

# The inverse podant $[\text{Li}_3(\text{NBu}^t)_3\text{S}]^+$ stabilises a single ethylene oxide $\text{OCH}=\text{CH}_2$ anion as a high- and low-temperature polymorph of $[(\text{thf})_3\text{Li}_3(\text{OCH}=\text{CH}_2)\{(\text{NBu}^t)_3\text{S}\}]$

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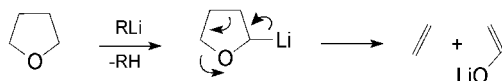
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A single ethylene oxide anion derived from the ether cleavage reaction of thf with  $\text{Bu}^t\text{Li}$  is stabilised by the inverse podant  $[\text{Li}_3(\text{NBu}^t)_3\text{S}]^+$  to give a high- and a low-temperature polymorph with a considerable difference in conformation and packing.

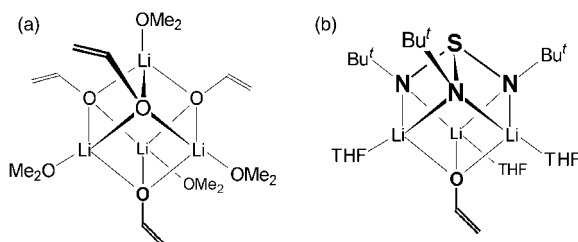
The ether cleavage reaction is one of the most common side reactions in organometallic chemistry as the  $\text{RLi}$  starting material is often dissolved in ethers.<sup>1</sup> Apart from the mostly unintended reaction to side products, cyclic ethers are deliberately employed in this reaction<sup>2–5</sup> as they give synthetically important lithium enolates<sup>6</sup> by an  $\alpha$ -metalation followed by a  $[\pi 4s + \pi 2s]$ -cycloreversion. In this reaction the most common cyclic ether tetrahydrofuran (thf) gives lithium ethylene oxide and ethene (Scheme 1).



**Scheme 1** Ether cleavage reaction of thf by lithium organics:  $\alpha$ -metalation is followed by a  $[\pi 4s + \pi 2s]$ -cycloreversion to give lithium ethylene oxide and ethene.<sup>1</sup>

Recently it was found that ethene can insert in the  $\text{Li}-\text{C}$  bond of non-reacted  $\text{Bu}^t\text{Li}$ , to give  $n$ -hexyllithium  $[(\text{thf})\text{LiCH}_2-\text{CH}_2\text{Bu}^t]_4$ .<sup>7</sup> Because the ionic character of the  $\text{Li}-\text{O}$  bond lithium enolates tend to aggregate in the solid state as solvated dimers, tetramers or even hexamers.<sup>6</sup> Although heteroatoms, like in the mixed lithium enolate/chiral amide structures<sup>8</sup> or adjacent double bonds,<sup>9</sup> help to coordinate the lithium atoms and to decrease the degree of aggregation, structurally characterised ethylene oxides generally form complex cage like structures.<sup>2–5,10</sup> The  $S_4$  symmetric tetrasolvated tetramer  $[(\text{Me}_2\text{O})(\text{LiOCH}=\text{CH}_2)]_4$  was computed to be the most stable oligomer (Scheme 2(a)).<sup>11</sup>

Here we report the solid state structure of  $[(\text{thf})_3\text{Li}_3(\text{OCH}=\text{CH}_2)\{(\text{NBu}^t)_3\text{S}\}]$  **1**. Formally it derives from the tetramer  $[(\text{Me}_2\text{O})(\text{LiOCH}=\text{CH}_2)]_4$  by replacement of the top  $[(\text{Me}_2\text{O})(\text{LiOCH}=\text{CH}_2)_3]^{2-}$  dianionic fragment by the diimido sulfite dianion  $[\text{S}(\text{NBu}^t)_3]^{2-}$  (Scheme 2(b)). This tripodal dia-

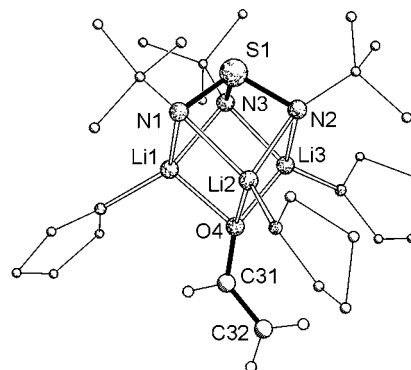


**Scheme 2** The computed  $S_4$  symmetric cubic tetramer  $[(\text{Me}_2\text{O})(\text{LiOCH}=\text{CH}_2)]_4$  is the most stable lithium enolate solvate (a).<sup>11</sup>  $[(\text{thf})_3\text{Li}_3(\text{OCH}=\text{CH}_2)\{(\text{NBu}^t)_3\text{S}\}]$  **1** mimics the same aggregation by replacement of the top  $[(\text{Me}_2\text{O})(\text{LiOCH}=\text{CH}_2)_3]^{2-}$  dianionic fragment by the triimido sulfite dianion  $[\text{S}(\text{NBu}^t)_3]^{2-}$  (b).

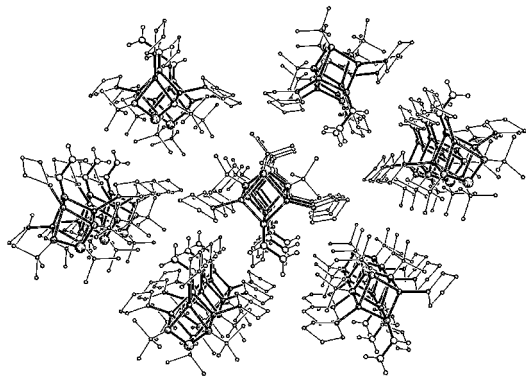
nion templates the  $\text{Li}_3$  triangle required for the oxygen atom of the single ethylene oxide ion to be  $\eta^3$  metal coordinated. By analogy to Mulvey's inverse crowns<sup>12</sup> like  $[\text{M}_2\text{Mg}_2(\text{NR}_2)_4]^{2+}$ ,  $\text{M} = \text{Li}, \text{Na}, \text{K}$ , the  $[\text{Li}_3(\text{NBu}^t)_3\text{S}]^+$  cationic motif in **1** can be regarded an inverse podant, capable of single-anion coordination to *e.g.* methanide.<sup>13</sup> In the attempted coordination of *tert*-butanide from  $\text{Bu}^t\text{Li}$  we isolated and crystallised **1** in a high-temperature (**1a**;  $D_c = 1.036 \text{ Mg m}^{-3}$ ) and a low-temperature phase (**1b**;  $D_c = 1.073 \text{ Mg m}^{-3}$ ).<sup>†</sup> For the first time an *in situ* generated, industrial important product is stabilised by the diimido sulfite dianion.

Both phases contain the cap shaped triimido sulfite dianion coordinated to three lithium atoms close to the  $\text{SN}_2$  bisectors. The single ethylene oxide anion is  $\eta^3$  coordinated *via* the oxygen atom to those three metal centres (Fig. 1). Thus, the oxygen atom forms one corner of a  $\text{SN}_3\text{Li}_3\text{O}$  cube. In both polymorphs the  $\text{H}_2\text{C}=\text{CHO}$  group is disordered. In **1a** it slots in between the three thf molecules with a 0.8/0.1/0.1 site occupation factor (SOF) each. In **1b** the ethylene group is only disordered over two positions: staggered between  $\text{Li}2$  and  $\text{Li}3$  (0.8 SOF) and eclipsed to  $\text{Li}1$  (0.2 SOF). The average  $\text{S}-\text{N}$  bond lengths of 165.3 and 166.4 pm for **1a** and **1b**, respectively, are almost identical. The  $\text{Li}_3\text{N}_3$  array is not a regular chair-shaped ring but shows alternating long and short  $\text{Li}-\text{N}$  bonds. The average  $\text{Li}\cdots\text{Li}$  distances in the cap shaped  $[\text{Li}_3(\text{NBu}^t)_3\text{S}]^+$  cation are 264.3 pm in **1a** and 265.5 pm in **1b** and are only marginally longer than the distances found in parent tetrameric lithium organics (241 ( $[\text{Bu}^t\text{Li}]_4$ ),<sup>14a</sup> 253 ( $[\text{EtLi}]_4$ ),<sup>14b</sup> 259 pm ( $[\text{MeLi}]_4$ )).<sup>14c</sup> The bond lengths similarities in both structures indicate that the different phases are not a result of severe changes in bond distances. However, the conformation of both molecules changes quite dramatically.<sup>‡</sup>

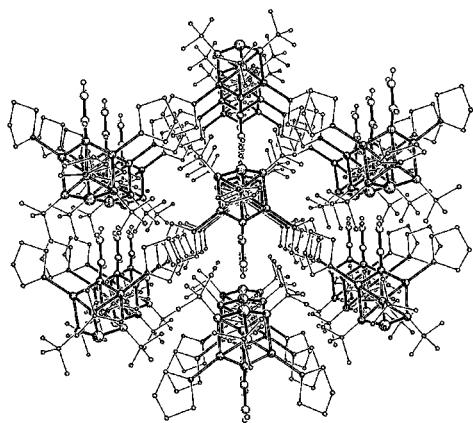
The most obvious difference between **1a** and **1b** is the more dense packing of the molecules in the low-temperature phase



**Fig. 1** Solid-state structure of  $[(\text{thf})_3\text{Li}_3(\text{OCH}=\text{CH}_2)\{(\text{NBu}^t)_3\text{S}\}]$  **1**. Selected average bond lengths (pm) and angles ( $^\circ$ ) [**1b** in square brackets]:  $\text{S}-\text{N}$  165.3(3) [166.4(2)], long  $\text{Li}-\text{N}$  210.9(7) [211.0(5)], short  $\text{Li}-\text{N}$  202.3(7) [200.4(5)],  $\text{Li}-\text{OCH}=\text{CH}_2$  195.7(8) [196.4(11)],  $\text{Li}\cdots\text{Li}$  264.3(10) [265.5(6)],  $\text{C}31-\text{O}4$  135.8(6) [133.1(6)],  $\text{C}31-\text{C}32$  136.5(13) [132.1(5)];  $\text{N}-\text{S}-\text{N}$  100.4(2) [100.38(11)].



**Fig. 2** Wide packing of the molecules in the high-temperature polymorph of **1a** with no interlocking at the periphery.



**Fig. 3** Dense packing of the low-temperature polymorph **1b**, with the thf donors zipping the molecular rods. The ethylene oxide moiety is locked in a groove provided by an adjacent rod.

compared to the high-temperature polymorph.<sup>15</sup> The average intermolecular distances in **1a** give the molecules considerably more room than in **1b**. Virtually no interlocking of the molecular periphery in the packing of **1a** tolerates the disordered orientation of the ethylene oxide over three positions, although the depicted one is favoured by eight of ten molecules (Fig. 2). In the packing of **1b** the molecular rods are zipped together by interlocking thf molecules (Fig. 3). This causes the ethylene oxide to slot in to the groove formed by two *tert*-butyl groups of an adjacent rod. The channel permits only two disordered orientations of the ethylene oxide group in **1b**. The position with the smaller SOF is disfavoured by the orientation of the CH<sub>2</sub> group eclipsed towards Li.

Evidently the beginning of the chain of cause and effect between the change in conformation and different packing can not be identified. The question whether the different packing causes the conformation or *vice versa* remains open. However, at temperatures lower than  $-36\text{ }^{\circ}\text{C}$  the ethylene oxide group clicks into the space between two thf molecules while it has more rotational freedom at higher temperatures.<sup>15c</sup>

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## Notes and references

† Preparation of [(thf)<sub>3</sub>Li<sub>3</sub>(OCH=CH<sub>2</sub>)](NBu<sup>t</sup>)<sub>3</sub> **1**: to a solution of 5.0 g [(thf)Li<sub>2</sub>(NBu<sup>t</sup>)<sub>3</sub>S]<sub>2</sub> (8.46 mmol) in 20 mL thf, 4.97 mL of a 1.7 M solution of *tert*-butyllithium (16.92 mmol) were slowly added at  $-78\text{ }^{\circ}\text{C}$

and stirred for 1 h. The mixture was stirred for 2 h at room temperature. The solvent was reduced by half under vacuum. Crystallisation at room temperature gives colourless pyrophoric crystals of the high temperature phase **1a**. Storage of the solution at  $-36\text{ }^{\circ}\text{C}$  for several days affords colourless pyrophoric crystals of **1b**; destructive phase transition from **1b** to **1a** was observed at  $-30\text{ }^{\circ}\text{C}$ ; spectroscopic data for both phases are identical (2.6 g, 78%). <sup>1</sup>H NMR (400.4 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.37 (12H, thf), 1.54 [s, 27H, C(CH<sub>3</sub>)<sub>3</sub>], 3.71 (12 H, thf), 4.03 [d, 2 H, OCHCH<sub>2</sub>], 7.45 (t, 1 H, OCHCH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  25.52, 68.40 (thf), 33.89 [C(CH<sub>3</sub>)<sub>3</sub>], 52.99 [C(CH<sub>3</sub>)<sub>3</sub>], 82.15 (OCHCH<sub>2</sub>), 159.68 (OCHCH<sub>2</sub>); <sup>7</sup>Li NMR (155.5 MHz, ext. sat. LiCl solution)  $\delta$  1.35, (br s, 3 Li).

‡ Crystal data were collected from shock-cooled crystals on a STOE IPDS (**1a**) or a Bruker SMART-APEX CCD diffractometer (**1b**) (Mo-K $\alpha$  radiation,  $\lambda = 71.073\text{ pm}$ ) at 193(2) and 173(2) K, respectively (D. Stalke, *Chem. Soc. Rev.*, 1998, **27**, 171). The structure of **1a** was solved by direct methods (SHELXS-97) and refined by full-matrix least squares methods against  $F^2$  (SHELXL-97); (G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467; G. M. Sheldrick, SHELXL-97, program for crystal structure refinement, 1996, Göttingen). The low-temperature phase **1b** crystallised as a non-merohedral twin. The matrices of both domains were determined and every domain was integrated independently. Subsequently, the structure was solved with the data of one domain by direct methods;  $R$  values defined as  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{0.5}$ ,  $w = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$ ,  $P = 1/3[\max(F_o^2, 0) + 2F_c^2]$ .

**1a**: C<sub>26</sub>H<sub>54</sub>Li<sub>3</sub>N<sub>3</sub>O<sub>4</sub>S,  $M = 525.60$ , monoclinic, space group  $P2_1/n$ ,  $a = 1003.5(2)$ ,  $b = 2331.1(5)$ ,  $c = 1469.6(3)\text{ pm}$ ,  $\beta = 101.55(3)$ ,  $U = 3.3683(12)\text{ nm}^3$ ,  $Z = 4$ ,  $D_c = 1.036\text{ Mg m}^{-3}$ ,  $\mu = 0.126\text{ mm}^{-1}$ ,  $F(000) = 1152$ , 22142 reflections measured, 5718 unique,  $R_{\text{int}} = 0.0558$ ,  $wR2$  (all data) = 0.1949,  $R1[I > 2\sigma(I)] = 0.0747$ , 520 parameters and 718 restraints.

**1b**: C<sub>26</sub>H<sub>54</sub>Li<sub>3</sub>N<sub>3</sub>O<sub>4</sub>S,  $M = 525.60$ , monoclinic, space group  $P2_1/c$ ,  $a = 1586.05(11)$ ,  $b = 1371.07(10)$ ,  $c = 1497.29(11)\text{ pm}$ ,  $\beta = 91.444(2)$ ,  $U = 3.2550(4)\text{ nm}^3$ ,  $Z = 4$ ,  $D_c = 1.073\text{ Mg m}^{-3}$ ,  $\mu = 0.130\text{ mm}^{-1}$ ,  $F(000) = 1152$ , 18299 reflections measured, 6989 unique,  $R_{\text{int}} = 0.0647$ ,  $wR2$  (all data) = 0.2113,  $R1[I > 2\sigma(I)] = 0.0775$ , 426 parameters and 305 restraints.

The disordered ethylene oxide moiety was refined with distance and ADP restraints to split occupancies of 0.79/0.10/0.11 (**1a**) and 0.79/0.21 (**1b**). The disordered thf molecules were refined with distance and ADP restraints to split occupancies. All hydrogen atom positions were refined using a riding model.

CCDC reference numbers 165029 and 165030. See <http://www.rsc.org/suppdata/cc/b105429p/> for crystallographic data in CIF or other electronic format.

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