Formation and co-coordination of lithium azide *via* lithium triazasulfite
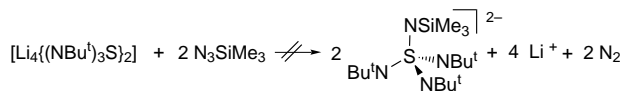
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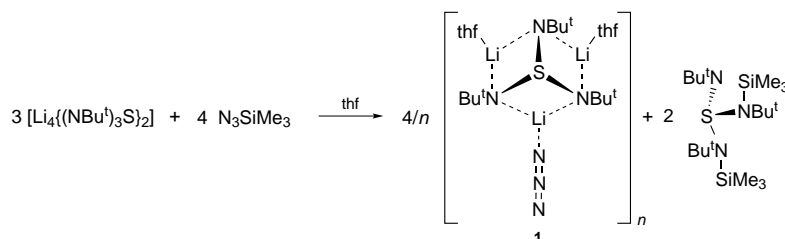
The triazasulfite [Li$_4${(NBu^t)$_3$S}$_2$] (the analogue of Li$_2$SO$_3$) provides the opportunity to complex *in situ* formed lithium azide and converts this inorganic solid into soluble monomeric residues.

Recently, we described the synthesis and structures of some nitrogen analogues of simple sulfur oxygen compounds. In these derivatives the oxygen atoms are substituted by isoelectronic NR groups to yield the dilithium triazasulfite dimer[1] [(thf)Li$_4${(NBu^t)$_3$S}$_2$] (the analogue of Li$_2$SO$_3$) and the dilithium tetraazasulfate monomer[2] [(thf)$_4$Li$_2$(NBu^t)$_4$S] (analogue to Li$_2$SO$_4$). Polyimido polyanions containing p-block element bridgeheads like [RSi(NSiMe$_3$)$_3$]$_2$$^{3-}$,[3] RE(E'R'$_2$NR'')$_3$$^{3-}$ (R,R' = H, alkyl; R'' = alkyl, aryl; E,E' = C, Si),[4] [Sb(NR)$_3$]$^{3-}$,[5a] [Sb$_2$(NR)$_4$]$^{2-}$,[5b] and [E(NBu^t)$_3$]$^{2-}$ (E = Se, Te)[6] furnish a new family of ligand systems to construct macromolecular architectures of mixed metal cages and clusters.[7] While the alkali metal salts of these polyanions are mostly employed in metal metathesis reactions little is known of their anion solvation behaviour to metal salts. The flexible electronic structure of their alkali metal derivatives, *i.e.* the ability to localise or delocalise the charge in the anion core backbone, should provide the opportunity to complex neutral metal salts.

We report here the reaction of dilithium *N,N',N''*-tris(*tert*-butyl)azasulfite [(thf)Li$_4${(NBu^t)$_3$S}$_2$] and trimethylsilyl azide to give the lithium azide adduct [(thf)$_2$Li$_3$(μ_4N$_3$){(NBu^t)$_3$S}]$_\infty$ **1**. Organo azides are mainly employed as oxidants in Staudinger type reactions.[8] In an attempt to obtain the aza analogue Me$_3$SiNS(NBu^t)$_3$$^{2-}$ of sulfate we added trimethylsilyl azide to a hexane solution of [(thf)Li$_4${(NBu^t)$_3$S}$_2$]. During the reaction at room temperature a slight rise in temperature was detected, although no evolution of gas (N$_2$) was observed (Scheme 1). In addition, silicon could not be detected in the ^{29}Si NMR spectrum of the product and the ^{7}Li NMR spectrum displayed two different lithium sites in the ratio 1:2. To further investigate the actual composition of the product, an X-ray structure analysis of the air-sensitive crystals (the compound turned dark blue when exposed to oxygen) was performed which established the formation of a polymeric lithium azide adduct **1** of monomeric [Li$_2$(NBu^t)$_3$S] (Scheme 2).

Obviously the trimethylsilyl azide acts as an acid rather than an oxidant in this reaction. That the byproduct Bu^{t}NS(Bu^{t}N-SiMe$_3$)$_2$ could not be isolated is presumably owing to its instability with respect to decomposition to S(NBu^t)$_2$ and Bu^{t}N(SiMe$_3$)$_2$ which were isolated from the reaction mixture† and identified by ^{1}H and ^{13}C NMR spectroscopy.

Compound **1** crystallises from thf–hexane within a few hours storage at room temperature to give colourless needles.‡ Within the monomeric units (Fig. 1), three lithium atoms are co-ordinated by the dianionic S(NBu^t)$_3$$^{2-}$ ligand. The dianion shows almost ideal local C_3 symmetry at sulfur. The three S–N distances are identical within e.s.d.s and are of typical length (av. 163.7 pm).[1] Li(1) and Li(1a) are tetrahedrally coordinated by two nitrogen atoms of the dianionic S(NBu^t)$_3$$^{2-}$ ligand, one azide nitrogen atom, and a single thf donor molecule. In addition to the two nitrogen atoms of the S(NBu^t)$_3$$^{2-}$ ligand Li(2) is coordinated by two azide nitrogen atoms [N(5) and N(5a)] of different N$_3$$^-$ anions completing the tetrahedral coordination sphere of Li(2). Each azide anion μ_4 bridges the three lithium atoms of one Li$_3$(NBu^t)$_3$S unit [av. Li–N 220(1) pm] and one lithium atom of a neighbouring monomeric residue

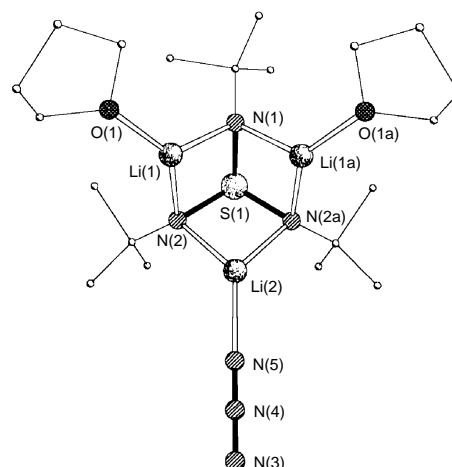**Fig. 1** Solid state structure of a monomeric unit of [(thf)$_2$Li$_3$(μ_4N$_3$){(N-Bu^t)$_3$S}]$_\infty$ **1**. Selected bond lengths (pm) and angles (°): S(1)–N(1) 163.3(5), S(1)–N(2) 164.2(4), Li(1)–N(1) 203.0(9), Li(1)–N(2) 200.3(8), Li(2)–N(2a) 203.3(8), Li(1)–N(5) 219.9(9), Li(2a)–N(5) 221.1(13), Li(2)–N(3) 195.9(12), Li(1)–O(1) 192.1(8), N(3)–N(4) 117.7(8), N(4)–N(5) 117.4(7); N(1)–S(1)–N(2) 100.5(2), N(2)–S(1)–N(2a) 100.8(3), N(3)–N(4)–N(5) 180.0(6), Li(2)–N(5)–N(4) 146.4(5).
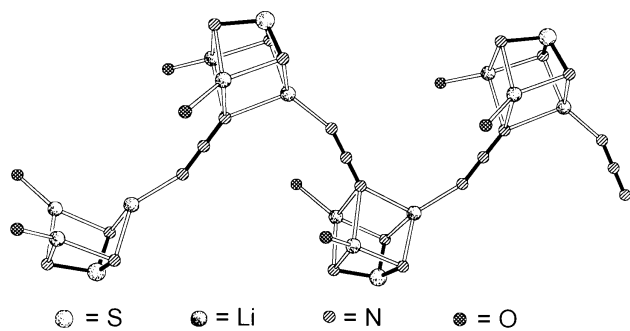
Scheme 1

Scheme 2

◎ = S   ◉ = Li   ⊘ = N   ● = O

Fig. 2 Arrangement of monomeric **1** to give polymeric wave shaped ribbons; carbon atoms omitted for clarity

[N(5)–Li(2) 196(1) pm] with both terminal nitrogen atoms, such that a polymeric solid state structure is generated (Fig. 2).

In the solid state structure of LiN_3 every lithium atom is octahedrally coordinated by eight nitrogen atoms.[9] Every terminal nitrogen atom of an azide anion μ_3 bridges three lithium atoms with one short (221.4 pm) and two longer (228.9 pm) Li–N distances. In contrast, the Li–N distances of the terminal azide nitrogen atoms [N(3) and N(5)] in **1** are equal within e.s.d.s.

The *in situ* generated lithium azide is incorporated in a metal salt cocoordination complex owing to the capability of the $S(NBu^t)_3{}^{2-}$ triazasulfite anion to coordinate more than two metal centres.[10] Although balanced in terms of charge the Li_2N_3S framework can accommodate another lithium atom to form a LiN_3 monomer. The polyimido polyanions in general seem to provide access to soluble mixed metal aggregates[11] *via* incorporation of *in situ* generated inorganic solids into complex residues.

Notes and References

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† *Preparation of* [(thf)$_2$Li$_3$\{μ_4N$_3$\}\{(NBu^t)$_3$S\}] **1**: a solution of trimethylsilyl azide (4 mmol, 0.46 g) in 5 ml hexane is added to a solution of [Li$_4$\{(NBu^t)$_3$S\}$_2$] (2 mmol, 1.18 g) in 5 ml hexane and stirred for 1 h. All volatiles are removed *in vacuo*. Crystallisation from thf–hexane (2:3) solution gives colourless needles. $M = 452.45$ g mol^{-1}, yield 1.14 g (63%). Mp 113 °C. NMR: ^{1}H (200 MHz, C$_6$D$_6$) δ 1.37 (s, 18 H, Bu^t), 1.40 (m, 8 H, thf), 1.49 (s, 9 H, Bu^t), 3.63 (m, 8 H, thf). ^{13}C (100 MHz, C$_6$D$_6$) δ 25.65 (OCH$_2$CH$_2$, thf), 34.00, 34.35 [C(CH$_3$)$_3$], 52.92, 53.49 [C(CH$_3$)$_3$], 68.09 (OCH$_2$, thf). ^{7}Li (100 MHz, C$_6$D$_6$) δ 1.31 (s, 1Li), 2.88 (s, 2Li).

‡ *Crystal data* for [(thf)$_2$Li$_3$\{μ_4N$_3$\}\{(NBu^t)$_3$S\}]·0.5 thf **1**: C$_{20}$H$_{43}$Li$_3$-N$_6$O$_2$S·0.5C$_4$H$_8$O, $M = 488.54$, orthorhombic space group *Pnma*, $a = 965.60(14)$, $b = 1593.2(4)$, $c = 2079.3(5)$ pm, $U = 3.1988(12)$ nm^3, $Z = 4$, $D_c = 1.014$ Mg m^{-3}, $F(000) = 1064$, $\lambda = 71.073$ pm, μ(Mo-Kα) = 0.128 mm^{-1}, $T = 153(2)$ K, data were collected on a Stoe-Siemens AED. Intensities of a 0.5 × 0.2 × 0.2 mm rapidly cooled crystal in an oil drop[12] were collected by the 2θ–ω method in the range of $4.33 \leqslant \theta \leqslant 22.55°$. Of a total of 3931 reflections, 2179 were independent and together with 608 restraints, were used to refine 322 parameters, largest difference peak and hole: 509 and -255 e nm^{-3}, $R1[F > 4\sigma(F)] = 0.0760$ and $wR2 = 0.2369$ (all data) with $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$ and $wR2 = \{\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2\}^{\frac{1}{2}}$; $w = 1/\{\sigma^2(F_o{}^2) + (0.153P)^2 + 1.81P\}$; $P = (F_o{}^2 + 2F_c{}^2)/3$. The

structure was solved by direct methods with SHELXS-96[13] and refined by full-matrix least squares on F^2.[14] The Bu^t moiety [C(21)–C(23)] exhibits a rotational disorder. It was refined to a split occupancy of 0.72/0.28. The twist disorder of the coordinated thf molecule [O(1), C(40)–C(43)] was modelled to a split occupancy of 0.61/0.39. Additionally, half an uncoordinated thf was found in the difference Fourier map. It is disordered over a special position and was refined to a split occupancy of 0.52/0.48. In the refinement of the Bu^t moiety [C(10)–C(13)], the symmetry (mirror plane) was suppressed. For the refinement of the disorder bond length and similarity restraints were applied. A riding model was applied in the refinement of the hydrogen atom positions. CCDC 182/720.

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