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Oxidation of $[Li_4\{(NBu^t)_3S\}_2]$: a new route to sulfur triimides‡

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The oxidation reactions of $[Li_4\{(NBu^t)_3S\}_2]$ with oxygen and halogens (bromine and iodine) were investigated. In all these reactions a radical intermediate $[Li_3\{(NBu^t)_3S\}_2]^\bullet$ was observed, which was investigated by ESR spectroscopy. While the reaction with oxygen leads to the dianionic sulfur(VI) species $[Li_2(NBu^t)_3SO]$, oxidation with halogens yields *N*,*N′*,*N″*-tris(*tert*-butyl)sulfur triimide $S(NBu^t)_3$. The latter reaction provides an easy access to sulfur triimides. Some intermediates from the reaction of $[Li_4\{(NBu^t)_3S\}_2]$ with halogens could be isolated and characterised by X-ray structure analyses. The intermediates can be rationalised as adducts of a lithium halide and a monomeric $[Li_2(NBu^t)_2S]$ unit to give $[(thf)_3Li_3(\mu_3\text{-}X)\{(NBu^t)_3S\}]$ (X = Br or I). In the presence of oxygen the oxidation reaction of $[Li_4\{(NBu^t)_3S\}_2]$ with iodine affords an adduct of lithium iodide and the sulfate analogue $[(thf)_3Li_3(\mu_3\text{-}I)\{(NBu^t)_3SO\}]$ is obtained. As revealed by X-ray structure analysis, this adduct is very similar to $[(thf)_3Li_3(\mu_3\text{-}I)\{(NBu^t)_3S\}]$ in the solid state.

Sulfur diimides were a major focus in the chemistry of sulfur–nitrogen compounds during the past twenty years.[1] Initially we were interested in $S(NR)_2$[2] to design $RS(NR)_2^-$ as monoanionic ligands by nucleophilic addition of alkali-metal alkyls or aryls to the S=N double bond of sulfur diimides.[3] In order to expand this initial work, a metal amide instead of a metal alkyl was used in the addition reaction, yielding a tripodal, dianionic $S(NR)_3^{2-}$ ligand.[4] There are only a couple of examples of these dianions described in the literature.[5] Although fascinating from the start, the use of such dianions as ligands in co-ordination chemistry was hampered by their confusing redox properties. Even traces of an oxidant like oxygen led to a deep blue colour of the compound, indicating the presence of radical species. Since the landmark synthesis of the first sulfur triimide $S(NR)_3$ by Glemser and Wegener in 1970[6] another versatile building block of sulfur–nitrogen chemistry, similar to the sulfur diimides is available. Unfortunately, sulfur triimides, in contrast to sulfur diimides, have not received general attention, all the reactions starting from sulfur triimides were reported by Glemser and Mews (for recent review see ref. 7). One of the reasons might be the limited synthetic access to the sulfur triimides. Until recently only two reactions were known in which the sulfur triimide backbone was formed. These syntheses starting from NSF_3[6,8] or OSF_4[9] are quite hazardous and give poor yields. Transimidation reactions provide limited access to asymmetrically substituted sulfur triimides.[9,10]

Sulfur-containing compounds show an ample redox chemistry. Many sulfur oxy acids are known with sulfur in oxidation states from III (dithionic acid $H_2S_2O_4$) to VI (sulfuric acid H_2SO_4).[11] They, as well as their salts, are related to each other by oxidation–reduction equilibria. Similar relationships between the corresponding sulfur–nitrogen compounds are expected, but while the redox properties of the sulfur–oxygen compounds are intrinsic, those of the sulfur–nitrogen compounds are dependent on the electronic properties of the nitrogen-bonded substituents. Therefore, the redox properties of the sulfur–nitrogen compounds are adjustable by variation of the electronic properties of the substituents. However, a detailed examination was hampered by the lack of convenient synthetic access to those species.

Results and Discussion

Iminosulfur diamides $S(NR)_3^{2-}$ are extremely sensitive to oxidation. Even traces of oxygen, *e.g.* if handled in an argon 5.0 atmosphere without additional oxygen absorption, led to a dark blue colour of the solution and the solid state, indicating the presence of radicals. These radicals[12] are as stable as the $S(NR)_2^{\bullet-}$ radical anion, reported by Hunter *et al.*[12a] and can be stored for several weeks. The nature of the radicals from the reaction of $[Li_4\{(NBu^t)_3S\}_2]$ **1** with oxygen was investigated earlier.[4] An ESR spectrum of the radical in hexane solution displayed a signal even at room temperature. The hyperfine splitting of the signal, to give a septet ($a = 8$ G, intensity ratio 1 : 3 : 6 : 7 : 6 : 3 : 1) confirms that the single electron interacts with three equivalent ^{14}N nuclei ($I = 1$). An additional hyperfine splitting (septet with $a = 0.8$ G, intensity ratio 1 : 2 : 3 : 4 : 3 : 2 : 1) was tentatively assigned to an interaction with two equivalent ^7Li nuclei ($I = \frac{3}{2}$), but the resolution was not high enough to be decisive.

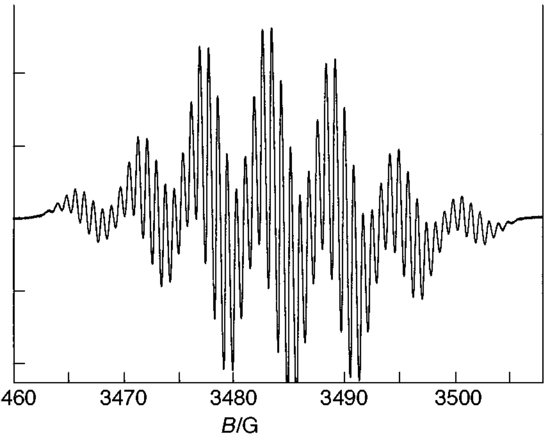

Fig. 1 The ESR spectrum of oxidised complex **1** in hexane solution

Reinvestigation, however, gave a better resolved ESR spectrum (Fig. 1). From this spectrum the second hyperfine splitting could be assigned to an interaction of the single electron with three equivalent ^7Li nuclei ($I = \frac{3}{2}$, decet with $a = 0.8$ G). Lineshape analysis and simulation of the spectrum confirms this assignment (Fig. 2). The structure therefore can be deduced from the ESR spectrum. In the dimer of the radical monoanion $S(NBu^t)_3^{\bullet-}$ and the dianionic $S(NBu^t)_3^{2-}$ three lithium cations are located between the cap-shaped ligands (Scheme 1).

Similar radicals can be generated with the heavier alkali metals sodium and potassium. These radicals are stable enough to be investigated by X-ray structure analysis,[13] revealing

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‡ *Non-SI unit employed*: G = 10^{-4} T.

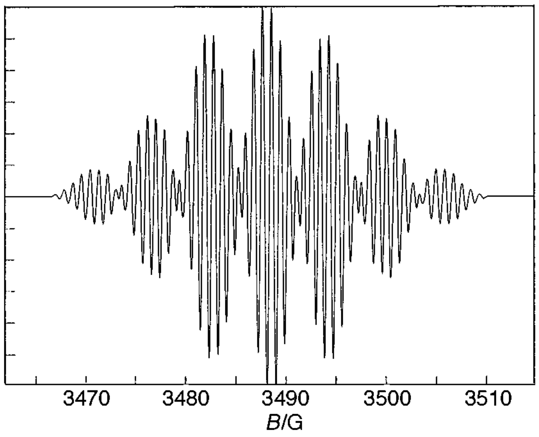
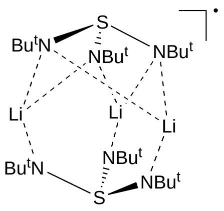


Fig. 2 Simulated ESR spectrum of the $[Li_3\{(NBu^t)_3S\}_2]^{\bullet}$ radical



Scheme 1 Proposed structure of $[Li_3\{(NBu^t)_3S\}_2]^{\bullet}$ **2** in solution

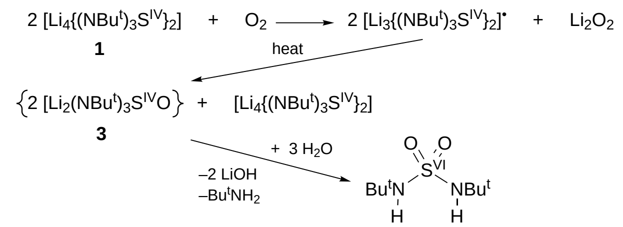
structures similar to that proposed for the radical lithium complex **2** shown in Scheme 1. Since the radical is not the final product of these oxidation reactions, quantitative oxidation reactions of complex **1** were carried out.

Reaction of $[Li_4\{(NBu^t)_3S\}_2]$ with oxygen

When dry oxygen is bubbled through a solution of complex **1** in hexane under otherwise inert gas conditions, the mixture instantaneously turns dark blue. Fast interruption of the oxygen gas supply and heating of the dark blue solution causes a colour change to green, then reddish brown and finally colourless again. The same sequence of colours can be initiated by continuous oxygen gas supply to the solution of **1**, although it stops at the reddish brown level. Unfortunately, no defined product could be isolated and purified either by distillation, or by crystallisation. Only after hydrolysis, could $O_2S(Bu^tNH)_2$ be isolated and characterised. Work-up of this reaction mixture is difficult because it is almost impossible to react solutions of **1** with stochiometric amounts of oxygen. These drawbacks have been overcome by employing other oxidants like the halogens bromine and iodine. A plausible tentative mechanism for the oxidation of **1** with oxygen is nevertheless formulated in Scheme 2. Although complex **3** could not be isolated in this reaction, there are hints for the existence of such a compound from other reactions as discussed later.

Reactions of $[Li_4\{(NBu^t)_3S\}_2]$ with halogens

Two products can be isolated when bromine (or iodine) is used in the oxidation of complex **1**. Dependent on the stochiometry, a lithium halide adduct of monomeric $[Li_2(NBu^t)_3S]$ and $S(NBu^t)_3$ **4** can be isolated in variable yields. Right after the addition of halogen to a solution of **1** in thf–hexane, the mixture instantaneously turns dark blue as in the reaction with oxygen, and a precipitate is formed. In contrast to the reaction with oxygen the radical formed in this reaction is not stable. When addition of the halogen is interrupted, the colour slowly vanishes, leaving a white suspension. Further addition of halogen causes the solution to turn blue and, subsequently, to become colourless again not until 2 equivalents are added at the end of the oxidation. It should be noted that the final product of this oxidation reaction is the *N*,*N*′,*N*″-tris(*tert*-butyl)sulfur triimide **4**. Hence, the reaction of **1** with 2 equivalents of halide provides easy access to sulfur triimides [equation (1), X = Br or I].



Scheme 2 Tentative mechanism for the oxidation of complex **1** with $O_2(g)$

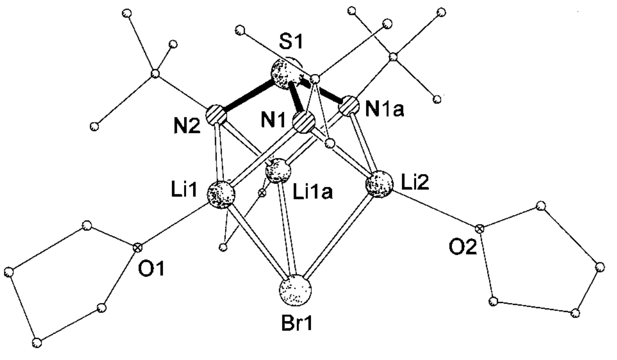


Fig. 3 Solid-state structure of $[(thf)_3Li_3(\mu_3\text{-}Br)\{(NBu^t)_3S\}]$ **5**

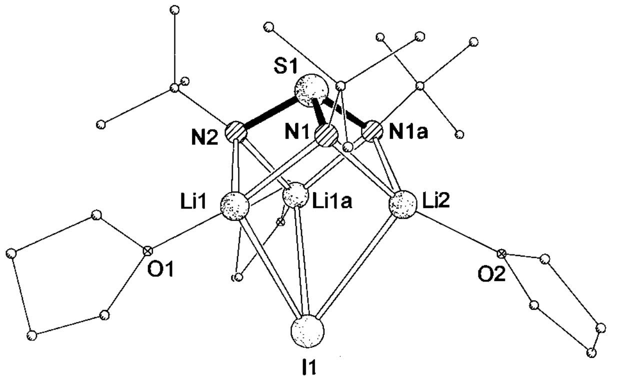


Fig. 4 Solid-state structure of $[(thf)_3Li_3(\mu_3\text{-}I)\{(NBu^t)_3S\}]$ **6**

$$[Li_4\{(NBu^t)_3S\}_2] + 2\,X_2 \longrightarrow S(NBu^t)_3 + 4\,LiX \qquad (1)$$

Structures of $[(thf)_3Li_3(\mu_3\text{-}X)\{(NBu^t)_3S\}]$ (X = Br or I)

In oxidation reactions [equation (1)] with both bromine and iodine, the intermediate lithium halide adducts $[(thf)_3Li_3(\mu_3\text{-}X)\{(NBu^t)_3S\}]$ (X = Br **5** or I **6**) can be isolated. Maximum yield is reached by slow addition of the halogen to the reaction mixture in a 4:3 (**1**:X_2) molar ratio. Crystallisation from thf–hexane solution yields X-ray quality crystals within 12 h storage at −20 °C. Complexes **5** and **6** crystallise in the orthorhombic space group *Pnma*. The isotypic monomeric structures are made up of one cap-shaped $S(NBu^t)_3^{2-}$ ligand, co-ordinating three lithium cations, and a halide, which is μ_3 bridging the metals. The co-ordination sphere of each lithium cation is completed by co-ordination of one thf molecule (Figs. 3 and 4 and Table 1). In both structures, ideal crystallographic C_3 symmetry is precluded, owing to the formation of two short [Br–Li 266.0(4), I–Li 291.2(8) pm] and one longer [Br–Li 269.3(6), I–Li 296.0(12) pm] Li–X bonds. Nevertheless, the negative charge is completely delocalised in the $S(NBu^t)_3^{2-}$ ligands, as indicated by equally long S–N bonds [**5** 167.2(2), **6** 165.6(5) pm, average]. Even the Li–N distances [**5** 206.1(4), **6** 204.2(9) pm, average] are not influenced by the different Li–X distances.

Compared to the Li–X distances in the solid-state structures

Table 1 Selected bond lengths (pm) and angles (°) for complexes **5**, **6** and **7**

	5	**6**	**7**
X	Br	I	I
S1–N1	167.2(2)	165.4(4)	157.7(6)
S1–N2	166.6(2)	165.9(6)	157.4(7)
S1–N3			158.2(7)
S1–O1s			145.5(5)
Li1–N1	205.5(4)	204.1(9)	215(2)
Li1–N2	204.9(4)	203.6(9)	
Li2–N1	207.1(4)	204.3(10)	
Li1–N3			201(2)
Li2–N2			199.7(13)
Li2–N3			214.5(14)
Li3–N1			196(2)
Li3–N2			215(2)
Li1–X1	266.0(4)	291.2(8)	285(2)
Li2–X1	269.3(6)	296.0(12)	285(1)
Li3–X1			285(1)
N1–S1–N2	100.37(8)	100.4(2)	102.9(4)
N1a–S1–N2	100.37(8)	100.4(2)	
N1–S1–N1a	100.37(12)	100.5(3)	
N2–S1–N3			102.3(4)
N3–S1–N1			103.9(4)

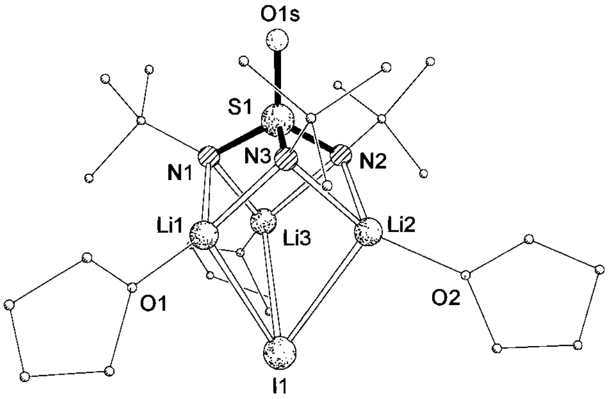


Fig. 5 Solid-state structure of $[(\mathrm{thf})_3\mathrm{Li}_3(\mu_3\text{-I})\{(\mathrm{NBu^t})_3\mathrm{SO}\}]$ **7**

of LiBr [274.4(7) pm] and LiI [300.0(7) pm],[14] the Li–X distances in **5** [266.0(4) and 269.3(6) pm] and **6** [291.2(8) and 296.0(12) pm] are shortened due to the decreased co-ordination number of the halogen atom (six in the solid-state structures of LiX, X = Br or I, and three in the complexes **5** and **6**). One hemisphere of the halide remains unco-ordinated in the complexes described and neither intra- nor inter-molecular long-range interactions have been detected.

Reaction of $[\mathrm{Li}\{\mathrm{S}(\mathrm{NBu^t})_3\}_2]$ with halogens in the presence of oxygen

When the oxidation reaction of complex **1** with iodine is carried out in the presence of oxygen, the lithium iodide adduct $[(\mathrm{thf})_3\mathrm{Li}_3(\mu_3\text{-I})\{(\mathrm{NBu^t})_3\mathrm{SO}\}]$ **7** (Fig. 5) is obtained. The reaction with oxygen as well as with iodine proceed simultaneously yielding a lithium iodide adduct of the sulfate analogue **3** and the sulfur triimide **4**. Complex **7** emulates the same structural features as **5** and **6**, although the complex contains a sulfur(VI) centre. The S1–O1s bond length of 145.5(5) pm is similar to the distance in the sulfate anion of 149.0 pm.[15] The average S–N distance of 157.8 pm is 8.5 pm shorter than the related distance in **5** and **6** (average 166.3 pm). This seems to be a surprisingly high difference, especially when taking into account that only a bond shortening of 1–2 pm due to the higher oxidation state of the sulfur atom in **7** is expected.[16]

Comparison of oxidation with oxygen and halogens

Although the oxidation of complex **1** with oxygen and halogens yields a radical after the first step, both reactions differ considerably afterwards. While in the first case the radical is quite stable, in the latter it is not. Presumably the structure of the radical is the same in both reactions, *i.e.* a dimer of the radical monoanion $\mathrm{S}(\mathrm{NBu^t})_3{}^{\bullet -}$ and the dianionic $\mathrm{S}(\mathrm{NBu^t})_3{}^{2-}$ with three lithium cations between the cap-shaped ligands, the crucial difference must be caused by the formation of another species, also present in the reaction mixture. If the dimeric structure of the radical is broken down by formation of the halide adduct **5** (**6**), a destabilised monomeric radical $\{[\mathrm{Li}(\mathrm{NBu^t})_3\mathrm{S}]^{\bullet}\}$ is left. This radical monomer, in contrast to the dimer, easily undergoes redox disproportion, to yield the sulfur triimide **4** and monomeric $[\mathrm{Li}_2(\mathrm{NBu^t})_3\mathrm{S}]$. In the reaction of halides with **1** four steps [equations (2)–(5), X = Br or I] can be distinguished. The

$$2\,[\mathrm{Li}_4\{(\mathrm{NBu^t})_3\mathrm{S}\}_2] + \mathrm{X}_2 \longrightarrow 2\,[\mathrm{Li}_3\{(\mathrm{NBu^t})_3\mathrm{S}\}_2]^{\bullet} + 2\,\mathrm{LiX} \quad (2)$$

$$2\,[\mathrm{Li}_3\{(\mathrm{NBu^t})_3\mathrm{S}\}_2]^{\bullet} + 2\,\mathrm{LiX} \longrightarrow 2\,[\mathrm{Li}_3\mathrm{X}(\mathrm{NBu^t})_3\mathrm{S}] + 2\,[\mathrm{Li}(\mathrm{NBu^t})_3\mathrm{S}]^{\bullet} \quad (3)$$

$$2\,[\mathrm{Li}(\mathrm{NBu^t})_3\mathrm{S}]^{\bullet} \longrightarrow \tfrac{1}{2}\,[\mathrm{Li}_4\{(\mathrm{NBu^t})_3\mathrm{S}\}_2] + \mathrm{S}(\mathrm{NBu^t})_3 \quad (4)$$

$$2\,[\mathrm{Li}_3\mathrm{X}(\mathrm{NBu^t})_3\mathrm{S}] + \mathrm{X}_2 \longrightarrow 2\,[\mathrm{Li}(\mathrm{NBu^t})_3\mathrm{S}]^{\bullet} + 3\,\mathrm{LiX} \quad (5)$$

first step of the reaction is a fast one-electron oxidation of **1**, to yield the dimeric radical $[\mathrm{Li}_3\{(\mathrm{NBu^t})_3\mathrm{S}\}_2]^{\bullet}$ and LiX [X = Br or I; equation (2)]. In the second step, the dimeric structure of the radical is broken down by formation of the halide adduct (**5** and **6**) and the radical monomer $\{[\mathrm{Li}(\mathrm{NBu^t})_3\mathrm{S}]^{\bullet}$; [equation (3)]}, followed by a redox disproportionation to give **4** and $\tfrac{1}{2}[\mathrm{Li}_4\{(\mathrm{NBu^t})_3\mathrm{S}\}_2]$ [equation (4)]. On further addition of halogen the halide adduct itself can undergo a similar one-electron oxidation to **1** resulting in the same radical monoanion [equation (5)]. However, it is stable enough to be isolated and characterised.

The reaction of **1** with oxygen is very different. Instead of breaking down the dimeric structure of the radical by formation of an adduct, $\mathrm{Li}_2\mathrm{O}_2$ oxidatively adds to the S=N double bond of the radical, upon heating. The intermediate product in this oxidation is proposed in Scheme 2.

Conclusion

The $\mathrm{S(NR)}_3{}^{2-}$ dianions have several very intriguing properties, which provide many further opportunities for both synthetic and co-ordination chemistry. The most important properties are: (i) *variable electronic structure.* Depending on the electronic requirements, different resonance forms of the ligand can be utilised, by which the charges of the co-ordinated cations are stabilised. The electronic flexibility also facilitates stabilisation of unusual electronic states such as radicals. (ii) *Easy oxidisability.* Metal activation in the $\mathrm{S(NR)}_3{}^{2-}$ complexes enables facile oxidation. In all oxidation reactions of $\mathrm{S}(\mathrm{NBu^t})_3{}^{2-}$, a stable radical intermediate is formed as shown previously, but the final products are dependent on the oxidant. In the reaction with molecular oxygen $(\mathrm{Bu^tN})_3\mathrm{SO}^{2-}$ is probably formed, while the neutral $\mathrm{S^{VI}}$ species, sulfur triimide, is formed when halogens are employed. The latter reaction is a straightforward synthesis for sulfur triimides $\mathrm{S(NR)}_3$ providing general access to this class of compounds. (iii) *Cap-shaped geometry.* The co-ordination chemistry of $\mathrm{S}(\mathrm{NBu^t})_3{}^{2-}$ is unique among the chelating nitrogen ligands due to the two negative charges and its cap-shaped geometry. The combination of cap-shaped geometry and steric demand of the nitrogen-bonded substituents should enable homoleptic metal(II) complexes to form. (iv) *Lewis-base character of the sulfur atom.* Owing to its oxidation state the central sulfur atom has a stereochemically active lone pair. This

Table 2 Crystal data and structure refinement for complexes **5**, **6** and **7**

	5	**6**	**7**
Empirical formula	$C_{24}H_{51}BrLi_3N_3O_3S$	$C_{24}H_{51}ILi_3N_3O_3S$	$C_{24}H_{51}ILi_3N_3O_4S$
M	562.47	609.46	625.46
T/K	193(2)	193(2)	153(2)
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	*Pnma*	*Pnma*	$P2_1/n$
a/pm	1463.43(2)	1423.1(5)	993.1(3)
b/pm	1610.63(1)	1638.8(2)	2265.0(7)
c/pm	1392.04(2)	1394.9(2)	1484.1(3)
β/°	90	90	99.18(2)
U/nm^3, Z	3.28110(7), 4	3.2532(13), 4	3.295(2), 4
D_c/Mg m^{-3}	1.139	1.244	1.261
μ/mm^{-1}	1.341	1.074	1.064
F(000)	1200	1272	1304
Crystal size/mm	0.5 × 0.4 × 0.4	0.5 × 0.5 × 0.3	0.8 × 0.4 × 0.4
θ Range/°	2.78–28.40	3.12–22.52	3.04–22.55
Limiting indices	$0 \leqslant h \leqslant 19$, $0 \leqslant k \leqslant 21$, $0 \leqslant l \leqslant 18$	$-15 \leqslant h \leqslant 15$, $0 \leqslant k \leqslant 17$, $-2 \leqslant l \leqslant 15$	$-10 \leqslant h \leqslant 10$, $-24 \leqslant k \leqslant 24$, $-16 \leqslant l \leqslant 16$
Reflections collected	45 785	2546	8770
Independent reflections	4239	2216	4319
R(int)	0.0339	0.1414	0.0841
Data, restraints, parameters	4239, 258, 257	2216, 249, 233	4318, 786, 469
Absorption correction	Semiempirical	Semiempirical	Semiempirical
Transmission (max., min.)	0.715, 0.651	0.773, 0.765	0.684, 0.410
Goodness-of-fit on F^2	1.335	1.047	1.050
$R1$ [$I > 2\sigma(I)$]	0.0441	0.0497	0.0680
$wR2$ (all data)	0.0964	0.1397	0.1915
g_1, g_2	0.023, 2.14	0.099, 0.80	0.097, 5.71
Largest difference peak, hole/e nm^{-3}	328, −280	978, −934	1305, −1535

lone pair not only causes the pyramidal geometry, which results in the cap shape of the ligand, but also gives rise to the Lewis-base character of the sulfur atom. Hence, it should be possible to facilitate S- as well as N-co-ordination. This dianion is therefore a prime candidate to host hard as well as soft Lewis acids each in a suitable fashion.

Experimental

All manipulations were performed under an inert gas atmosphere of dry N_2 with Schlenk techniques or in an argon glovebox. All solvents were dried over Na–K alloy and distilled prior to use. The NMR spectra were obtained on Bruker AM 250, MS 400 or DMX 300 instruments at 25 °C using $SiMe_4$ as external standard. Melting points and decomposition temperatures were measured by differential thermoanalysis using a DuPont Thermal Analyzer TA 9000. Owing to the easy oxidisability no mass spectra were recorded and no elemental analysis is available.

Syntheses

$S(NBu^t)_3$ 4. Compound **1** was prepared according to a literature procedure.[4] A solution of bromine (50 mmol, 8.0 g) in pentane 50 ml was added dropwise to a solution of complex **1** (25 mmol, 14.8 g) in pentane (50 ml) at −78 °C and additionally stirred for 1 h. The solvent was removed under vacuum and the crude product condensed in a cold trap. Crystallisation of the resulting yellow oil from *tert*-butylamine yielded a colourless solid: $M = 245.41$ g mol^{-1}; yield 6.81 g (55%), m.p. 57.5 °C. NMR: ^1H (400 MHz, C_6D_6) δ 1.31 (s, 27 H, Bu^t); ^{13}C (100 MHz, C_6D_6) δ 30.33 [s, $C(CH_3)_3$], 56.99 [s, $C(CH_3)_3$].

$[(thf)_3Li_3(\mu_3\text{-}Br)\{(NBu^t)_3S\}]$ 5. A solution of bromine (3 mmol, 0.48 g) in thf (10 ml) was added dropwise to a solution of complex **1** (4 mmol, 2.36 g) in hexane (10 ml) at 0 °C and stirred for 1 h at room temperature. Crystallisation from the resulting solution at −20 °C yielded colourless crystals: $M = 562.44$ g mol^{-1}; yield 1.10 g (63%); m.p. 115 °C. NMR: ^1H (300 MHz, C_6D_6) δ 1.27 (s, 9 H, Bu^t), 1.66 (m, 4 H, thf), 3.60 (m, 4 H, thf); ^{13}C (75 MHz, C_6D_6) δ 25.95 (OCH_2CH_2, thf), 34.60 [$C(CH_3)_3$], 53.81 [$C(CH_3)_3$], 68.30 (OCH_2, thf).

$[(thf)_3Li_3(\mu_3\text{-}I)\{(NBu^t)_3S\}]$ 6. A solution of iodine (3 mmol, 0.76 g) in thf (10 ml) was added dropwise to a solution of complex **1** (4 mmol, 2.36 g) in hexane (10 ml) at 0 °C and stirred for 1 h. The reaction mixture was stored at −20 °C and after 12 h colourless crystals were obtained: $M = 609.44$ g mol^{-1}; yield 1.33 g (73%); m.p. 117 °C. NMR: ^1H (200 MHz, C_6D_6) δ 1.29 (s, 9 H, Bu^t), 1.68 (m, 4 H, thf), 3.62 (m, 4 H, thf); ^{13}C (100 MHz, C_6D_6) δ 26.35 (OCH_2CH_2, thf), 34.58 [$C(CH_3)_3$], 53.95 [$C(CH_3)_3$], 68.22 (OCH_2, thf).

Crystal data for complexes 5–7

Crystal data for the three structures are presented in Table 2. Data for all structures were collected at low temperature using oil-coated shock-cooled crystals[17] on a Stoe-Siemens AED (**6** and **7**) or Stoe-Huber-Siemens-Eigenbau diffractometer fitted with a Siemens CCD detector (**5**) using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Semiempirical absorption correction was applied.[18,19] The structures were solved by Patterson or direct methods using SHELXS 96.[20] All structures were refined by full-matrix least-squares procedures on F^2, using SHELXL 96.[21] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions. The denoted *R* values are defined as follows: $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; $w = 1/\{\sigma^2(F_o^2) + (g_1P)^2 + g_2P\}$; $P = (F_o^2 + 2F_c^2)/3$.

Complex **5** crystallises in the orthorhombic space group *Pnma*. Space group symmetry (mirror plane) was suppressed for the refinement of the *tert*-butyl group (C20–C23). The co-ordinating thf molecule (O2, C35–C38) was refined to a split occupancy of 0.57:0.43, suppressing the symmetry. Bond length and similarity restraints were used in the refinement of both groups.

Complex **6** is isostructural with **5**. The disordered *tert*-butyl moiety (C20–C23) was refined to a split occupancy of

0.79 : 0.21. The space group symmetry (mirror plane) was suppressed. The co-ordinating thf molecule (O2, C35–C38) was treated likewise. Refinement of a split occupancy for the thf molecule was attempted but did not give a better model. Bond length and similarity restraints were applied.

The disordered thf molecules in **7** were refined to split occupancies of 0.5 : 0.5 (O1, C13–C16 and O2, C17–C20) and 0.45 : 0.55 (O3, C21–C24). Bond length and similarity restraints were used in the refinement.

Selected bond lengths and angles are presented in Table 1.

CCDC reference number 186/809.

See http://www.rsc.org/suppdata/dt/1998/193/ for crystallographic files in .cif format.

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