Inorg. Chem. **2003**, *42*, 3849–3855

Inorganic Chemistry

Article

Structural Diversity of Lithium Sulfenamides: ^{7}Li NMR Studies in Solution and Crystal Structures of $[Li_2(\eta^2\text{-}(CH_3)_3C{-}NS{-}C_6H_4CH_3\text{-}4)_2(THF)_2]$ and $[Li_2(\eta^1\text{-}4\text{-}CH_3C_6H_4{-}NS{-}C_6H_4CH_3\text{-}4)_2(THF)_4]$

Amir H. Mahmoudkhani, Sarah Rauscher, Brian Grajales, and Ignacio Vargas-Baca*

Department of Chemistry, McMaster University, 1280 Main Street West, Hamilton, Ontario L8S 4M1, Canada

Received December 13, 2002

Two lithium sulfenamides were prepared by reaction of $(CH_3)_3C{-}N(H){-}S{-}C_6H_4CH_3$-4 (**1**) and 4-$CH_3C_6H_4{-}N(H){-}S{-}C_6H_4CH_3$-4 (**2**) with an alkyllithium. The unsolvated sulfenamide $Li[(CH_3)_3C{-}NS{-}C_6H_4CH_3\text{-}4]$ **(3)** was soluble enough for variable-temperature (VT) ^{7}Li NMR to provide evidence of a dynamic exchange of oligomers in solution. The crystal structures of the solvated sulfenamides of $[Li_2(\eta^2\text{-}(CH_3)_3C{-}NS{-}C_6H_4CH_3\text{-}4)_2(THF)_2]$ (**4**) and of $[Li_2(\eta^1\text{-}4\text{-}CH_3C_6H_4{-}NS{-}C_6H_4CH_3\text{-}4)_2(THF)_4]$ (**6**) consisted of dimers in which the anions display different hapticities. The VT ^{7}Li NMR spectra of **4** suggest that the two different structures exist in equilibrium in toluene–THF mixtures. These compounds are easily oxidized to the neutral thioaminyl radicals as identified by EPR spectroscopy.

Introduction

There is currently interest in ligands that contain negatively charged nitrogen directly bound to softer main-group donor atoms. Their ambidentate character and the polarity of the N−E bond often result in fascinating structures and reactivity. Several studies have examined the chemistry of various nitrogen−phosphorus anions.[1−7] There is comparatively less information available on the sulfenamido anion $[R{-}S{-}N{-}R]^-$. The chemistry of its transition-metal derivatives is complicated. The dihapto coordination mode has been observed in homo- and heteroleptic complexes of Zr(IV), Ti(IV), Mo(VI), W(VI), and U(IV).[8−10] In the crystal structure of a Ni(II) derivative there are two nonequivalent sulfenamido anions, with two different S−Ni distances; but these cannot be distinguished by NMR due to fast exchange in solution. Moreover, the reaction of sulfenamido anions with halides of transition elements goes beyond simple metathesis. It is frequently observed that the sulfur−nitrogen bond is cleaved to form thiolato and imido ligands with simultaneous oxidation of the metal; oxidation of the ancillary ligands has also been observed.[11] Although the lithium sulfenamides have been the most frequent starting point of the reactions with transition elements, the structures of derivatives of s-block elements have not been examined in detail until now. Here we present synthetic and structural studies of lithium sulfenamides in their unsolvated form and their adducts with THF. The spectroscopic data point to a polymeric nature of unsolvated compounds; the crystal structures of the solvated lithium salts are examples of these anions binding the cation with different hapticities.

Experimental Section

Materials and Methods. All manipulations were performed under an atmosphere of dry argon or nitrogen with standard Schlenk and glovebox techniques. All solvents and reagents were dried and

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* Author to whom correspondence should be addressed. Phone: (905) 525-9140, ext 23497. Fax: (905) 522-2509. E-mail: vargas@chemistry.mcmaster.ca.

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10.1021/ic026269w CCC: $25.00

purified by standard procedures immediately before each experiment. The concentration of commercial solutions of *n*-butyllithium was established by titration of diphenylmethanol.[12] Elemental analyses were performed by Guelph Chemical Laboratories Inc. (Guelph, Ontario, Canada).

Spectroscopic Instrumentation. IR spectra were recorded using a Bio-Rad FTS-40 FT-IR spectrometer. Each spectrum was acquired from KBr pellets with a resolution of 8 cm^{-1}, and the background, which was simultaneously subtracted, was recorded prior to a spectral acquisition.

FT Raman spectra were recorded at ambient temperature in sealed Pyrex melting point capillaries using a Bruker RFS 100 spectrometer equipped with a quartz beam splitter and a liquid nitrogen cooled Ge diode detector. The 1064 nm line of a Nd:YAG laser (350 mW maximum output) was used for excitation of the sample with a spot of ca. 0.2 mm at the sample using 10−300 mW of power, and the backscattered radiation was sampled. The actual usable Stokes range was 100−3500 cm^{-1} with a spectral resolution of 2 cm^{-1}. The Fourier transformations were carried out by using a Blackman−Harris four-term apodization and a zero-filling factor of 4.

EPR spectra were acquired with a Bruker SMX-EPR and processed with the program WINEPR. The instrument was standardized with a Bruker strong pitch standard, and the spectra were referenced to a sample of MgO doped with Mn^{2+}. The samples were prepared under an argon atmosphere in thoroughly degassed toluene and measured at ambient temperature in quartz tubes sealed with a rubber septum.

The ^{1}H, $^{13}C\{^{1}H\}$, and ^{7}Li NMR spectra in soluton were recorded on a Bruker Avance AV200 (200.13 MHz) or AV300 (300.13 MHz) spectrometer. Chemical shifts are reported in parts per million and were referenced to the residual proton peak of C_6D_6 (δ 7.16, ^{1}H NMR; δ 128.06, $^{13}C\{^{1}H\}$ NMR) or an external standard solution of LiCl in D_2O (δ 0.0, ^{7}Li NMR). Variable-temperature (VT) ^{7}Li NMR studies were performed using a Bruker DRX500 probing ^{7}Li nuclei operating at 194.37 MHz. The temperature at the position of the sample was calibrated using an external thermocouple and maintained within ±1 °C. The benzene-d_6 solvent for NMR spectroscopic measurements was degassed by successive “freeze−pump−thaw” cycles and dried over freshly washed and activated 4 Å molecular sieves. Solid-state NMR experiments were performed on a Bruker Avance 300 spectrometer, with a 4 mm magic angle spinning (MAS) probe tuned to a ^{7}Li frequency of 116.59 MHz. A maximum MAS rotor frequency of 9 kHz was chosen. A single 30° pulse, of 3 μs, was used to obtain the spectra, with 8192 transients acquired. This large number of transients provided a good signal-to-noise ratio in the broad sideband manifold. A recycle delay of 2 s was used. All shifts were referenced to solid LiCl. The maximum available spectral width of 150 kHz was selected. Together with the spinning frequency, this allowed for acquisition of the entire spinning-sideband manifold, with sidebands outside the 150 kHz sweep width folding back between the lower order sidebands. In this paper we discuss exclusively the relative isotropic shifts. A full description of the quadrupolar tensors, based on simulation of the sideband pattern, will be published elsewhere.

The sulfenamides $(CH_3)_3C{-}N(H){-}S{-}C_6H_4CH_3$-4 (**1**) and 4-$CH_3C_6H_4{-}N(H){-}S{-}C_6H_4CH_3$-4 (**2**) were prepared with modifications to Miura’s procedure[13] by reaction of 4-$CH_3C_6H_4SCl$ with the corresponding amine in diethyl ether. In a typical reaction, the sulfenyl chloride (15.85 g, 100 mmol) was dissolved in 30 mL of solvent. This was added dropwise to a stirred solution containing an excess of amine (250 mmol) in 50 mL at −100 °C. The mixture was stirred for 1 h, removed from the cooling bath, and left stirring overnight. After filtration the solvent was evaporated to yield a crude product which was subject to further purification.

$(CH_3)_3C{-}N(H){-}S{-}C_6H_4CH_3$-4 (1). The pure substance distilled as a colorless oil at 77−79 °C (200 mbar). Yield: 75%. The pure material crystallizes upon standing. ^{1}H NMR (200 MHz, C_6D_6): δ 0.99 (s, 9H, $(CH_3)_3C$); 2.09 (s, 3H, $CH_3C_6H_4$); 2.36 (s, 1H, N*H*); 6.96, 7.00, 7.37, 7.41 (q, 4H, aryl). $^{13}C\{^{1}H\}$ NMR (50 MHz, C_6D_6): δ 20.94 ($(CH_3)_3C$); 29.12 ($CH_3C_6H_4$); 54.60 ($(CH_3)_3C$); 123.24, 129.58, 134.20, 141.68 (aryl). Raman (cm^{-1}): 3331vw, 3050s, 3036m, 3032s, 3029m, 2972s, 2948m, 2921s, 2907s, 2872m, 2736vw, 2708w, 1598s, 1491w, 1445w, 1379w, 1210m, 1177w, 1083vs, 920w, 809w, 794m, 747w, 637w, 627w, 300w, 253w, 165vw. IR (cm^{-1}): 3329w, 3016w, 2970m, 2930w, 2870w, 1599w, 1491m, 1472w, 1398w, 1378w, 1362m, 1226m, 1205m, 1178w, 1114w, 1083w, 1016w, 939w, 921w, 835w, 805s, 627w, 488w. MS (EI): *m*/*z* (rel intens) 195 (M^+, 100), 180 ($M^+ - CH_3$, 6), 139 (40), 107 (20), 91 (14), 57 (18), 41 (6).

4-$CH_3C_6H_4{-}N(H){-}S{-}C_6H_4CH_3$-4 (2). After evaporation a dark red-brown viscous oil was obtained. This was stored under nitrogen at ambient temperature, and in a few days, pale yellow crystals of pure **2** grew large enough to be filtered off and washed with cold hexanes. Yield: 70%. Mp: 57−60 °C. ^{1}H NMR (200 MHz, C_6D_6): δ 2.00 (s, 3H, $CH_3C_6H_4N$); 2.06 (s, 3H, $CH_3C_6H_4S$); 6.79−7.09 (m, 8H, aryl). $^{13}C\{^{1}H\}$ NMR (50 MHz, C_6D_6): δ 20.52 ($CH_3C_6H_4N$); 20.84 ($CH_3C_6H_4S$); 115.10, 123.17, 129.85, 129.93, 130.02, 135.16, 138.87, 144.88 (aryl). Raman (cm^{-1}): 3345w, 3052s, 3032m, 2973w, 2918s, 2869w, 2732w, 1610s, 1596m, 1567w, 1509w, 1491w, 1376m, 1302w, 1281w, 1231w, 1211s, 1177m, 1118w, 1082s, 835w, 811m, 793m, 637m, 635m, 620w, 442w, 391w, 352w, 328w, 307w, 267w, 192w, 116vs. IR (cm^{-1}): 3346m, 3031w, 2917w, 2862w, 1881w, 1610m, 1508m, 1491m, 1437m, 1372m, 1280m, 1229m, 1176w, 1112w, 1080w, 1040w, 1014w, 908m, 833w, 806s, 704w, 617w, 542w, 507m, 492m, 441w. MS (EI): *m*/*z* (rel intens) 228 (M^+, 100), 213, 180, 123, 106, 77, 65.

$Li[(CH_3)_3C{-}NS{-}C_6H_4CH_3$-4] (3). A solution of **1** (0.336 g, 1.720 mmol) in 5 mL of hexanes was cooled to −100 °C, and *n*-butyllithium (0.86 mL of 2.0 M in pentane, 1.720 mmol) was carefully added. The mixture was stirred in the cooling bath for 30 min and then allowed to warm to room temperature. A white solid slowly formed and settled after 2 h. The liquid was removed by cannula; the precipitate was washed with hexanes (3 × 5 mL) and dried gently under vacuum. Yield: 0.187 g (54%). Anal. Calcd for $C_{11}H_{16}LiNS$: C, 65.65; H, 8.01; N, 6.95. Found: C, 65.02; H, 8.31; N, 6.50. The material is sparingly soluble in aliphatic hydrocarbons and dissolves slowly in aromatic solvents. ^{1}H NMR (200 MHz, C_6D_6): δ 1.13 (s, 9H, $(CH_3)_3C$); 2.06 (s, 3H, $CH_3C_6H_4$); 6.93−7.21 (br m, 4H, aryl). $^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6): δ 20.86 ($(CH_3)_3C$); 32.38 ($CH_3C_6H_4$); 55.48 ($(CH_3)_3C$); 122.26, 130.33, 133.67, 148.40 (aryl). ^{7}Li (116 MHz, C_6D_6): δ 0.88. Raman (cm^{-1}): 3046m, 2958m, 2919m, 2902w, 2860w, 2734vw, 2688vw, 1597m, 1564w, 1488w, 1454w, 1440w, 1379w, 1299w, 1275w, 1234w, 1211m, 1187w, 1176w, 1075s, 1015vw, 1011vw, 938vw, 932vw, 910vw, 899vw, 795m, 728w, 702w, 637m, 624m, 535w, 499w, 440w, 412vw, 399vw, 376vw, 338vw, 304w, 266vw, 225m, 184w, 158w, 116s, 100sh. The reaction provided a clear solution when performed with an excess of alkyllithium; NMR spectra were acquired from the residue of solvent evaporation of a 1:2 mixture. ^{1}H NMR (200 MHz, C_6D_6): δ −0.94 (br s, 2H, $CH_2CH_2CH_2CH_3$),

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0.95 (br s, 3H, $CH_2CH_2CH_2CH_3$); 1.20 (s, 9H, $(CH_3)_3C$); 1.37 (br m, 4H, $CH_2CH_2CH_2CH_3$), 2.11 (s, 3H, $CH_3C_6H_4$); 6.93−7.15 (m, 4H, aryl). ^{7}Li (116 MHz, C_6D_6): δ 2.11.

$[Li_2(\eta^2\text{-}(CH_3)_3C{-}NS{-}C_6H_4CH_3\text{-}4)_2(THF)_2]$ (4). The lithium sulfenamide **3** was dissolved in a mixture of hexanes and THF (20:0.5). After one night of standing at room temperature, colorless crystals of **4** were formed in quantitative yield. The crystals were stored in the mother liquor until transferred for characterization. ^{1}H NMR (300 MHz, C_6D_6): δ 1.23 (THF); 1.37(s, 9H, $(CH_3)_3C$); 2.18 (s, 3H, $CH_3C_6H_4$); 3.74 (THF); 6.95, 6.97, 7.46, 7.49 (q, 4H, aryl). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 21.04 ($(CH_3)_3C$); 25.49 (THF), 32.52 ($CH_3C_6H_4$); 55.81 ($(CH_3)_3C$); 69.05 (THF), 123.16, 129.04, 132.03, 150.96 (aryl). ^{7}Li (116 MHz, C_6D_6): δ 1.05. ^{7}Li MAS: δ 1.40. Raman (cm^{-1}): 3049m, 3031m, 3014w, 2960m, 2954m, 2918m, 2883m, 1597s, 1565w, 1488w, 1463w, 1448w, 1439w, 1376m, 1299w, 1276w, 1229w, 1209m, 1178w, 1072vs, 1036w, 1014w, 919w, 900w, 793m, 740w, 637w, 620w, 360w, 337w, 305w, 266w, 239w, 192w, 122m.

$Li[4\text{-}CH_3C_6H_4{-}NS{-}C_6H_4CH_3\text{-}4]$ (5) and $[Li_2(\eta^1\text{-}4\text{-}CH_3C_6H_4{-}NS{-}C_6H_4CH_3\text{-}4)_2(THF)_4]$ (6). The unsolvated lithium salt **5** was prepared from the reaction of **2** and *n*-butyllithium as described for its analogue **3**. The washed precipitate was dissolved in THF and hexanes (1:4). The solvate **6** appeared as colorless crystals after several days. ^{1}H NMR (300 MHz, C_6D_6): δ 1.21 (THF), 2.09 (s, 3H, $CH_3C_6H_4N$); 2.21 (s, 3H, $CH_3C_6H_4S$); 3.39 (THF); 6.89, 6.92, 7.05, 7.07, 7.30, 7.33, 7.48, 7.51 (m, 8H, aryl). $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): δ 20.68 ($CH_3C_6H_4N$); 20.97 ($CH_3C_6H_4S$); 25.50 (THF); 68.25 (THF); 116.93, 122.93, 124.61, 129.42, 130.22, 132.49, 144.91, 157.24 (aryl). ^{7}Li (116 MHz, C_6D_6): δ 0.86. ^{7}Li MAS: δ 0.60. Both **5** and **6** are strongly fluorescent, and their Raman spectra could not be obtained.

X-ray Crystallography. Crystals of **4** and **6** were handled immersed in a low-viscosity perfluoropolyether oil using the cryotechnique described by Håkansson.[14] Suitable crystals of **4** (0.12 × 0.10 × 0.08 mm^3) and **6** (0.40 × 0.25 × 0.20 mm^3) were mounted in nylon loops (Hampton, CA) using a perfluoropolyether glass. Mounted samples were stored in liquid nitrogen until installed in the diffractometer. Data were collected on a P4 Bruker diffractometer upgraded with a Bruker SMART 1000 CCD detector and a rotating anode utilizing Mo Kα radiation (λ = 0.71073 Å, graphite monochromator) equipped with an Oxford cryosystem. For each compound, a full sphere of reciprocal lattice was scanned by 0.36° steps in ω with a crystal-to-detector distance of 4.97 cm. Preliminary orientation matrixes were obtained from the first frames using SMART.[15] The collected frames were integrated using the preliminary orientation matrixes, which were updated every 100 frames. Final cell parameters were obtained by refinement on the positions of reflections with $I > 10\sigma(I)$ after integration of all the frames using SAINT.[15] The data were empirically corrected for absorption and other effects using SADABS.[16] The structures were solved by direct methods and refined by full-matrix least squares on all F^2 data using SHELXTL.[17] The non-H atoms were refined anisotropically, while H atoms were constrained to idealized positions using appropriate riding models. Analysis of the molecular structures determined by X-ray diffraction was assisted by comparison to related structures compiled in the Cambridge Structural Database (CSD), updated in April 2002, with a total of 257162 entries.[18] Molecular graphics were produced using ORTEP-3[19] and PovRay.

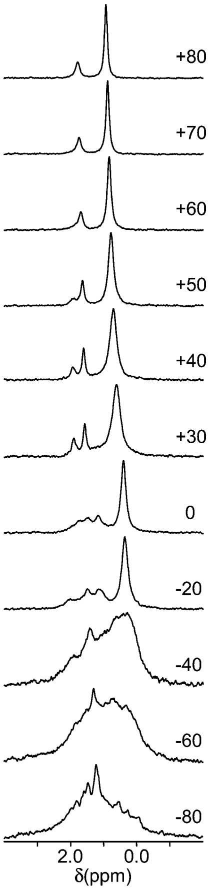

Figure 1. VT ^{7}Li NMR spectra of $Li[(CH_3)_3C{-}NS{-}C_6H_4CH_3\text{-}4]$ **(3)** in toluene.

Results and Discussion

The unsolvated sulfenamides **3** and **5** were produced by low-temperature treatment of the parent sulfenamides **1** and **2** with butyllithium and precipitated from hexanes. Compound **3** dissolves slowly in benzene and toluene. Although its ^{1}H and ^{13}C NMR spectra are simple and suggest that a single species is present in solution, observations in ^{7}Li NMR (Figure 1) portray a completely different situation. At ambient temperature the ^{7}Li spectrum of a dilute sample in toluene reveals three signals at δ 1.90, 1.57, and 0.61 ppm with approximate ratio 1:2:8, respectively. Upon warming, the two lower field peaks appear to coalesce at 60 °C while the other signal becomes narrower and shifts downfield progressively. At 80 °C the remaining two signals are located at 1.78 and 0.93 ppm. Upon cooling, all the signals broaden and split further into multiple peaks that could not be fully resolved at −80 °C. These changes are fully reversible and suggest the existence of a complex equilibrium between several oligomeric structures. In the absence of other donor groups to complete the coordination sphere of the metal, formation of an extended network in the solid state is

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Table 1. Crystallographic and Refinement Data for **4** and **6**

	4	**6**
empirical formula	$C_{15}H_{24}LiNOS$	$C_{22}H_{30}LiNO_2S$
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	10.535(3)	9.25(2)
b (Å)	8.343(2)	15.28(4)
c (Å)	18.352(5)	15.00(4)
7β (deg)	99.25(1)	100.94(6)
V (Å^3)	1592.0(7)	2082(9)
Z, ρ(calcd) [g·cm^{-3}]	4, 1.140	4, 1.211
T (K)	173(1)	173(1)
μ (mm^{-1})	0.194	0.171
θ range	2.10−23.25	1.92−25.00
limiting indices	$-11 \leq h \leq +11$ $-9 \leq k \leq +9$ $-20 \leq l \leq +20$	$-10 \leq h \leq +10$ $-17 \leq k \leq +18$ $-17 \leq l \leq +17$
no. of reflns collected/unique	10070/2287	13842/3655
R(int)	0.183	0.139
no. of params	173	247
R1[a]/wR2[a] ($I > 2\sigma(I)$)	0.085/0.169	0.072/0.166
R1[a]/wR2[a] for all data	0.170/0.175	0.160/0.209
GOF on F^2	1.026	1.024
largest diff peak/hole (e·Å^{-3})	0.394/−0.302	0.477/−0.488

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$.

Table 2. Selected Bond Distances and Angles (Å, deg) for **4** and **6**

	4	**6**		**4**	**6**
Li···Li[a]	2.47(2)	2.68(2)	Li−S	3.185(11)	
N···N[a]	3.134(7)	3.24(2)	Li−S[a]	2.609(10)	3.034(11)
Li−N	1.974(11)	2.044(9)	S−N	1.687(5)	1.686(6)
Li−N[a]	2.018(10)	2.165(9)	C−N	1.507(7)	1.414(6)
Li−O	1.984(11)	2.010(8)	C−S	1.788(6)	1.766(6)
Li−O		2.034(9)			
Li−N−Li[a]	76.5(5)	79.2(4)	O−Li−S[a]	98.8(4)	
N−Li−N[a]	103.5(5)	100.8(4)	N[a]−Li−S[a]	40.3(2)	
O−Li−O		94.0(4)	N−Li−S[a]	120.7(5)	
O−Li−N	131.9(5)	119.1(4) 118.6(4)	S−N−C1 N−S−C8	114.1(4) 110.2(3)	115.8(3) 106.9(2)
O−Li−N[a]	124.6(6)	115.0(4) 110.1(4)			
C−S−N−C	95.0(4)	76.5(3)			

[a] Symmetry code: $-x, -y, -z + 1$.

expected. Aromatic rings can solvate lithium cations, as has been observed in phenyl hydrazides such as $Li[(Me_3Si)_2N-NPh]$,[20] but the interaction is weak and oligomers form easily in toluene solution. Detailed studies for the aggregation of LDA and Et_2NLi have been published recently.[21,22]

The limited solubility of lithium sulfenamides in aliphatic hydrocarbons facilitates their isolation. However, **3** is solubilized in the presence of an excess of organolithium. The possible formation of a mixed sulfenamide−alkyllithium cluster was investigated with ^1H NMR by mixing **1** with 2 equiv of *n*-butyllithium. After the solvents were removed and the precipitate was redissolved in benzene, a remarkably simple spectrum was obtained in which the protons of the sulfenamide and the alkyl group were easily identified and were only slightly shifted since most of those nuclei are far from the metal. The largest shift corresponds to the signal of the *n*-butyl α protons at −0.94 ppm from −0.85 ppm observed for *n*-BuLi in the same conditions. The ^7Li resonance (2.11 ppm) is also shifted with respect to that of *n*-BuLi (2.63). Similar shifts are known for mixed complexes of alkyllithiums.[23] Such species also provide explanation for the slow formation of the precipitate of **3** even at temperatures close to 0 °C. On the other hand, **5** is virtually insoluble in all hydrocarbons and could not be characterized by spectroscopic methods in solution; it precipitates immediately during the synthesis and cannot be dissolved with an excess of organolithium.

Both sufenamides are soluble in ethers, including diethyl ether, THF, and dioxane. Colorless single crystals suitable for X-ray diffraction were obtained from THF−hexanes mixtures. The crystalline products were identified as the solvated sulfenamides $[Li_2(\eta^2\text{-}(CH_3)_3C-NS-C_6H_4CH_3\text{-}4)_2(THF)_2]$ (**4**) and $[Li_2(\eta^1\text{-}4\text{-}CH_3C_6H_4-NS-C_6H_4CH_3\text{-}4)_2(THF)_4]$ (**6**). The corresponding crystallographic and refinement data are summarized in Table 1; a comparison of selected bond distances and angles of **4** and **6** is given in Table 2. The crystalline structures of **4** and **6** are presented in Figures 2 and 3, respectively.

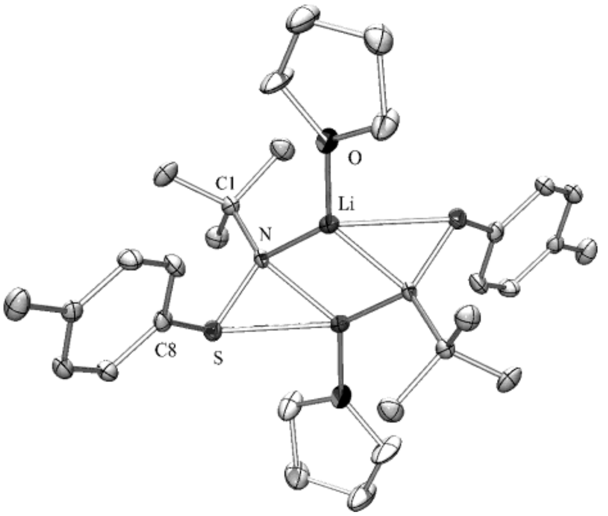

Figure 2. Molecular structure of $[Li_2(\eta^2\text{-}(CH_3)_3C-NS-C_6H_4CH_3\text{-}4)_2(THF)_2]$ (**4**). Displacement ellipsoids are shown at the 30% probability level. The hydrogen atoms are omitted for clarity.

In both crystals the unit cell contains two molecules; each is a dimer sitting in a screw axis. Thus, the asymmetric unit consists of only one solvated lithium sulfenamide. Figure 4 contains a comparison of the cores of the two different structures. Both molecular structures have a central Li_2N_2 square ring, which is the characteristic feature of most dimeric lithium amides. The Li_2N_2 rings of **4** and **6** are planar, as is commonly observed in structures without any special steric demands.

In the molecular structure of **4** there is one molecule of THF coordinating each metal atom, while in **6** there are two. In the latter case the sulfur atoms are located out of the ring plane; their distances to each of the lithium atoms, 3.034(11) and 3.092(11) Å, are nearly identical and too long to consider any bonding interaction. Thus, the lithium atoms have a coordination number of 4 and an approximately

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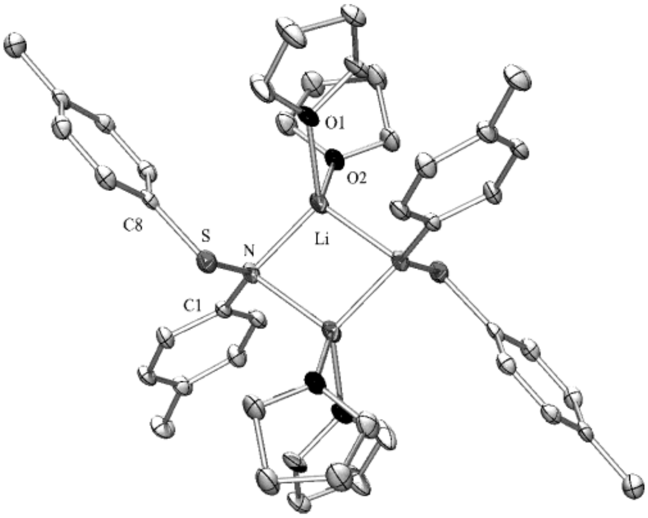


Figure 3. Molecular structure of $[Li_2(\eta^1\text{-}4\text{-}CH_3C_6H_4{-}NS{-}C_6H_4CH_3\text{-}4)_2(THF)_4]$ (**6**). Displacement ellipsoids are shown at the 30% probability level. The hydrogen atoms are omitted for clarity.

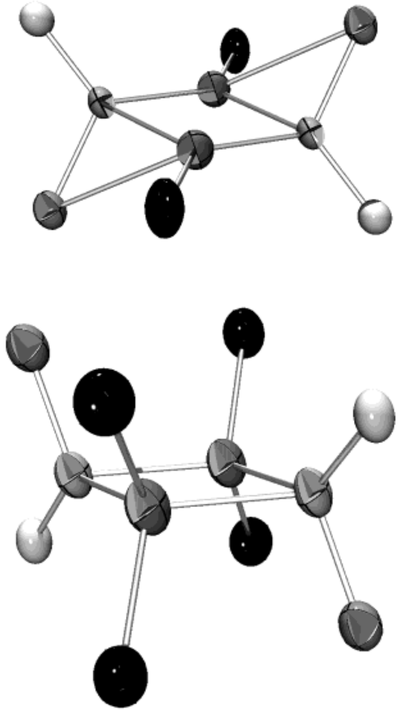
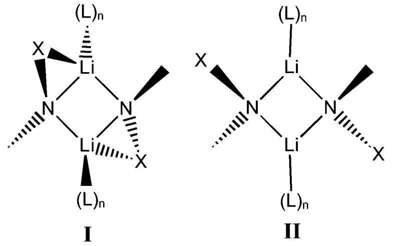


Figure 4. Comparison of the cores of the crystal structures of **4** (top) and **6** (bottom).

tetrahedral geometry. The dimensions of the Li_2N_2 ring in **6** are comparable to those of other solvated dimers with a similar structure.[24−27] However, the O−Li−O angle of 94.0(4)° is significantly smaller than the 100.78−104.06° angle observed in the other cases.

Chart 1



A more significant difference in the structure of **4** is the position of the sulfur atoms. These are located 1.430(2) Å above and below the annular plane and are leaning toward one metal atom each. The Li_2N_2–LiNS interplanar angle is 58.0(5)°, and the molecular conformation resembles a chair. The shortest Li−S distance is 2.609(10) Å. This is longer than the average $Li{-}S_{anionic}$ bond length, 2.481(8) Å, obtained from 212 CSD records. However, the distance is comparable to the average calculated for $Li{-}S_{neutral}$ bonds, 2.55(3) Å, from 19 structures deposited in the CSD. Therefore, coordination of the sulfenamido anion in **4** is best described as η^2, toward one lithium, and μ between the two metal atoms.

Although there are some published examples of unsolvated dimeric lithium amides,[28−32] in most cases the metals are coordinated by other donor groups, most commonly ethers, amines, nitriles, or phosphoramides. Coordination numbers as large as 5[33] have been observed when the additional donors are part of a chelating amide. A ligand that contains the additional donor atom (X) directly bound to nitrogen could be considered as the shortest case of a chelating amide; the proximity to the metal favors the η^2 binding mode (Chart 1, **I**) over the η^1 mode (Chart 1, **II**). Such coordination has been observed in $[Li_2((CH_3)_3Si{-}N{-}N(Si(CH_3)_3))_2]$ (**7**),[34] $[Li_2((CH_3)_2((CH_3)_3C)Si{-}N{-}N(H)Si(C(CH_3)_3)(CH_3)_2)_2(THF)_2]$ (**8**),[35] $[Li_2((CH_3)_3Si{-}N{-}N(H)C(CH_3)_3)_2(THF)_2]$ (**9**),[35] $[Li_2((CH_3)_3Si{-}N{-}N(CH_2C_6H_5)Si(CH_3)_3)_2]$ (**10**),[20] $[Li_2(C_6H_5{-}N{-}N(H)Si(CH_3)_3)_2(Et_2O)_2)]$ (**11**),[20] and $[Li_2(F{-}((CH_3)_3C)_2Si{-}N{-}N(CH_3)_2)_2(THF)_2]$ (**12**).[36] Softer X atoms are less effective in coordinating a hard cation; the only other structure of an amide featuring a third-period donor and η^2 coordination is that of $[Li_2(PhN{-}PPh_2)_2(OEt_2)_2]$ (**13**)[37] with a Li−P distance of 2.684(3) Å.

The Li−O and Li−N bond distances in **6** are slightly longer than in **4**, but do not deviate from the average bond

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lengths and angles of typical Li_2N_2 squares. The difference in C−S−N−C torsion angles between **4** and **6**, −95.0(4)° and −76.5(3)°, respectively, is the only structural difference between these two structures that can be unequivocally attributed to sulfur coordination. The sum of bond angles subtending at Li, N, N^a (at $-x$, $-y$, $-z + 1$), and O is 360°; thus, these atoms are coplanar. This trigonal unit is not symmetrical; the O−Li−N and O−Li−N^a angles differ by 7.3(6)°. This is not only the result of the side-on coordination by the sulfur atom; the dimers of other asymmetric lithium amides can display even larger O−Li−N angle differences, e.g., 21° in $[Li_2(C_6H_5CH_2{-}N{-}C_6H_5)_2(Et_2O)_2]$.[38] One last noteworthy feature in the structure of **6** is the N−Li−S bond angle of 40.3(2)°, slightly smaller than the 41.8(2)° measured for the analogous N−Li−N angle in the structures **7**−**12** but not as acute as the 38.47(1)° for the N−L−P angle of **13**.

The difference in lithium coordination environments in the two characterized structures was reflected in the solid-state isotropic ^7Li NMR chemical shifts, 1.40 ppm for **4** and 0.60 ppm for **6**. In solution, the ambient-temperature spectrum of **6** displayed a single ^7Li resonance whose position is solvent dependent. It was observed at 0.86 ppm in toluene and at 0.69 ppm in THF; intermediate values were observed in mixtures of the two solvents. The difference in chemical shifts, 0.17 ppm, is small and can be attributed to the change in the polarity of the medium but not to a change in the coordination sphere; thus, the molecular structure of **6** is maintained throughout.

In contrast, more complicated changes were observed in the solution ^7Li NMR spectrum of **4**. At ambient temperature, a single peak was observed at 1.00 ppm in benzene or toluene and at 0.36 ppm in pure THF. The large difference in chemical shifts suggests a change in the coordination sphere and is comparable to the difference observed in the solid-state spectra of **4** and **6**. Moreover, up to two peaks can be observed in solvent mixtures; their positions and relative intensities depend on temperature and THF concentration. This phenomenon is best exemplified with the observations made in a 1:0.3 toluene−THF mixture (Figure 5). The two signals exhibit a thermal drift of ca. 0.005 ppm/°C. At 30 °C a single peak is observed at 0.92 ppm. Upon cooling, this peak shifts to high field and broadens. At −30 °C the second peak is clearly distinguishable at higher field. As the temperature decreases, the new signal grows at the expense of the first and becomes predominant at −50 °C. At −70 °C only the second peak is visible at −0.23 ppm; this position approximates that of the signal observed in pure THF once the thermal drift is considered. These temperature-induced changes are fully reversible, and the higher field species becomes predominant as the proportion of THF increases. The large difference in chemical shifts of the two species is close to that observed between the spectra of the crystalline lithium sulfenamides **4** and **6**. These observations suggest that the higher field species has the structure observed in the crystal of **6**, with η^1 coordination and four coordinated THF molecules, and the other species observed in the solution spectrum of **4** corresponds to the η^2 structure found in the crystal structure. If these structures actually exist in equilibrium in the THF−toluene mixture (Scheme 1), the exchange rate constant would be less than 150 s^{-1} below −30 °C since the two resonances are observed instead of the average peak. The equilibrium is strongly dependent on temperature, with estimated values of $\Delta H = -68$ kJ mol^{-1} and $\Delta S = -250$ J mol^{-1} K^{-1}. While in this case the type **II** structure is enthalpically favored by the preference of lithium for the hard THF donor, the type **I** structure is entropically favored because of the loss of two THF molecules facilitated by the bulk of the *tert*-butyl group. The equilibrium observed in the solutions of **4** must be present under the conditions used for crystallization; thus, the η^2 structure was isolated due to its lower solubility.

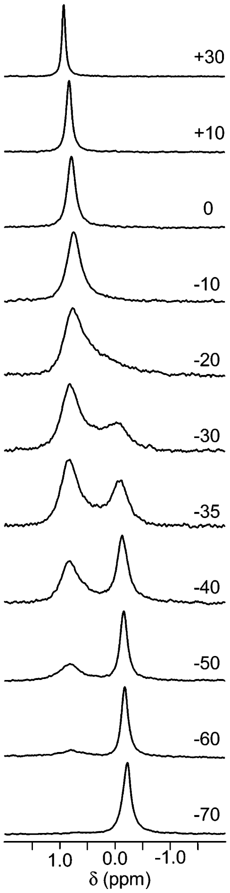
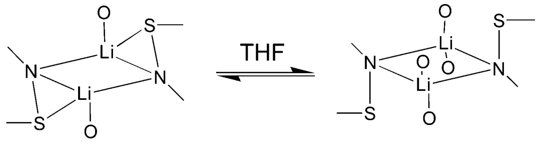


Figure 5. VT ^7Li NMR spectra of **4** in toluene−THF, 1:0.3 (v/v).

Scheme 1



Solvated and unsolvated sulfenamides are very sensitive, and a satisfactory elemental analysis was obtained only for **3**. These materials are very reactive, not only toward hydrolysis by adventitious moisture but also to oxidation by air as well. Upon exposure to an atmosphere containing less than 20 ppm oxygen, solid and solution samples of **4** and **6** undergo color changes from colorless to blue and finally to

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orange-red. EPR of samples in solution treated with dry oxygen displayed a poorly resolved spectrum of a free radical. Samples of **3** and **5** are more tolerant of small amounts of oxygen, but under an atmosphere of the pure gas their EPR spectra consisted of the three-line signal characteristic of the nitrogen-centered thioaminyl neutral radical $[(CH_3)_3C{-}NS{-}C_6H_4CH_3\text{-}4]\bullet$ ($g = 2.0070$, $a_N = 11.7$ G).[39] Such persistent radicals have been prepared before by oxidation of sulfenamides with strong oxidizers and by photolysis of bissulfenamides; they are known to decay to colored diazenes and phenazines.[40] These radicals may be behind the complicated reactions of lithium sulfenamides with some transition-metal complexes.

Conclusions

These initial investigations of the sulfenamido complexes of lithium revealed that the unsolvated compounds exist in solution as a collection of oligomers in dynamic equilibrium; very likely the solid sulfenamide has a polymeric structure. The lithium sulfenamides are readily solubilized by ethers through the formation of discrete solvated dimers. In the structures of the derivatives **4** and **6**, the sulfenamides act as bridging ligands between two metals. Simultaneously, these structures are examples of two different hapticities of the sulfenamido ligand toward one metal atom. The dynamic exchange of these structures is a plausible explanation for the observed behavior in the VT ^{7}Li NMR of **4** in toluene−THF mixtures.

Acknowledgment. We thank Dr. James F. Britten for help with X-ray data collection, Dr. Brian G. Sayer and Dr. Gillian Goward for assistance with NMR measurements, and Dr. Gary J. Schrobilgen for FT-Raman measurements. We thank Dr. Vratislav Langer (Chalmers University of Technology, Sweden) for kindly providing us with a sample of perfluoropolyether oil for cryocrystallography. The financial support of McMaster University, the Natural Sciences and Engineering Research Council of Canada, the Canada Foundation for Innovation, and the Ontario Innovation Trust is gratefully acknowledged.

Supporting Information Available: Tables listing detailed crystallographic data, atomic positions, parameters, and bond lengths and angles for **4** and **6** and MAS ^{7}Li NMR spectra of these compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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