Template Effects of Lithium Salts on the Crystallization of Diazasulfates: X-ray Structures of $\{THF\cdot Li_2[O_2S(N^tBu)_2]\}_8\cdot 2LiOH\cdot 2LiCl$ and $\{(THF\cdot Li)_2[O_2S(N^tBu)_2]\cdot(THF)LiCl\}_2$

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The addition of 2 equiv of ^nBuLi to solutions of $O_2S[N(H)R]_2$ (R = ^iPr, ^tBu) produces the dilithium diazasulfates $\{Li_2[O_2S(N^iPr)_2]\}_n$ (**2**) and $\{THF\cdot Li_2[O_2S(N^tBu)_2]\}_n$ (**3**), which were characterized by solid-state ^7Li and ^{13}C NMR spectroscopy. Crystals were obtained from a THF/*n*-hexane solution of **3** and determined by X-ray crystallography to be $\{THF\cdot Li_2[O_2S(N^tBu)_2]\}_8\cdot 2LiOH\cdot 2LiCl$ (**4**), which consists of a 64-atom ($Li_{20}S_8N_{16}O_{18}Cl_2$) cluster composed of two Li_4O_4 cubes and a central Li_4O_4 step-shaped ladder. The eight $[O_2S(N^tBu)_2]^{2-}$ dianions in **4** exhibit three distinct modes of bonding to the Li^+ cations: (a) bis-(*N*,*O*),(*N*′,*O*′)-chelate, (b) *N*,*O*-chelate, bis-*N*′,*O*′-monodentate, and (c) bis-(*N*,*O*),(*N*,*N*′)-chelate, *O*′-monodentate. The synthesis of **3** in the presence of 1 equiv of LiCl produces the dimer $\{(THF\cdot Li)_2[O_2S(N^tBu)_2]\cdot(THF)LiCl\}_2$ (**5**). The structure of **5** incorporates an 18-atom ($Li_6S_2N_4O_4Cl_2$) quinary cluster in which two $\{[THF\cdot Li(\mu\text{-}O)(\mu\text{-}N^tBu)]_2S\}$ molecules are held together by two (THF·LiCl) units. The mean Li−Cl distance (2.348 Å) linking the $\{[THF\cdot Li(\mu\text{-}O)(\mu\text{-}N^tBu)]_2S\}$ molecules to the (THF·LiCl) units is significantly shorter than the corresponding value of 2.483 Å within these units. Crystal data: **4**, monoclinic, $P2_1/n$, $a = 18.557(1)$ Å, $b = 15.731(1)$ Å, $c = 28.063(2)$ Å, $\beta = 107.381(1)°$, $V = 7817.9(9)$ Å^3, and $Z = 2$; **5**, monoclinic, $P2_1/n$, $a = 11.583(3)$ Å, $b = 17.126(5)$ Å, $c = 13.891(4)$ Å, $\beta = 94.613(4)°$, $V = 2747(1)$ Å^3, and $Z = 2$.

Introduction

In the past few years, several aza analogues of the common oxo anions sulfite, i.e., $[S(N^tBu)_3]^{2-}$ [1] and $[OS(N^tBu)(NR)]^{2-}$ (R = ^tBu, $SiMe_3$),[2] and sulfate, i.e., $[S(N^tBu)_4]^{2-}$ [3] and $[OS(N^tBu)_3]^{2-}$,[4] have been structurally characterized as their dilithium derivatives and their ligand behavior has been investigated.[5,6] Significant consequences result from the replacement of a bulky imido (RN^{2-}) group in a homoleptic system by an oxo (O^{2-}) ligand. For example, $\{Li_2[S(N^tBu)_3]\}_2$ is dimeric in the solid state[1a] and forms a ternary $Li_4S_2N_6$ hexagonal prism, cf. $\{Li_2[E(N^tBu)_3]\}_2$ (E = Te[7] and Se[8]). By contrast, a hexameric structure is found for $\{Li_2[OS(N^tBu)_2]\}_6$.[2] This 36-atom ($Li_{12}S_6N_{12}O_6$) quaternary cluster is formed by the aggregation of three $Li_4S_2N_4O_2$ hexagonal prisms via their sterically unencumbered Li_2O_2 faces.

In this context, extension of these ideas to the heteroleptic azasulfite $[O_2S(N^tBu)]^{2-}$ and diazasulfate $[O_2S(NR)_2]^{2-}$ (R = alkyl) dianions, which contain *two* oxo ligands, may lead to structurally unique clusters. For example, we have suggested that the dilithium derivative of $[O_2S(N^tBu)]^{2-}$ may give rise to extended structures by aggregation via the *two* Li_xO_x (x = 2, 3) faces of the fundamental building block.[9] In a preliminary report on diazasulfates,[10] we described the use of a heterobimetallic strategy involving partial magnesiation and subsequent lithiation of $O_2S[N(H)^tBu]_2$ to produce crystalline $\{(THF)_4Li_4Mg[O_2S(N^tBu)_2]_3\}_2$ (**1**). An Li_4O_4 ladder is the central feature of the centrosymmetric dimer **1**, which incorporates a 36-atom ($Li_6Mg_2S_6N_{12}O_{10}$) quinary cluster, in which six $[O_2S(N^tBu)_2]^{2-}$ ligands are coordinated to the Li^+ and Mg^{2+} cations via *N*,*O*-chelation.

The templation of organic and inorganic molecules by added salts is an established and reasonably well understood phenomenon.[11] For example, the lithium amidinate $\{Li[(^nBu)C(N^tBu)_2]\}$ acts as a neutral lithioligand in the entrapment of LiX (X = OH, Cl, Br, I) molecules.[12] Herein we report the syntheses of

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$\{Li_2[O_2S(N^iPr)_2]\}_n$ (**2**) and $\{THF\cdot Li_2[O_2S(N^tBu)_2]\}_n$ (**3**), the first dilithium diazasulfates. The serendipitous generation of the novel cluster $\{THF\cdot Li_2[O_2S(N^tBu)_2]\}_8\cdot 2LiOH\cdot 2LiCl$ (**4**) during these studies suggested that templation with added lithium salts, e.g., LiCl, may provide a viable and, perhaps, necessary approach to the crystallization of $\{Li_2[O_2S(NR)_2]\}_n$ which are amorphous, gel-forming solids. This concept has been confirmed by the deliberate preparation and structural characterization of the highly solvated, LiCl-templated dimer $\{(THF\cdot Li)_2[O_2S(N^tBu)_2]\cdot(THF)LiCl\}_2$ (**5**).

Experimental Section

Reagents and General Procedures. Solvents were dried and distilled before use: tetrahydrofuran, toluene, *n*-hexane, *n*-pentane (Na/benzophenone). *n*-Butyllithium (2.5 M solution in hexanes, Aldrich) was used as received. $^iPrNH_2$ and $^tBuNH_2$ (Aldrich) were predried over KOH and then distilled from CaH_2 onto molecular sieves. SO_2Cl_2 (Aldrich) was distilled immediately prior to use. Anhydrous LiCl was prepared by heating a hydrated sample (Fisher Scientific) at 130 °C in vacuo for 4 days. The compounds $O_2S[N(H)R]_2$ (R = ^iPr,[13] ^tBu[14]) were prepared by the literature procedures. The handling of air- and moisture-sensitive reagents was performed under an atmosphere of argon gas using Schlenk techniques or a glovebox.

Instrumentation. ^1H NMR spectra were collected on a Bruker AM-200 spectrometer, and chemical shifts are reported relative to Me_4Si in $CDCl_3$. ^7Li NMR spectra were recorded on a Varian XL-200 instrument operating at 77.75 MHz; chemical shifts are reported relative to 1 M LiCl in D_2O. Solid-state ^7Li and ^{13}C NMR studies were performed on a Bruker AMX-300 spectrometer (operating at 116.64 and 75.48 MHz, respectively) using a BL4 probe; chemical shifts are reported relative to LiCl and Me_4Si, respectively. Elemental analyses were provided by the Analytical Services Laboratory of the Department of Chemistry, University of Calgary.

Preparation of $\{Li_2[O_2S(N^iPr)_2]\}_n$ (2). *n*-Butyllithium (13.3 mL, 33.3 mmol) was added slowly to a stirred slurry of $O_2S[N(H)^iPr]_2$ (3.00 g, 16.6 mmol) in *n*-hexane (60 mL) cooled to 0 °C. After 0.5 h, the cooling bath was removed and the reaction mixture was stirred for a further 3 h at 23 °C. Removal of all volatiles in vacuo and subsequent washing of the white residue with *n*-pentane (2 × 15 mL) yielded, upon drying, **2** (3.00 g, 15.6 mmol, 94%); mp 255 °C dec. Anal. Calcd for $C_6H_{14}Li_2N_2O_2S$: C, 37.51; H, 7.34; N, 14.58. Found: C, 37.57; H, 7.42; N, 14.38. Solid-state ^7Li NMR (spin at 15 kHz): δ 1.58 (s). Solid-state ^{13}C NMR (spin at 10 kHz): δ 47.10 [s, $(CH_3)_2CH$], 44.81 [s, $(CH_3)_2CH$], 26.67 [br, $\Delta\nu_{1/2} = 313$ Hz, $(CH_3)_2CH$].

Preparation of $\{THF\cdot Li_2[O_2S(N^tBu)_2]\}_n$ (3). *n*-Butyllithium (1.96 mL, 4.90 mmol) was added slowly to a stirred solution of $O_2S[N(H)^tBu]_2$ (0.51 g, 2.45 mmol) in toluene (25 mL) cooled to −78 °C. After 0.5 h, the cooling bath was removed and the reaction mixture was stirred for a further 6 h at 23 °C. After all volatiles were removed in vacuo, the white residue was dissolved in THF (20 mL) to give a colorless gel from which **3** (0.64 g, 2.20 mmol, 90%) was obtained following evaporation of THF and subsequent washing with *n*-pentane (10 mL); mp 160 °C dec. Anal. Calcd for $C_{12}H_{26}Li_2N_2O_3S$: C, 49.31; H, 8.97; N, 9.58. Found: C, 49.02; H, 9.06; N, 9.72. Solid-state ^7Li NMR (spin at 15 kHz): δ 1.69 (s) and 0.53 (s) (approximately 1:1). Solid-state ^{13}C NMR (spin at 10 kHz): δ 67.94 [s, $O(CH_2)_2(CH_2)_2$], 51.03 [s, $C(CH_3)_3$], 32.33 [s, $\Delta\nu_{1/2} = 145$ Hz, $C(CH_3)_3$], 24.73 [s, $O(CH_2)_2(CH_2)_2$].

Preparation of $\{(THF\cdot Li)_2[O_2S(N^tBu)_2]\cdot(THF)LiCl\}_2$ (5). *n*-Butyllithium (1.92 mL, 4.80 mmol) was added slowly to a stirred mixture of $O_2S[N(H)^tBu]_2$ (0.50 g, 2.40 mmol) and LiCl (0.10 g, 2.40 mmol) in THF (35 mL) at 23 °C. The clear, colorless reaction mixture was stirred for 3 h. Removal of all volatiles in vacuo yielded white microcrystalline **5** (0.98 g, 1.02 mmol, 85%); mp 200 °C dec (loss of THF solvate occurs at ca. 75 °C). Anal. Calcd for $C_{20}ClH_{42}Li_3N_2O_5S$: C, 50.16; H, 8.84; N, 5.85. Found: C, 49.31; H, 8.73; N, 5.84. ^1H NMR (in d_8-THF at 23 °C): δ 3.58 [m, 24H, $O(CH_2)_2(CH_2)_2$], 1.73 [m, 24H, $O(CH_2)_2(CH_2)_2$], 1.21 (s, 36H, ^tBu). ^7Li NMR (in d_8-THF at 23 °C; locked on downfield signal): δ 1.20 (s, $\Delta\nu_{1/2} = 13$ Hz).

Table 1. Crystallographic Data for $\mathbf{4}\cdot 2THF\cdot n\text{-}C_6H_{14}$ and **5**

	$\mathbf{4}\cdot 2THF\cdot n\text{-}C_6H_{14}$	**5**
formula	$C_{110}H_{240}Cl_2Li_{20}N_{16}O_{28}S_8$	$C_{40}H_{84}Cl_2Li_6N_4O_{10}S_2$
fw	2701.36	957.77
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	18.557(1)	11.583(3)
b, Å	15.731(1)	17.126(5)
c, Å	28.063(2)	13.891(4)
β, deg	107.381(1)	94.613(4)
V, Å^3	7817.9(9)	2747(1)
Z	2	2
T, °C	−70.0	−70.0
λ, Å	0.710 73	0.710 73
d_{calcd}, g cm^{-3}	1.148	1.158
μ, cm^{-1}	2.12	2.44
$F(000)$	2916	1032
R1^a	0.0554	0.0586
wR2^b	0.1718	0.1170

^{a} $R1 = [\sum||F_o| - |F_c||]/[\sum|F_o|]$ for $[I > 2\sigma(I)]$. ^{b} $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$ (all data).

X-ray Analyses. All data were collected on a Bruker AX SMART 1k CCD diffractometer. Crystallographic data are summarized in Table 1.

Compound 4. Colorless crystals of $\{THF\cdot Li_2[O_2S(N^tBu)_2]\}_8\cdot 2LiOH\cdot 2LiCl$ cocrystallized with two *noncoordinating* THF molecules and one *n*-hexane molecule were formed in 3 days at 23 °C by filtering a sample of **3** in THF and layering the resulting solution with 1 equiv of *n*-hexane. A flash-cooled crystal (0.10 × 0.10 × 0.10 mm), mounted with viscous oil onto a thin glass fiber, was measured using 0.3° ω-scans at 0°, 90°, and 180° in ϕ in the range $1.50° \leq 2\theta \leq 21.00°$. Semiempirical absorption corrections ($t_{max}/t_{min} = 1.49$) based on equivalent reflections were applied.[15] Of a total of 19 294 reflections collected, 8396 were independent ($R_{int} = 0.0959$) and were used to refine 827 parameters, with 5913 reflections considered observed [$I > 2\sigma$]. Systematic absences in the diffraction data were uniquely consistent for the space group $P2_1/n$ (No. 14). The structure was solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. With the exception of the *n*-hexane carbon atoms, each of which was disordered equally over two positions, all non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions.

Compound 5. Colorless crystals of $\{(THF\cdot Li)_2[O_2S(N^tBu)_2]\cdot(THF)LiCl\}_2$ were formed in 24 h at 23 °C by layering *n*-hexane onto a solution of **5** in THF. A flash-cooled crystal (0.20 × 0.20 × 0.20 mm), mounted with viscous oil onto a thin glass fiber, was measured using 0.3° ω-scans at 0°, 90°, and 180° in ϕ in the range $1.89° \leq 2\theta \leq 28.70°$. Semiempirical absorption corrections ($t_{max}/t_{min} = 1.92$) based on equivalent reflections were applied.[15] Of a total of 14 903 collected reflections, 6368 were independent ($R_{int} = 0.0917$) and were used to refine 289 parameters, with 2642 reflections considered observed [$I > 2\sigma$]. Systematic absences in the diffraction data were uniquely consistent for the space group $P2_1/n$ (No. 14). Structure solution and refinement procedures were the same as those described for **4**.

All scattering factors and anomalous dispersion factors are contained in the SHELXTL 5.1 program library (Brüker AXS, Inc., Madison, WI, 1997).

Results and Discussion

Preparation and Solid-State ^{7}Li and ^{13}C NMR Spectra of $\{Li_2[O_2S(N^iPr)_2]\}_n$ and $\{THF\cdot Li_2[O_2S(N^tBu)_2]\}_n$. The first dilithium derivatives of the diazasulfate dianion, $\{Li_2[O_2S(N^iPr)_2]\}_n$ (**2**) and $\{THF\cdot Li_2[O_2S(N^tBu)_2]\}_n$ (**3**), are prepared

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in excellent yields (94% and 90%, respectively) from the facile reactions of 2 equiv of ^{n}BuLi with the appropriate *N,N′*-dialkylsulfamide (eq 1).

$$2\ {}^{n}\mathrm{BuLi} + \mathrm{O_2S[N(H)R]_2} \rightarrow 1/n\ \{(\mathrm{THF})_x\cdot\mathrm{Li_2[O_2S(NR)_2]}\}_n + 2\ {}^{n}\mathrm{BuH} \quad (1)$$

2, R = ^{i}Pr, $x = 0$
3, R = ^{t}Bu, $x = 1$

The solid-state ^{13}C NMR spectrum of **2** shows two singlets of approximately equal intensity at δ 47.10 and 44.81 ppm for the α-carbon atoms and a broad ($\Delta\nu_{1/2} = 313$ Hz) resonance at δ 26.67 ppm for the methyl carbon atoms of the isopropyl groups [cf. $\Delta\nu_{1/2} = 145$ Hz for methyl carbon atoms in **3** (vide infra)], indicating two significantly different isopropylimido environments. The ^{7}Li NMR spectrum revealed a singlet at δ 1.58 ppm. The complex **2** is insoluble in *n*-pentane and *n*-hexane, but forms very viscous gels in aromatic solvents, e.g., benzene and toluene, and in coordinating solvents, e.g., THF, diethyl ether, and TMEDA, possibly resulting from the incorporation of solvent molecules in the channels or cavities of an extended structure. Consequently, crystals suitable for X-ray crystallography could not be obtained.

Although **3** is also insoluble in alkanes and produces gels similar to those formed by **2** in aromatic solvents, this complex forms a much less viscous, colorless gel in THF. In addition to resonances for the ^{t}Bu groups in the ^{13}C NMR spectrum, resonances for coordinated THF molecules are observed at δ 67.94 and 24.73 ppm in the approximate ratio of one THF molecule:one $\{\mathrm{Li_2[O_2S(N^tBu)_2]}\}$ unit. Consistent with this observation, the ^{7}Li NMR spectrum displayed two singlets at δ 1.69 (unsolvated) and 0.53 (solvated) ppm in an approximate 1:1 ratio. Interestingly, the ^{13}C NMR spectrum shows only one singlet for the α-carbon atoms (δ 51.03 ppm) as well as for the methyl carbon atoms (δ 32.33 ppm) of the *tert*-butyl groups, indicating one type of *tert*-butylimido environment.

The solvated complex $\{[(\mathrm{THF})_2\cdot\mathrm{Li}(\mu\text{-}\mathrm{N^tBu})_2]_2\mathrm{S}\}$ is monomeric.[3] Although X-ray quality crystals of **3** could not be obtained, it is clear that the replacement of two imido groups in the homoleptic dianion $[\mathrm{S(N^tBu)_4}]^{2-}$ with oxo ligands has significant structural consequences. As well, it is evident from a comparison of the NMR data for **2** and **3** that small changes to the size of the alkyl groups in $[\mathrm{O_2S(NR)_2}]^{2-}$ may result in additional structural differences.

Formation and X-ray Structure of $\{\mathrm{THF\cdot Li_2[O_2S(N^tBu)_2]}\}_8\cdot$2LiOH·2LiCl (4). During a preliminary investigation of the dilithiation of $\mathrm{O_2S[N(H)^tBu]_2}$ with 2 equiv of ^{n}BuLi (eq 1), filtration of the gel and subsequent layering of the resulting THF solution with 1 equiv of *n*-hexane afforded a few crystals. Surprisingly, X-ray structure analysis revealed the LiCl- and LiOH-templated octamer $\{\mathrm{(THF)Li_2[O_2S(N^tBu)_2]}\}_8\cdot$2LiCl·2LiOH (**4**), which contains a 64-atom ($\mathrm{Li_{20}S_8N_{16}O_{18}Cl_2}$) quinary cluster (Figure 1). Selected bond distances and bond angles are listed in Table 2. The presence of LiCl in **4** is attributed to lithiation of trace amounts of ${}^{t}\mathrm{BuNH_3Cl}$ in $\mathrm{O_2S[N(H)^tBu]_2}$.[14] The source of LiOH is likely to be commercial ^{n}BuLi.[16]

The 64-atom cluster **4** contains eight $[\mathrm{O_2S(N^tBu)_2}]^{2-}$ dianions together with 16 Li^{+} counterions. All Li^{+} ions are four-coordinate with the exception of Li(1), which is three-coordinate. Three $\mathrm{Li_4O_4}$ units, a central step-shaped ladder connected by $\mathrm{S(N^tBu)_2}$ units to two broken cubes, provide the structural framework for this novel cluster arrangement (Figure 2). Furthermore, the four-runged $\mathrm{Li_4O_4}$ ladder is extended to a six-runged, S-shaped ladder via S(2)−N(3) rungs at either end. A similar ladder is observed in the core of $\{\mathrm{(THF)_4Li_4Mg[O_2S(N^tBu)_2]_3}\}_2$ (**1**).[10] The $\mathrm{Li_4O_4}$ cubes are opened along their Li(9)−O(4) edges in order to accommodate the LiOH [Li(8)−O(14)] units, thus forming six-membered $\mathrm{Li_3O_3}$ rings (Figure 1). The inner four $[\mathrm{O_2S(N^tBu)_2}]^{2-}$ ions [containing S(1), S(1*), S(2), and S(2*)] each contribute one O atom to the ladder and one to their respective cube, while the outer four dianions [containing S(3), S(3*), S(4), and S(4*)] each contribute one O atom to the cube and one to the periphery of the cluster. These peripheral O atoms [O(5), O(5*), O(7), and O(7*)] are two-coordinate while all remaining O atoms in the cluster are three- or four-coordinate.

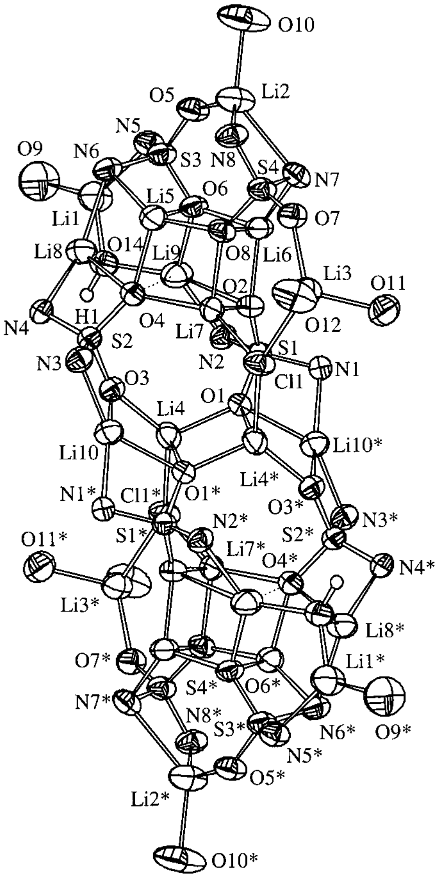

Figure 1. Molecular structure of $\{\mathrm{THF\cdot Li_2[O_2S(N^tBu)_2]}\}_8\cdot$2LiOH·2LiCl (**4**). For clarity, the ^{t}Bu groups are omitted and only the oxygen atoms of the THF molecules are shown. Displacement ellipsoids are plotted at the 50% probability level. Starred atoms are related by the symmetry transformation $-x + 1, -y, -z + 2$.

Interestingly, the $[\mathrm{O_2S(N^tBu)_2}]^{2-}$ ions in **4** exhibit three distinct modes of metal cation coordination. The dianions involving S(1) and S(2) *N,O*-chelate two Li^{+} ions (Figure 3a); those containing S(3) are coordinated to three cations via *N,O*-chelation of Li(5) and monodentate coordination through an N atom to Li(1) and through an O atom to Li(2) (Figure 3b); and those containing S(4) are also coordinated to three cations, but via *N,N′*-chelation of Li(2), *N,O*-chelation of Li(6), and monodentate coordination through an O atom to Li(3) (Figure 3c). Bischelation has previously been observed for the related ligands $[\mathrm{S(N^tBu)_4}]^{2-}$ [3,6] and $[\mathrm{SO_4}]^{2-}$,[17] as well as for $[\mathrm{O_2S(N^tBu)_2}]^{2-}$.[10] However, the other two coordination modes exhibited by $[\mathrm{O_2S(N^tBu)_2}]^{2-}$ in **4** (Figure 3b,c) are novel for this series of dianions.

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for $\{THF{\cdot}Li_2[O_2S(N^tBu)_2]\}_8{\cdot}2LiOH{\cdot}2LiCl$ (**4**)[a]

S(1)−O(1)	1.512(3)	Li(4)−O(1)	1.934(8)
S(1)−O(2)	1.491(3)	Li(4)−O(1*)	2.245(9)
S(1)−N(1)	1.550(3)	Li(5)−O(8)	1.922(8)
S(1)−N(2)	1.549(4)	Li(5)−O(4)	1.929(8)
S(2)−O(3)	1.496(3)	Li(5)−N(6)	2.103(8)
S(2)−O(4)	1.514(3)	Li(5)−O(6)	2.167(9)
S(2)−N(3)	1.555(4)	Li(6)−O(6)	1.905(8)
S(2)−N(4)	1.554(3)	Li(6)−O(2)	1.934(7)
S(3)−O(5)	1.476(3)	Li(6)−N(7)	1.988(8)
S(3)−O(6)	1.512(3)	Li(6)−O(8)	2.127(8)
S(3)−N(5)	1.547(4)	Li(7)−O(2)	1.955(8)
S(3)−N(6)	1.576(4)	Li(7)−O(8)	1.990(7)
S(4)−O(7)	1.469(3)	Li(7)−O(4)	2.047(8)
S(4)−O(8)	1.520(3)	Li(8)−O(14)	1.861(9)
S(4)−N(7)	1.566(4)	Li(8)−N(4)	1.979(8)
S(4)−N(8)	1.557(4)	Li(8)−N(6)	2.137(8)
Cl(1)−Li(3)	2.348(8)	Li(8)−O(4)	2.290(8)
Cl(1)−Li(7)	2.294(7)	Li(9)−O(14)	1.890(9)
Cl(1)−Li(4*)	2.367(7)	Li(9)−O(6)	1.967(8)
Li(1)−O(14)	1.806(9)	Li(9)−N(2)	1.975(8)
Li(1)−N(5)	1.958(9)	Li(9)−O(2)	2.528(9)
Li(2)−O(5)	1.890(9)	Li(10)−N(3)	1.949(8)
Li(2)−N(7)	2.362(10)	Li(10)−N(1*)	1.965(8)
Li(2)−N(8)	1.993(9)	Li(10)−O(3)	2.059(8)
Li(3)−O(7)	1.914(8)	Li(10)−O(1*)	2.099(8)
Li(4)−O(3)	1.892(8)	Li(9)···O(4)	2.996(9)

O(1)−S(1)−O(2)	107.28(16)	S(1)−O(1)−Li(4)	132.2(3)
O(1)−S(1)−N(1)	100.55(17)	S(1)−O(1)−Li(10*)	91.9(2)
O(2)−S(1)−N(1)	114.11(17)	Li(4)−O(1)−Li(10*)	128.9(3)
O(1)−S(1)−N(2)	113.30(17)	S(1)−O(1)−Li(4*)	134.2(2)
O(2)−S(1)−N(2)	101.91(17)	Li(4)−O(1)−Li(4*)	83.2(3)
N(1)−S(1)−N(2)	119.6(2)	Li(10*)−O(1)−Li(4*)	79.7(3)
O(3)−S(2)−O(4)	108.51(17)	S(1)−O(2)−Li(6)	145.4(3)
O(3)−S(2)−N(3)	100.76(17)	S(1)−O(2)−Li(7)	125.9(3)
O(4)−S(2)−N(3)	113.46(19)	Li(6)−O(2)−Li(7)	88.6(3)
O(3)−S(2)−N(4)	113.62(18)	S(1)−O(2)−Li(9)	86.8(2)
O(4)−S(2)−N(4)	101.26(17)	Li(6)−O(2)−Li(9)	82.3(3)
N(3)−S(2)−N(4)	119.3(2)	Li(7)−O(2)−Li(9)	102.0(3)
O(5)−S(3)−O(6)	107.34(17)	S(2)−O(3)−Li(4)	154.1(3)
O(5)−S(3)−N(5)	112.80(19)	S(2)−O(3)−Li(10)	92.4(2)
O(6)−S(3)−N(5)	112.08(19)	Li(4)−O(3)−Li(10)	89.5(3)
O(5)−S(3)−N(6)	113.7(2)	S(2)−O(4)−Li(5)	150.4(3)
O(6)−S(3)−N(6)	99.79(17)	S(2)−O(4)−Li(7)	121.0(3)
N(5)−S(3)−N(6)	110.4(2)	Li(5)−O(4)−Li(7)	84.8(3)
O(7)−S(4)−O(8)	107.74(16)	S(2)−O(4)−Li(8)	88.9(2)
O(7)−S(4)−N(8)	113.95(19)	Li(5)−O(4)−Li(8)	75.9(3)
O(8)−S(4)−N(8)	110.81(19)	Li(7)−O(4)−Li(8)	141.5(3)
O(7)−S(4)−N(7)	115.38(19)	S(3)−O(5)−Li(2)	137.0(3)
O(8)−S(4)−N(7)	101.57(18)	S(3)−O(6)−Li(6)	136.8(3)
N(8)−S(4)−N(7)	106.7(2)	S(3)−O(6)−Li(9)	122.5(3)
Li(7)−Cl(1)−Li(3)	96.9(3)	Li(6)−O(6)−Li(9)	100.1(3)
Li(7)−Cl(1)−Li(4*)	92.9(3)	S(3)−O(6)−Li(5)	89.3(2)
Li(3)−Cl(1)−Li(4*)	152.8(3)	Li(6)−O(6)−Li(5)	86.9(3)
S(1)−N(1)−Li(10*)	96.0(3)	Li(9)−O(6)−Li(5)	103.6(3)
S(1)−N(2)−Li(9)	108.0(3)	S(4)−O(7)−Li(3)	132.7(3)
S(2)−N(3)−Li(10)	94.9(3)	S(4)−O(8)−Li(5)	128.6(3)
S(2)−N(4)−Li(8)	100.1(3)	S(4)−O(8)−Li(7)	144.2(3)
S(3)−N(5)−Li(1)	109.9(3)	Li(5)−O(8)−Li(7)	86.6(3)
S(3)−N(6)−Li(5)	89.9(3)	S(4)−O(8)−Li(6)	91.7(2)
S(3)−N(6)−Li(8)	112.0(3)	Li(5)−O(8)−Li(6)	87.6(3)
Li(5)−N(6)−Li(8)	75.9(3)	Li(7)−O(8)−Li(6)	82.5(3)
S(4)−N(7)−Li(6)	95.7(3)	Li(1)−O(14)−Li(8)	102.5(4)
S(4)−N(7)−Li(2)	82.2(3)	Li(1)−O(14)−Li(9)	112.1(4)
Li(6)−N(7)−Li(2)	100.9(3)	Li(8)−O(14)−Li(9)	89.8(4)
S(4)−N(8)−Li(2)	95.9(3)		

[a] Bond angles centered at Li atoms are contained in the Supporting Information.

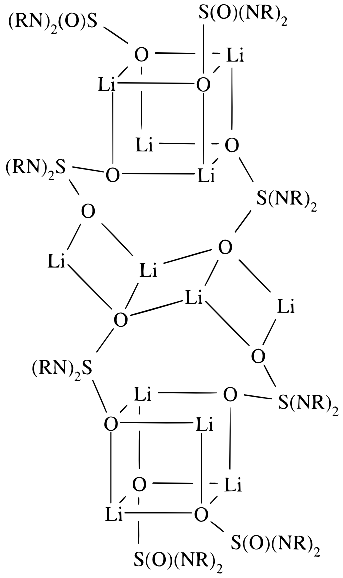

Figure 2. Schematic drawing of the cluster $\{THF{\cdot}Li_2[O_2S(N^tBu)_2]\}_8{\cdot}2LiOH{\cdot}2LiCl$ (**4**) (R = ᵗBu). The three Li_4O_4 units (two broken cubes and one step-shaped ladder) are highlighted.

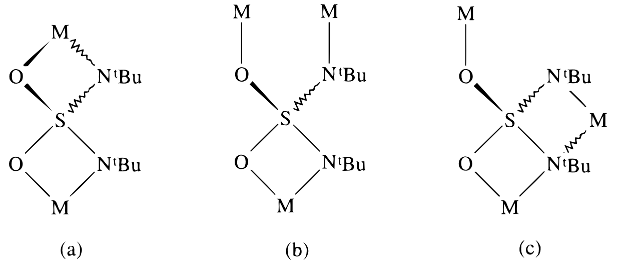

Figure 3. Different coordination modes of the $[O_2S(N^tBu)_2]^{2-}$ dianions in **4**: (a) bis-(*N,O*),(*N′,O′*)-chelate; (b) *N,O*-chelate, bis-*N′,O′*-monodentate; (c) bis-(*N,O*),(*N,N′*)-chelate, *O′*-monodentate.

Formation and X-ray Structure of $\{(THF{\cdot}Li)_2[O_2S(N^tBu)_2]{\cdot}(THF)LiCl\}_2$ (5). In light of the fortuitous crystallization of **4**, we turned our attention to the intentional use of lithium salts as templates for the crystallization of diazasulfates. Lithium chloride was chosen in view of its proven effectiveness for the templation of related systems.[12,18] Accordingly, $\{(THF{\cdot}Li)_2[O_2S(N^tBu)_2]{\cdot}(THF)LiCl\}_2$ (**5**) is prepared in 85% yield from the reaction of 2 equiv of ⁿBuLi with $O_2S[N(H)^tBu]_2$ and anhydrous LiCl in THF. Although the formation of **5** requires a 1:1 stoichiometry of LiCl and the sulfamide (eq 2), it is the first product to crystallize when 0.5 equiv of LiCl is utilized and **5** is the only product formed when more than 1 equiv of LiCl is used.

$$2\,{}^nBuLi + O_2S[N(H)^tBu]_2 + LiCl \rightarrow \tfrac{1}{2}\,\{(THF{\cdot}Li)_2[O_2S(N^tBu)_2]{\cdot}(THF)LiCl\}_2 + 2\,{}^nBuH \quad (2)$$

The highly solvated structure of **5** contains two $\{(THF{\cdot}Li)_2[O_2S(N^tBu)_2]\}$ molecules and two [(THF)LiCl] units in an 18-atom ($Li_6S_2N_4O_4Cl_2$) quinary cluster (Figure 4). Selected bond distances and bond angles are listed in Table 3. Crystallographically related by a center of inversion, each $[O_2S(N^tBu)_2]^{2-}$ ion *N,O*-chelates two $(THF{\cdot}Li)^+$ ions, and the O atoms further exhibit monodentate coordination to the Li atoms of the LiCl

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(17) (a) Rudert, R.; Czichocki, G. *Acta Crystallogr.* **1996**, *C52*, 1670. (b) Hori, T.; Himeno, S.; Tamada, O. *J. Chem. Soc., Dalton Trans.* **1996**, 2083.

(18) LiCl was intentionally added to a THF solution of $(Me_2AlOLi)_4$ in order to enhance crystallization, resulting in formation of crystals of the complex $(Me_2AlOLi)_4{\cdot}7THF{\cdot}LiCl$. Storre, J.; Schnitter, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Fleischer, R.; Stalke, D. *J. Am. Chem. Soc.* **1997**, *119*, 7505.

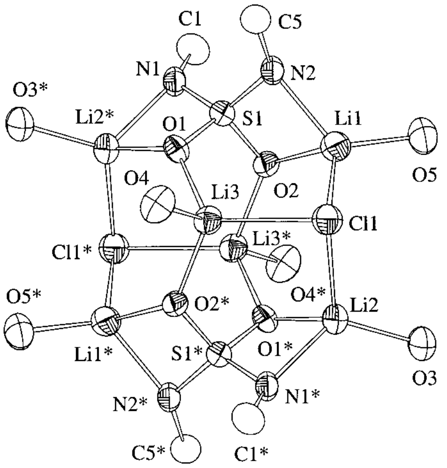


Figure 4. Molecular structure of $\{(THF\cdot Li)_2[O_2S(N^tBu)_2]\cdot(THF)LiCl\}_2$ (**5**). For clarity, only the α-carbon atoms of the ^{t}Bu groups and the oxygen atoms of the THF molecules are shown. Displacement ellipsoids are plotted at the 50% probability level. Starred atoms are related by the symmetry transformation $-x, -y, -z + 1$.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for $\{(THF\cdot Li)_2[O_2S(N^tBu)_2]\cdot(THF)LiCl\}_2$ (**5**)

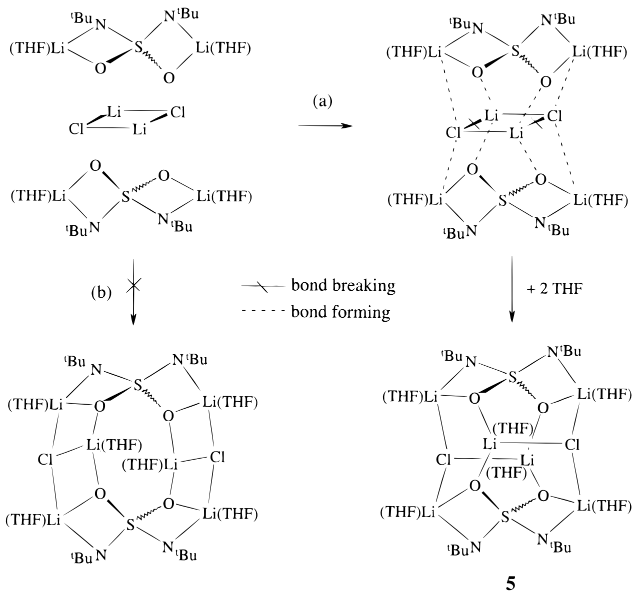
S(1)−O(1)	1.5080(17)	O(2)−Li(1)	1.973(5)
S(1)−O(2)	1.5098(17)	N(1)−Li(2*)	2.000(5)
S(1)−N(1)	1.555(2)	N(2)−Li(1)	1.989(5)
S(1)−N(2)	1.558(2)	Li(1)−Cl(1)	2.333(5)
O(1)−Li(3)	1.953(5)	Li(2)−Cl(1)	2.362(5)
O(1)−Li(2*)	1.999(5)	Li(3)−Cl(1)	2.483(5)
O(2)−Li(3*)	1.938(5)		

O(1)−S(1)−O(2)	107.65(10)	S(1)−N(2)−Li(1)	89.21(17)
O(1)−S(1)−N(1)	100.64(11)	O(2)−Li(1)−N(2)	72.84(18)
O(2)−S(1)−N(1)	113.74(11)	O(2)−Li(1)−Cl(1)	110.5(2)
O(1)−S(1)−N(2)	113.52(11)	N(2)−Li(1)−Cl(1)	115.3(2)
O(2)−S(1)−N(2)	100.17(11)	O(1*)−Li(2)−N(1*)	72.24(18)
N(1)−S(1)−N(2)	120.99(12)	O(1*)−Li(2)−Cl(1)	107.8(2)
S(1)−O(1)−Li(3)	120.44(17)	N(1*)−Li(2)−Cl(1)	114.2(2)
S(1)−O(1)−Li(2*)	91.07(16)	O(2*)−Li(3)−O(1)	110.1(2)
Li(3)−O(1)−Li(2*)	130.6(2)	O(2*)−Li(3)−Cl(1)	113.9(2)
S(1)−O(2)−Li(3*)	121.70(17)	O(1)−Li(3)−Cl(1)	115.0(2)
S(1)−O(2)−Li(1)	91.20(17)	Li(1)−Cl(1)−Li(2)	98.76(18)
Li(3*)−O(2)−Li(1)	129.0(2)	Li(1)−Cl(1)−Li(3)	86.80(16)
S(1)−N(1)−Li(2*)	89.68(17)	Li(2)−Cl(1)−Li(3)	88.46(16)

molecules. The S−O [mean 1.509(2) Å, range 1.508(2)−1.510(2) Å] and S−N [mean 1.557(2) Å, range 1.555(2)−1.558(2) Å] distances fall in the range for those of **1** and **4** (cf. S−O 1.47−1.52 Å and S−N 1.54−1.59 Å).[10] The ^{1}H NMR spectrum of **5** in d_8-THF exhibits one ^{t}Bu environment at δ 1.21 ppm consistent with the C_{2h} symmetry of the solid-state structure. Interestingly, the ^{7}Li NMR spectrum contains only one relatively sharp singlet ($\Delta\nu_{1/2} = 13$ Hz) at δ 1.20 ppm despite the two distinct environments for Li$^+$ ions in **5**.

The mode of templation of the $\{(THF\cdot Li)_2[O_2S(N^tBu)_2]\}$ molecules by LiCl is illustrated in Scheme 1 (pathway a). The presence of Li−O edges[19] and Li$_x$O$_x$ faces (x = 2, 3)[2] in heteroleptic oxo/imido systems results in the aggregation of various fundamental building blocks to give higher oligomers. The formation of **5** involves the encumbrance of both Li−O edges in $\{(THF\cdot Li)_2[O_2S(N^tBu)_2]\}$ via interactions with the polar LiCl molecules, thus inhibiting further aggregation. Perhaps the most surprising feature of this templation is the formation of structure **5** in preference to the laddered arrangement (Scheme 1, pathway b). Significantly, the Li(3)−Cl(1) distance of 2.483(5) Å is considerably longer than the Li(1)−Cl(1) and Li(2)−Cl(1) distances of 2.333(5) and 2.362(5) Å, respectively, indicating a strained bond.

Scheme 1



Conclusions

In contrast to the highly solvated tetraazasulfate complex $\{[(THF)_2\cdot Li(\mu\text{-}N^tBu)_2]_2S\}$, the first examples of dilithium derivatives of the diazasulfate dianion, i.e., $\{Li_2[O_2S(N^iPr)_2]\}_n$ and $\{THF\cdot Li_2[O_2S(N^tBu)_2]\}_n$, are amorphous in the solid state. The unexpected crystallization of $\{THF\cdot Li_2[O_2S(N^tBu)_2]\}_8\cdot 2LiOH\cdot 2LiCl$ led to the deliberate use of LiCl as a template for the crystallization of alkali metal diazasulfate clusters. This templation methodology may be effective for the structural characterization of lithium derivatives of hitherto unknown isoelectronic oxo/imido anions of p-block elements, e.g., $[O_xP(NR)_{4-x}]^{3-}$ and $[O_xSi(NR)_{4-x}]^{4-}$.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **4**·2THF·n-C$_6$H$_{14}$ and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Chivers, T.; Downard, A.; Yap, G. P. A. *Inorg. Chem.* **1998**, *37*, 5708.