Heteroaromatic-Substituted Mono- and Bis(triimidosulfonates)

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Dedicated to the memory of Ron Snaith

Keywords: Heterocycles / Lithium / N ligands / S ligands / Sulfur

In this paper we present the syntheses and structures of the metal complexes [(THF)$_2$Li{(N*t*Bu)$_3$S(C$_4$H$_3$NMe)}] (**1**), [(tmeda)Li{(N*t*Bu)$_3$S(C$_4$H$_3$S)}] (**2**), [(tmeda)Li{(N*t*Bu)$_3$S(C$_4$H$_3$Se)}] (**3**), [(THF)$_4$Li$_2${(*t*BuN)$_3$S(SC$_4$H$_2$)S(N*t*Bu)$_3$}] (**4a**) and [(tmeda)$_2$Li$_2${(*t*BuN)$_3$S(SC$_4$H$_2$)S(N*t*Bu)$_3$}] (**4b**). The lithium salts form non-aggregated soluble molecules rather than infinite insoluble solid-state lattices like their oxo analogues. The metals are *N*,*N*-chelated rather than tripodally coordinated. Although the S–N bond to the one pendant spectator *t*BuN group is considerably shorter than in the metal-coordinated *t*BuN groups, conjugation of the S–N bonds to the heteroaromatic rings could not be deduced unambiguously from the experimental structures.

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Introduction

Arylsulfonates (ArSO$_2^-$) and arylsulfamides [ArS(NR)$_2^-$] are used in various fields of modern chemistry. Sulfonic acids (RSO$_2$OH) and their metal salts (RSO$_3$M) are versatile catalysts used on a large scale for industrial cyclization and polymerization processes. A catalytic transfer-hydrogenation process is provided by sulfonates.[1] The preparation of inclusion compounds based on lamellar host frameworks constructed from guanidinium and organodisulfonate ions has been reported.[2] With this and the recent progress in isoelectronic replacement of oxygen atoms in simple *p*-block element oxoanions in mind, we aimed to synthesise aryltriimidosulfonates ArS(NR)$_3^-$ with Ar = MeNC$_4$H$_3$, SC$_4$H$_3$ and SeC$_4$H$_3$. To envisage oligo- or even polymeric molecules two S(NR)$_3^-$ moieties were linked by a 2,5-disubstituted thiophenyl ring. Thiophenesulfonamides and their alkali metal or non-toxic acid addition salts are useful as insecticides, acaricides and larvicides.[3] Molecules like 5-substituted thiophene-2-sulfonamides are promising drugs that are currently being used as carbonic anhydrase inhibitors for the treatment of glaucoma.[4] This industrial relevance combined with the recent progress in isoelectronic replacement of oxygen atoms in simple *p*-block element oxoanions[5] encouraged us to generate the unprecedented aryltriimidosulfonates ArS(NR)$_3^-$. Substitution of the oxygen atom in the aryloxoanions ArSiO$_3^{3-}$, ArPO$_3^{2-}$, ArAsO$_3^{2-}$, ArSbO$_3^{2-}$, ArPO$_2^{2-}$, ArSO$_2^-$, ArSeO$_3^-$ or ArTeO$_3^-$ by an NR imido group gives the polyimido anions ArP(NR)$_2^{2-}$, ArS(NR)$_2^-$, ArSi(NR)$_3^{3-}$, ArP(NR)$_3^{2-}$ and ArAs(NR)$_2^{2-}$.[6] However, to the best of our knowledge, related species with Sb, Se, Te and S^{VI} have not yet been reported in the literature. By contrast to the simple oxoanions, these species should be soluble because they form contact ion pairs in cage complexes surrounded by a lipophilic layer of organic residues rather than infinite solid-state lattices by multiple oxygen/cation contacts. Furthermore, their redox potential and coordination behaviour is tuneable by variation of the organic substituents.

To date the *S*-alkyl-[7] [MeS(NR)$_2$]$^-$ and *S*-phenyl diimidosulfinates[8] [PhS(NR)$_2$]$^-$ and *S*-alkyltriimidosulfonates[9] [MeS(NR)$_3$]$^-$ have been studied in detail. The CH-acidic organic substituent at the sulfur atom in the first and the latter species can be deprotonated to give dianionic alkylenediimidosulfites[10] and alkylenetriimidosulfates[11] in which the CR$_2$ group replaces the oxygen or NR group isoelectronically. They can both be rationalized as S^{IV}- and S^{VI}-ylides. Until recently the direct reaction of thiols with chloroamines or, better, bromoamines was the only known synthetic access to *S*-alkyltriimidosulfonates.[12] In this paper we present a new straightforward synthetic route which involves the nucleophilic addition of aryllithiums to the formal S=N double bond of sulfur triimides.[13] Presumably due to the steric crowding in the products, only sterically less-demanding alkyls could be added (e.g. MeLi) to the few structurally known sulfur triimides [S(NR)$_3$, R = *t*Bu, SiMe$_3$).[14] Addition reactions with *n*BuLi and *t*BuLi failed. In principle, the resulting [MeS(NR)$_3$]$^-$ anion possesses C_{3v} symmetry prompting feasible tripodal cap-shaped metal coordination. While the triimidosulfite[15] S(NR)$_3^{2-}$ and the triimidosulfate[16] OS(NR)$_3^{2-}$ dianions show this

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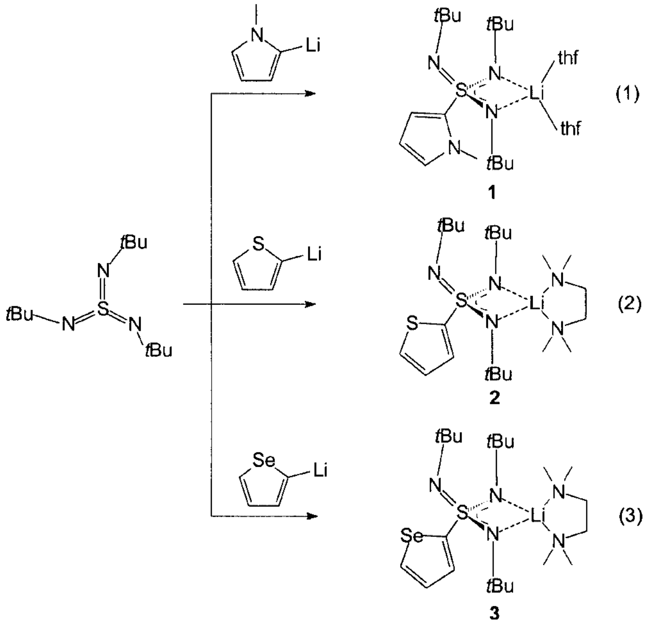
anticipated tripodal behaviour even in mixed-metal complexes,[17] only (*N*,*N*)-SN_2 chelation has been observed for the $[MeS(NR)_3]^-$ monoanion.[18]

In this paper we aimed both to evaluate the reactivity of the sulfur triimide towards organolithium reagents and to introduce an additional coordination site in the S-bound organic substituent. Experimental charge-density investigations of $S(N\textit{t}Bu)_3$ suggested that only flat carbanions are suitable for addition across the polar S−N bond as the reactive surface at $\nabla^2\rho(\mathbf{r}) = 0$ shows holes in the SN_3 plane on the NSN bisectors and maxima above and below the central sulfur atom. Hence, the carbanion needs to approach the electrophilic sulfur along the bisectors and slot in between the *t*BuN groups.[19] Thus we decided to react $S(N\textit{t}Bu)_3$ with lithiated furan, pyrrole, thiophene and selenophene.



Scheme 1. Preparation of $[(THF)_2Li\{(N\textit{t}Bu)_3S(C_4H_3NMe)\}]$ (**1**), $[(tmeda)Li\{(N\textit{t}Bu)_3S(C_4H_3S)\}]$ (**2**), and $[(tmeda)Li\{(N\textit{t}Bu)_3S(C_4H_3Se)\}]$ (**3**)

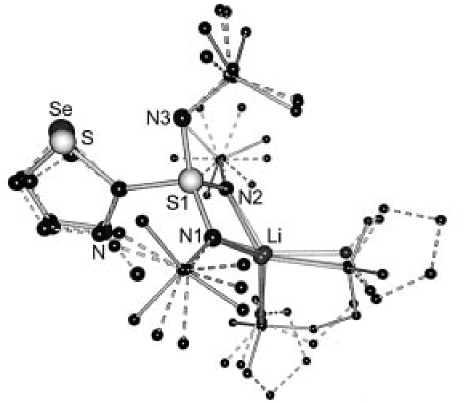


Figure 1. Superposition plot of the solid-state structures of **1**−**3**

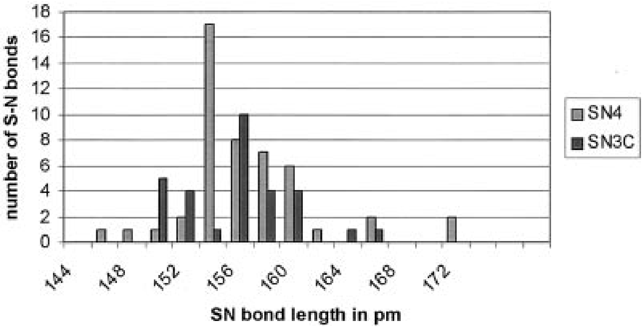
Results and Discussion

[Li{(N*t*Bu)$_3$SAr}] Complexes

The aromatic heterocycles were lithiated first with BuLi and then reacted at low temperatures with a stoichiometric amount of the sulfur triimide. Although addition reactions of organolithiums like *n*BuLi and *t*BuLi to $S(N\textit{t}Bu)_3$ failed in the past, presumably because of steric crowding in the sulfonates, methylpyrrolyl-, thiophenyl-, and selenophenyllithium react smoothly to give the related products $[(THF)_2Li\{(N\textit{t}Bu)_3S(C_4H_3NMe)\}]$ (**1**), $[(tmeda)Li\{(N\textit{t}Bu)_3S(C_4H_3S)\}]$ (**2**), and $[(tmeda)Li\{(N\textit{t}Bu)_3S(C_4H_3Se)\}]$ (**3**). Due to the reactivity and thermal instability of 2-lithiofuran all attempts to add it to sulfur triimide failed. Upon addition of $S(N\textit{t}Bu)_3$ to $Li(C_4H_3O)$ the reaction mixture polymerises instantaneously. The organic substituents (C_4H_3NMe), (C_4H_3S) and (C_4H_3Se) bond in the 2-position to the electropositive sulfur while the lithium cation is coordinated to the nitrogen atoms (Scheme 1). This reactivity is not surprising in view of the S^{2+} charge and the sp^3-hybridization of the nitrogen atoms.[20]

Structures of 1−3

The solid-state structures of the lithium *S*-aryl-tri(*tert*-butyl)triimidosulfonates **1**, **2** and **3** (Figure 1) show that neither tripodal coordination nor additional coordination of the heteroatom in the aromatic five-membered ring to the lithium cations is accomplished. Like in the coordination of $PhS(NSiMe_3)_2^-$ [8] and $PhCCS(N\textit{t}Bu)_3^-$,[18] the ligand coordinates one hemisphere of the metal, leaving the two THF donor molecules coordinated to the other in **1**. In **2** and **3** the tetragonal coordination sphere is completed by one tmeda molecule each. Like the methyl derivatives, these anions coordinate in a bidentate manner with only two nitrogen atoms orientated towards the metal. No further coordination of the third *t*BuN group could be detected. In all three complexes one *tert*-butyl group is turned in the direction of the N_3 face, away from the heteroaromatic group, so one nitrogen atom is blocked from conceivable metal coordination. The methyl group of the heteroaromatic ring in **1** points towards the chelated lithium atom while the sulfur and selenium atoms in the heterocycles of **2** and **3** point towards the pendant *t*BuN group. The negative charge is distributed over both nitrogen atoms of the chelating SN_2 unit, as indicated by the almost ideal planar arrangement of the C1−N1−S1−N2−C5−Li1 moiety (mean deviation from best plane only 4.6 pm for **1**, 8.31 pm for **2** and 8.45 pm for **3**) and the S−N bond lengths, half-way between an S−N single and an S−N double bond [**1**: av. 158.5(6) pm; **2**: av. 157.7(4) pm; **3**: av. 157.91(30) pm]. The nitrogen atoms of the pendant *t*BuN group show significantly shorter S−N distances [**1**: 153.6(3) pm; **2**: 154.3(2) pm; **3**: 154.72(14) pm]. They are similar to the S=N double bonds in $S(N\textit{t}Bu)_2$ (153.2 pm),[21] but notably longer than in $S(N\textit{t}Bu)_3$ (151.5 pm).[14] In general, the S−N bond lengths in **1**, **2** and **3** match the standard range for S^{VI}−N



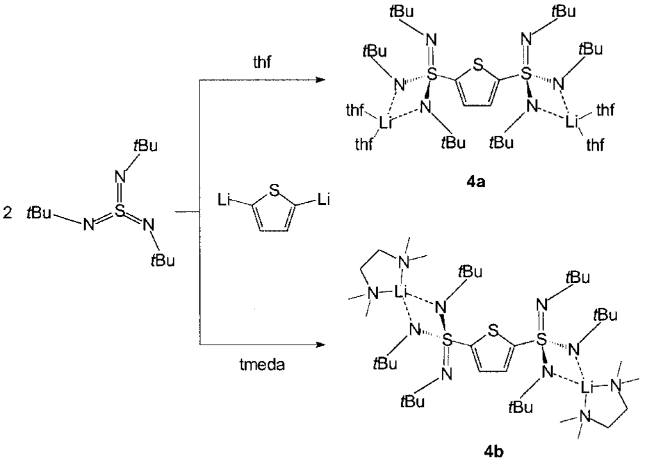
Scheme 2. $S^{VI}-N$ bond lengths from the CCDC (dark: SN_3C compounds; light: SN_4 compounds).

bond lengths found in the CCDC (Scheme 2).[22] The S−N bond lengths of non-coordinating nitrogen atoms are in the range of 150−156 pm, and the S−N bond lengths of coordinating nitrogen atoms are in the range of 156−168 pm. The S−C bond lengths of 179.6(3) pm in **1**, 179.2(3) pm in **2** and 179.29(19) pm in **3** are only marginally longer than a typical S−C(sp^2) single bond of 176 pm.[23] The Li−N bond lengths of about 200 pm match those normally observed in lithium amides.[24] The geometrical features of **1**, **2** and **3** (Table 1) reveal that the mean metric parameters of the $ArS(N\mathit{t}Bu)_3^-$ anion (i.e. S−N and S−C-distances, N−S−N and S−N−C-angles, etc.) are almost independent of the nature of the aromatic system. In addition, the delocalisation in the heteroaromatic ring seems not to be perturbed by the metalated $S(N\mathit{t}Bu)_3$ moiety.

In all known metal complexes the alkyltriimidosulfonate chelates as a bidentate ligand,[18] although tripodal coordination occurs with the triimidosulfite[13,15] and the oxotriimidosulfate $OS(N\mathit{t}Bu)_3^{2-}$.[15] In these dianions, tripodal coordination is facilitated by all the *tert*-butyl groups pointing towards the sulfur atom, leaving the lone pairs of the nitrogen atoms pointing in the opposite direction. A comparison with the tripodal $OS(N\mathit{t}Bu)_3^{2-}$ dianion proves that tripodal coordination is primarily caused by the higher negative charge than by steric or electronic effects:[18] for a single negative charge in the triimidosulfonates it is sufficient to be distributed over two nitrogen atoms rather than over all three. To stabilise a double negative charge in the triimidosulfite and the oxotriimidosulfate three S-bound nitrogen atoms are required.

[Li{(N*t*Bu)$_3$S(C$_4$H$_3$S)S{(N*t*Bu)$_3$}Li] Complexes

Thiophene was lithiated twice with BuLi and subsequently reacted with two equivalents of sulfur triimide. Despite the anticipated steric strain in the disubstituted product the reaction works under mild conditions. The non-optimised yields for both complexes were about 65%. Dependant on the donating solvent used in the reaction, two different complexes $[(THF)_4Li_2\{(\mathit{t}BuN)_3S(SC_4H_2)S(N\mathit{t}Bu)_3\}]$ (**4a**), and $[(tmeda)_2Li_2\{(\mathit{t}BuN)_3S(SC_4H_2)S(N\mathit{t}Bu)_3\}]$, (**4b**) could be obtained (Scheme 3).



Scheme 3. Preparation of $[(THF)_4Li_2\{(\mathit{t}BuN)_3S(SC_4H_2)S(N\mathit{t}Bu)_3\}]$ (**4a**), and $[(tmeda)_2Li_2\{(\mathit{t}BuN)_3S(SC_4H_2)S(N\mathit{t}Bu)_3\}]$ (**4b**)

Table 1. Selected bond lengths [pm] and angles [°] of **1**−**3**

	1 R = *N*-methylpyrrolyl	**2** R = thiophenyl	**3** R = selenophenyl
S1−C13	179.6(3)	179.2(3)	179.29(19)
C13−C14	137.4(5)	140.2(4)	138.5(3)
C14−C15	142.0(6)	143.5(4)	142.4(3)
C15−C16	135.6(6)	134.8(5)	134.2(3)
C16−E	137.0(5) (E = N4)	170.0(4) (E = S2)	186.5(2) (E = Se1)
E−C13	138.5(5) (E = N4)	171.1(3) (E = S2)	186.11(17) (E = Se1)
S1−N1	158.4(3)	157.8(2)	157.94(15)
S1−N2	158.5(3)	157.6(2)	157.88(15)
S1−N3	153.6(3)	154.3(2)	154.72(14)
Li−N1	201.9(7)	198.9(5)	198.5(3)
Li−N2	196.9(6)	201.3(5)	201.6(3)
N1−S1−N2	96.52(15)	97.85(9)	97.63(8)
N2−S1−N3	122.03(6)	122.46(11)	122.14(8)
N1−S1−N3	123.79(17)	121.77(12)	121.71(8)
C13−S1−N1	109.24(15)	109.34(12)	109.54(8)
C13−S1−N2	108.97(16)	108.97(12)	109.61(8)
C13−S1−N3	95.85(16)	96.04(12)	95.99(8)
N1−Li−N2	72.7(2)	72.91(16)	72.88(12)

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Crystal Structures of 4a and 4b

Each central thiophenyl ring is 2,5-disubstituted by a triimidosulfite group coordinated to a single lithium atom. Like in the complexes **1−3** only two nitrogen atoms of each (tBuN)$_3$S moiety chelate the metal while the third tBuN group acts as a pendant spectator. The preferred tetragonal coordination of each lithium cation is completed by two THF molecules (**4a**) or one tmeda molecule (**4b**; Figure 2).

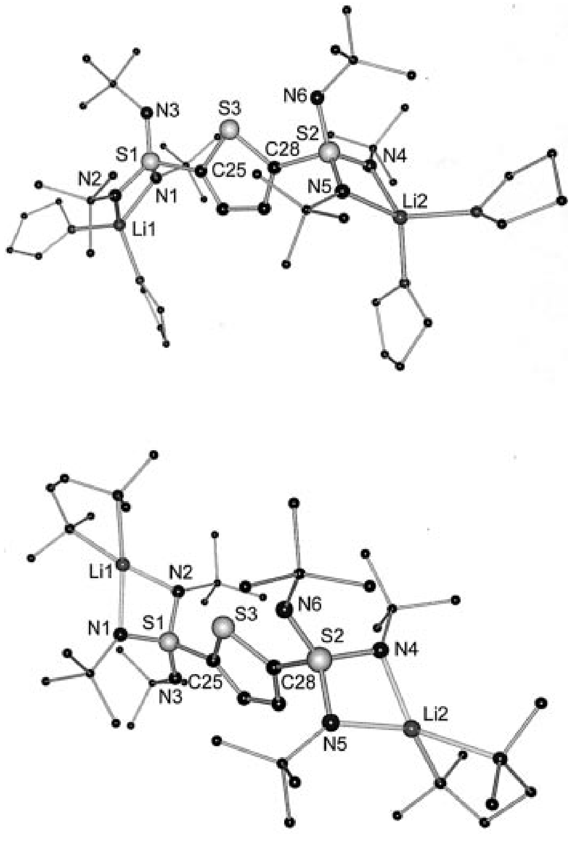

Figure 2. Solid-state structures of [(THF)$_4$Li$_2${(tBuN)$_3$S(SC$_4$H$_2$)S(NtBu)$_3$}] (**4a**; top), and [(tmeda)$_2$Li$_2${(tBuN)$_3$S(SC$_4$H$_2$)S(NtBu)$_3$}] (**4b**; bottom); selected bond lengths [pm] and angles [°] are compiled in Table 2

Although **4a** and **4b** are isostructural they differ in the arrangement of the NtBu groups. In **4a** the uncoordinated NtBu groups are pointing exactly in the same direction toward the thiophene ring sulfur atom S3, while in **4b** they are located opposite to each other like the lithium atoms. The S1−N3 and the S2−N6 bonds of both molecules are in the same plane as the thiophene ring. In addition, the N1−S1−N2 and the N4−S2−N5 bisectors are almost coplanar with the thiophene plane.

The negative charge in the (tBuN)$_3$S sulfonate unit is distributed over both nitrogen atoms of the chelating N−S−N unit [(S−N(av.): **4a** 157.2(5); **4b** 156.7(3) pm], and therefore the S−N bonds are equal to those in the monosubstituted aryltriimidosulfonates **1−3**. The S−N bonds of the pendant NtBu group are much shorter than the other S−N bonds [S−N(av.): **4a** 151.4(3); **4b** 153.8(5) pm]. Most remarkably, the S1−N3 bond in **4b** of 149.4(3) pm is the shortest S−N bond ever observed in SN$_3$C moieties (see Scheme 2), possibly due to hyperconjugation[25] to the SC$_4$ thiophenyl perimeter, as it is the only one in-plane and next to a C=C bond in the C$_4$S perimeter. Donation of the electron density via p(N3) → σ*(C25) in the S(NR)$_3^-$ moiety (anionic or negative hyperconjugation[25d]) would result in shortening of the S1−N3 bond and an elongation of the S1−C25 bond. The latter, however, could not be confirmed experimentally. Clearly NBO and NRT analysis are required to elucidate that problem. In [(THF)Li$_2${O$_2$S(NtBu)$_2$}]$_8$·2LiOH·2LiCl [av. S−N: 155.0(4) pm] and [{(THF)Li}$_2${O$_2$S(NtBu)$_2$]·(THF)LiCl}$_2$ [av. S−N: 155.7(2) pm] the S−N bonds are about 6 pm longer.[26] The S−C$_{\mathrm{ipso}}$ distances in **4a** and **4b** of 180.1(5) and 178.8(4) pm, respectively, are considerably longer than the S−C bond in [(tmeda)$_2$Li$_2${(CH$_2$)S(NtBu)$_3$}] of 172.5(2) pm (see also Table 2).[11]

Table 2. Selected bond lengths [pm] and angles [°] of [(THF)$_4$Li$_2${(tBuN)$_3$S(SC$_4$H$_2$)S(NtBu)$_3$}] (**4a**), and [(tmeda)$_2$Li$_2${(tBuN)$_3$S(SC$_4$H$_2$)S(NtBu)$_3$}] (**4b**)

	4a	**4b**
S1−N1	157.4(5)	156.5(3)
S1−N2	157.0(5)	156.9(3)
S1−N3	153.3(5)	149.4(3)
S3−N4	156.9(5)	156.9(3)
S3−N5	157.1(5)	156.3(3)
S3−N6	154.4(5)	153.4(3)
S1−C25	180.1(5)	178.8(4)
C25−C26	134.3(8)	136.7(5)
C26−C27	139.2(8)	141.4(5)
C27−C28	135.5(8)	135.4(5)
S3−C28	173.4(6)	170.3(4)
S3−C25	172.4(6)	171.9(4)
S2−C28	178.7(6)	178.2(4)
Li1−N1	197.7(11)	198.6(7)
Li1−N2	196.2(11)	196.6(8)
Li2−N4	198.5(11)	198.4(7)
Li2−N5	196.3(12)	198.7(8)
N1−S1−N2	97.0(2)	98.02(17)
N2−S1−N3	122.7(3)	122.64(19)
N1−S1−N3	122.6(3)	122.42(19)
N4−S3−N5	97.9(3)	97.91(17)
N5−S3−N6	121.1(3)	123.16(17)
N4−S3−N6	121.6(3)	121.97(17)

Conclusions from the Structural Comparisons

Comparison of the structures of **1**, **2** and **3** reveals that the geometrical features of the ES(NtBu)$_3^-$ unit (e.g. S−N distances, N−S−N and N−S−C angles) are almost independent of the nature of the heteroaromatic substituent and vice versa. The S or Se atom in the heteroaromatic ring is not involved in lithium coordination. Linkage of two sulfonate units via an S-heteroaromatic ring is possible, but conjugation of the S−N bonds to the SC$_4$ perimeter seems unlikely as the S−C and C−C bonds match the range of the related bond lengths in the parent thiophene. The negative charge in each sulfonate unit is distributed over both

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nitrogen atoms of the chelating N−S−N unit; the third N*t*Bu group remains non-coordinating. Tripodal metal coordination of the SN_3 unit is necessary for a double negative charge in the $S(NR)_3^{2-}$ triimidosulfite and the oxotriimidosulfate $OS(NR)_3^{2-}$, whereas for a single negative charge in $RS(NR)_3^-$ *N*,*N*-chelation seems to be sufficient.

Experimental Section

All manipulations were performed under inert-gas atmosphere of dry N_2 with Schlenk techniques or in an argon glove box. All solvents were dried over Na/K alloy and distilled prior to use. NMR spectroscopic data were obtained on either a Bruker AMX 400 or a Bruker AMX 300 instrument in the FT mode in C_6D_6 solvent. Elemental analyses were performed by the Microanalytisches Labor der Universität Würzburg. $S(NtBu)_3$ was obtained as described previously in ref. 15.

[(THF)$_2$Li{(H$_3$CNC$_4$H$_3$)S(N*t*Bu)$_3$}] (1): A solution of butyllithium in hexane (1.6 M, 2.44 mmol, 1.52 mL) was added dropwise to a solution of *N*-methylpyrrole (2.44 mmol, 0.2 g) in 3.5 mL THF at −78 °C. The reaction mixture was allowed to warm to room temperature and finally refluxed gently for 30 min. *N*,*N*′,*N*′′-Tris(*tert*-butyl)sulfur triimide (2.44 mmol, 0.6 g) was added to the solution and stirred for 12 h. All volatile material was removed under vacuum and the residue was dissolved in 3 mL of hexane and 1 mL of THF. Crystallisation at −36 °C gave colourless crystals. Yield: 0.76 g (65%). ^{1}H NMR (400 MHz, C_6D_6): δ = 1.31 [q, 4 H, $(CH_2CH_2)_2O$], 1.44 [s, 18 H, $C(CH_3)_3$], 1.50 [s, 9 H, $C(CH_3)_3$], 3.47 [t, 4 H, $(CH_2CH_2)_2O$], 3.52 (s, 3 H, NCH_3), 6.02 (t, 1 H, H2), 6.19 (t, 1 H, H4), 6.83 (q, 1 H, H3) ppm. ^{7}Li (155 MHz, C_6D_6): δ = 0.87 ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 25.48 [$(CH_2CH_2O)_2$], 30.57 [$C(CH_3)_3$], 33.11 [$C(CH_3)_3$], 37.05 (N-CH_3), 53.83 [$C(CH_3)_3$], 54.82 [$C(CH_3)_3$], 68.23 [$(CH_2CH_2O)_2$], 105.76 (C3), 114.91 (C4), 126.00 (C2), 128.28 (C1) ppm. $C_{25}H_{49}LiN_4O_2S$ (476.37): calcd. C 62.99, H 10.36, N 11.75, S 6.73; found C 60.69, H 9.6, N 12.77, S 7.12. Mp.: 60 °C.

[(tmeda)Li{(SC$_4$H$_3$)S(N*t*Bu)$_3$}] (2): Thiophene (5 mmol, 0.42 g) was added slowly to a mixture of tmeda (5 mmol, 0.58 g), 2 mL of diethyl ether and butyllithium in hexane (1.6 M, 5 mmol, 3.125 mL) and stirred for 30 min. A solution of *N*,*N*′,*N*′′-tris(*tert*-butyl)sulfur triimide (4.5 mmol, 1.1 g) in 2 mL of hexane was added to the solution and stirred for 12 h. After the small amount of precipitate was filtered off, 5 mL of hexane and 1.5 mL of THF were added. The solution was stored at +6 °C and after 1 day colourless crystals were obtained. Yield: 1.60 g (70%). ^{1}H NMR (400 MHz, C_6D_6): δ = 1.42 [s, 18 H, $C(CH_3)_3$], 1.74 [s, 9 H, $C(CH_3)_3$], 1.82 (s_{br}, 4 H, $Me_2NCH_2CH_2NMe_2$), 1.99 (s, 12 H, $Me_2NCH_2CH_2NMe_2$), 6.80, 6.95, 7.26 (C_4H_3S) ppm. ^{7}Li (155 MHz, C_6D_6): δ = 0.64 (s) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 33.02 [$C(CH_3)_3$], 33.83 [$C(CH_3)_3$], 46.72 ($Me_2NCH_2CH_2NMe_2$), 51.82 [$C(CH_3)_3$], 56.80 ($Me_2NCH_2CH_2NMe_2$) ppm. $C_{22}H_{46}LiN_5S_2$ (451.34): calcd. C 58.50, H 10.26, N 15.50, S 14.20; found C 55.63, H 9.45, N 14.11, S 13.01. Mp.: 141 °C.

[(tmeda)Li{(SeC$_4$H$_3$)S(N*t*Bu)$_3$}] (3): A solution of selenophene (3.8 mmol, 0.5 g) in 4.77 mL of hexane was added dropwise to a solution of tmeda (3.8 mmol, 0.45 g) and butyllithium in hexane (1.6 M, 3.8 mmol, 2.4 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. *N*,*N*′,*N*′′-Tris(*tert*-butyl)sulfur triimide (3.8 mmol, 0.94 g) in 1 mL hexane was added at 0 °C. After 12 h stirring at room temperature, the small amount of precipitate was filtered off. Crystallisation from the resulting solution at +6 °C yielded colourless crystals after 1 day. M = g/mol. (yield 1.74 g, 91%). ^{1}H NMR (400 MHz, C_6D_6): δ = 1.45 [s, 18 H, $C(CH_3)_3$], 1.72 (s_{br}, 4 H, $Me_2NCH_2CH_2NMe_2$), 1.80 [s, 9 H, $C(CH_3)_3$], 1.97 (s, 12 H, $Me_2NCH_2CH_2NMe_2$), 7.15 (s_{br}, 1 H, H2), 7.34 (s_{br}, 1 H, H4), 7.66 (dd, 1 H, H3) ppm. ^{7}Li NMR (155.5 MHz, ext. sat. LiCl solution): δ = 0.62 (s) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 33.69 [$C(CH_3)_3$], 33.98 [$C(CH_3)_3$], 46.71 ($Me_2NCH_2CH_2NMe_2$), 51.82 [$C(CH_3)_3$], 53.17 [$C(CH_3)_3$], 56.75 ($Me_2NCH_2CH_2NMe_2$), 127.87, 128.11, 128.35, 129.06 (C_4H_3Se) ppm. $C_{22}H_{46}LiN_5SSe$ (499.30): calcd. C 53.00, H 9.30, N 14.05, S 6.43; found C 49.21, H 8.57, N 13.62, S 6.01. Mp.: 134 °C (dec).

[(THF)$_4$Li$_2${(*t*BuN)$_3$S(SC$_4$H$_2$)S(N*t*Bu)$_3$}] (4a): Thiophene (2.08 mmol, 0.18 g) was added slowly to a mixture of tmeda (4.15 mmol, 0.48 g), 2 mL of diethyl ether and butyllithium in hexane (1.6 M, 4.15 mmol, 2.60 mL) and stirred for 30 min. A solution of *N*,*N*′,*N*′′-tris(*tert*-butyl)sulfur triimide (4.15 mmol, 1.0 g) in 1 mL of hexane was added to the solution and stirred for 3 days. The suspension was dissolved by addition of 4 mL of THF and 1 day storage at +6 °C yielded yellow crystals. M = 875.28 g/mol. (yield 1.43 g, 84%). All spectroscopic and analytical data are virtually identical to those of the tmeda derivative **4b**.

[(tmeda)$_2$Li$_2${(*t*BuN)$_3$S(SC$_4$H$_2$)S(N*t*Bu)$_3$}] (4b): Thiophene (2.08 mmol, 0.18 g) was added slowly to a mixture of tmeda (4.15 mmol, 0.48 g), 2 mL of diethyl ether and butyllithium in hexane (1.6 M, 4.15 mmol, 2.60 mL) and stirred for 30 min. A solution of *N*,*N*′,*N*′′-tris(*tert*-butyl)sulfur triimide (4.15 mmol, 1.0 g) in 1 mL of hexane was added to the solution and stirred for 3 days. The white precipitate was filtered off. The clear reaction mixture was stored at +6 °C and after 1 day light-yellow crystals could be obtained. M = g/mol. (yield 1.46 g, 86%). ^{1}H NMR (400.13 MHz, C_6D_6): δ = 1.55 [s, 18 H, $C(CH_3)_3$], 1.77 (s, 4 H, $Me_2NCH_2CH_2NMe_2$), 1.83 [s, 9 H, $C(CH_3)_3$], 2.07 (s, 12 H, $Me_2NCH_2CH_2NMe_2$), 6.95, 7.34 (2s, 2 H, C_4H_2S) ppm. ^{7}Li NMR (155.5 MHz, ext. sat. LiCl solution): δ = 0.70 (s) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 33.10 and 33.92 [$C(CH_3)_3$], 46.58 ($Me_2NCH_2CH_2NMe_2$), 51.91 [$C(CH_3)_3$], 53.58 [$C(CH_3)_3$], 55.03 ($Me_2NCH_2CH_2NMe_2$), 130.27, 130.69, 133.16, 148.89 (C_4H_2S). $C_{40}H_{88}Li_2N_{10}S_3$ (819.26): calcd. C 58.64, H 10.83, N 17.10, S 11.74; found C 55.33, H 10.42, N 15.54, S 10.98. Mp.: 152 °C (dec).

Crystal Structure Determinations: Crystal data for the structures **1**−**4b** are presented in Table 3. Data for structures were collected on a Bruker Apex CCD diffractometer at low temperature using oil-coated shock-cooled crystals[27] and Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS 97.[28] The structures were refined by full-matrix least-squares procedures on F^2, using SHELXL 97.[29] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions. Data were corrected for absorption using SADABS2.[30] In complex **2** one disordered tmeda molecule (C20−C22) was refined to a split site occupancy factor of 0.51/0.49. In complex **4a** the disordered THF molecule (O4−C44) was refined to a split site occupancy factor of 0.51/0.32/0.17, and the *tert*-butyl groups to 0.51/0.49 (C2−C4), 0.67/0.33 (C14−C16) and 0.78/0.22 (C22−C24), respectively. In complex **4b** the disordered tmeda molecule (C32−C34) was refined to a split site occupancy factor of 0.67/0.33, and the *tert*-butyl groups to 0.85/0.15 (C5−C8) and 0.69/0.31 (C13−C16), respectively. In all these refinements bond length and similarity restraints were applied.

Table 3. Crystal data and structure refinement for complexes **1**−**4** at T = 173(2) K

	1	**2**	**3**	**4a**	**4b**
Empirical formula	$C_{25}H_{49}LiN_4O_2S$	$C_{22}H_{46}LiN_5S_2$	$C_{22}H_{46}LiN_5SSe$	$C_{44}H_{88}Li_2N_6O_4S_3$	$C_{40}H_{88}Li_2N_{10}S_3$
M	476.37	451.70	498.60	875.26	819.26
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a [pm]	1012.92(9)	995.32(8)	9970.1(9)	1092.68(8)	1060.86(10)
b [pm]	1601.06(14)	1591.64(13)	1606.39(15)	1769.00(14)	1787.60(16)
c [pm]	1796.99(16)	1779.67(14)	1773.06(17)	2755.8(2)	2727.6(3)
β [°]	91.5070(10)	91.5970(10)	92.610(2)	94.869(2)	92.533(2)
V [nm^3], Z	2.9133(4), 4	2.8182(4), 4	2.8368(5), 4	5.3076(7), 4	5.1676(8), 4
D_c [Mg·m^{-3}]	1.087	1.065	1.167	1.095	1.053
μ [mm^{-1}]	0.137	0.205	1.413	0.182	0.179
θ range [°]	1.70 to 25.07	1.72 to 25.03	1.71 to 26.40	1.37 to 23.82	1.36 to 23.26
Data/restraints/parameter	5128/0/308	4973/126/323	5796/0/284	8147/712/736	7400/396/641
$R1$[a] [$I > 2\sigma(I)$]	0.0901	0.0627	0.0336	0.1225	0.0540
$wR2$[b] (all data)	0.1796	0.1468	0.0930	0.2619	0.1171
Largest diff. peak and hole [e nm^{-3}]	418, −301	365, −327	427, −266	670, −500	288, −175
CCDC no	208432	208429	208430	208431	208428

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ with $w = 1/[\sigma^2(F_o^2) + (g_1P)^2 + g_2P$ and $P = (F_o^2 + 2F_c^2)/3$.

CCDC-208432, -208429, -208430, -208431 and -208428 (see also Table 3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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