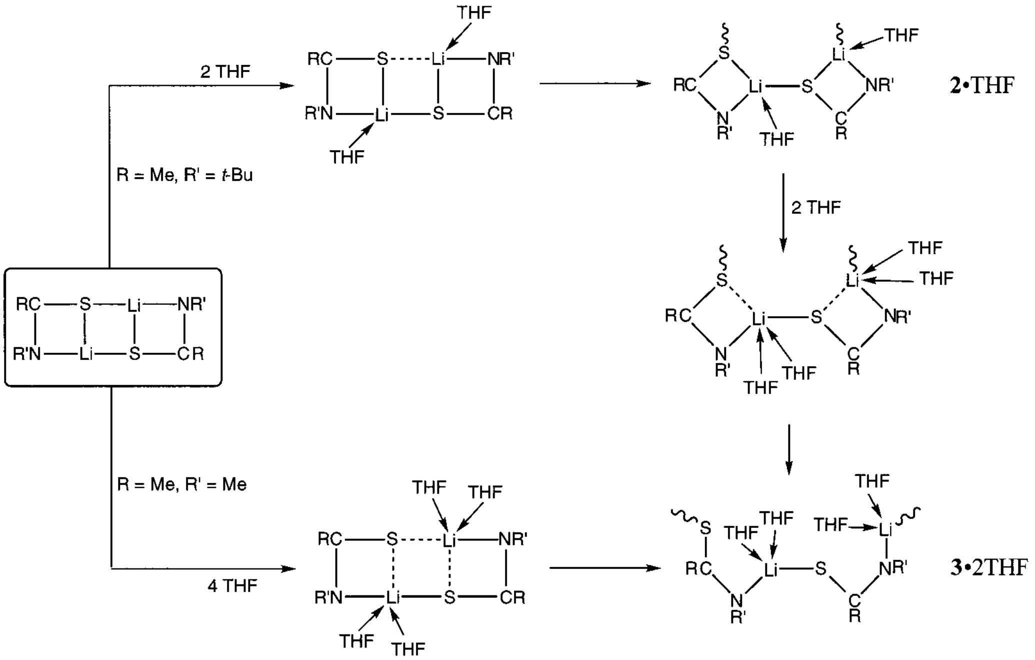

Figure 4. Schematic depiction of the generation of **2**•THF and **3**•2THF from a common dimeric precursor {Li[RCS(NR′)]}$_2$ (dashed lines indicate bonds being broken). For clarity, multiple bonding involving three-coordinated carbon atoms is omitted in the structural drawings (see also Schemes 1 and 2).

the thioamidate. In direct analogy to the relationship between **1** and **2**•THF, the reduced bulk of the NR′ group in **3** compared to that in **2** apparently allows solvent molecules to enter the coordination sphere of lithium more easily. Thus, solvation becomes the most efficient way of dispersing electronic charge at lithium and a linear fragment is produced. The polymeric arrangement of **3**•2THF can be generated from **2**•THF by visualizing a second molecule of solvent attaching to the lithium centers and concomitant breaking of the Li−S bonds within the four-membered rings. Thus, in contrast to previous reports which have indicated that donor solvents can disrupt or limit organolithium polymers,[5e,7b−c,20,21] solvation appears to promote polymerization for lithium thioamidates when it is not sterically prohibited.

The three structures **1**, **2**•THF, and **3**•2THF can be viewed as discrete points along a continuum. At one extreme, the bulky substituents in **1** prevent (sterically) solvation and yield an unsolvated, oligomeric structure; at the other extreme, very small substituents in **3** allow solvent molecules to enter the coordination sphere of lithium freely, producing the solvated, single-strand polymer **3**•2THF. Intermediate between these termini, the use of one small and one bulky substituent in **2** produces partial solvation of lithium by THF and yields a polymeric array **2**•THF in which the thioamidate units chelate lithium in a bidentate fashion. Aggregation in all three systems can be conceptualized to occur via a dimeric precursor unit under the control of solvation effects, which are in turn directed by steric factors related to the organic substituents employed.

Conclusions

The degree of solvation of lithium thioamidates by THF depends heavily on the steric environment around lithium. When bulky organic substituents are employed, solvation is hindered and unsolvated, finite oligomers result. For smaller substituents, solvation at lithium occurs readily and, in contrast to previously reported organolithium systems, actually *promotes* polymer formation. In all three cases presented here, the observed solid-state structure can be rationalized by considering the effects of sterically directed solvation on a dimeric unit. The implications of this observation for related systems such as alkali-metal amidinates and other heteroamidates—as well as for the reaction chemistry of these and other reagents—is a topic that we are currently investigating.

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Supporting Information Available: X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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