Polyimido sulphur anions $S(NR)_n^{m-}$: Free radicals and coordination behaviour

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Abstract. In a reaction sequence of amide addition followed by halogen oxidation the triazasulphite $S(NR)_3^{2-}$ and the tetrazasulphate $S(NR)_4^{2-}$ are readily accessible from sulphur diimide $S(NR)_2$ via sulphur triimide $S(NR)_3$. Addition of lithium organics to sulphur triimide provides a general route to triazasulphonates $RS(NR)_3^{2-}$. All these anions resemble potential tripodal coordination behaviour because of their nitrogen donor centres. Furthermore, the sulphur polyimido ligands are capable of responding to the various requirements of different metals (even in mixed metal species) by charge (de)localization. This paper deals with the synthetic routes of the sulphur nitrogen anions and their coordination behaviour. Their reactivity, mainly towards main group metal synthons, is also discussed.
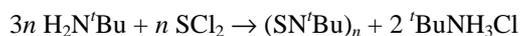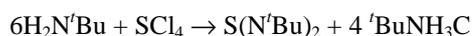
Keywords. Sulphur nitrogen anions; sulphur triimide metal synthons; tripodal coordination behaviour; halogen oxidation.
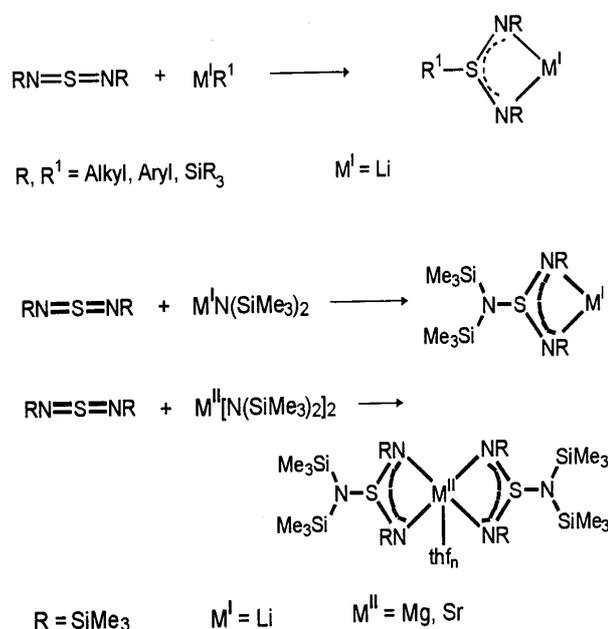
1. Introduction

Unequivocally, sulphur is one of the most versatile elements in main group chemistry. Classical inorganic chemistry was originally most concerned with sulphur oxides and related anions. Sulphur nitrogen compounds attracted much research interest from the 1950s to the 1980s. In the 1970s interest in S-N chemistry increased [1].

Sulphur dioxide	Sulphur trioxide	Sulphite	Sulphate
SO_2	SO_3	SO_3^{2-}	SO_4^{2-}
$S(NR)_2$	$S(NR)_3$	$S(NR)_3^{2-}$	$S(NR)_4^{2-}$
Sulphur diimide	Sulphur triimide	Triazasulphite	Tetrazasulphate

The isoelectronic sulphur nitrogen analogues of the simple sulphur oxygen compounds have shown to be very fruitful synthons in inorganic and organic synthesis [2]. Many sulphur oxygen/nitrogen compounds including their acids have been synthesized. In these compounds, the oxygen atoms are formally, either fully or partially isoelectronically substituted by NR groups (R = H, alkyl, aryl, silyl, sulphonyl, and others). Sulphur diimides $S(NR)_2$ are known since the mid 1950s [2]. They can be obtained in the reaction of either sulphur tetra [2,3] or dichloride [4,5] with primary amines. The reaction with sulphurdioxide and sodium *bis*(trimethylsilyl)amide yields the *bis*(trimethylsilyl) sulphur diimide [5a].
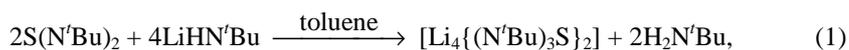
$6H_2N^tBu + SCl_4 \rightarrow S(N^tBu)_2 + 4\ ^tBuNH_3C$

$3n\ H_2N^tBu + n\ SCl_2 \rightarrow (SN^tBu)_n + 2\ ^tBuNH_3Cl$

$(Sn^tBu)_n \xrightarrow{\Delta T} n/2(S(N^tBu)_2 + 1/8S_8).$

$SO_2 + 2\ NaN(SiMe_3)_2 \rightarrow S(NSiMe_3)_2 + O(SiMe_3)_2 + 2\ Na_2SO_3.$

The formal double bonds in sulphurdiimides are exposed to nucleophilic addition reactions. Due to the considerable S^+–N^- bond polarization, the nucleophile R^- always bonds to the sulphur while the metal is chelated by the two nitrogen atoms of the diazasulphinate anion. With alkali metals, these fragments tend to dimerize via one M–N bond to furnish M_2N_2 four-membered ring systems [6,7].

$RN{=}S{=}NR\ +\ M^IR^1\ \longrightarrow$

$R, R^1 =$ Alkyl, Aryl, SiR_3 $M^I =$ Li

$RN{=}S{=}NR\ +\ M^IN(SiMe_3)_2\ \longrightarrow$

$RN{=}S{=}NR\ +\ M^{II}[N(SiMe_3)_2]_2\ \longrightarrow$

$R = SiMe_3$ $M^I =$ Li $M^{II} =$ Mg, Sr

2. The triazasulphite dianion

By analogy to the nucleophilic addition of alkali metal organics to sulphur diimides, primary lithium amides can be reacted with sulphur diimides. Dilithium triazasulphite and amine are obtained in a 1:2 ratio (1). Even in donating solvents like thf the product dimerizes to a cage structure (2) [8].

$$2S(N^tBu)_2 + 4LiHN^tBu \xrightarrow{\text{toluene}} [Li_4\{(N^tBu)_3S\}_2] + 2H_2N^tBu, \qquad (1)$$

$$2S(N^tBu)_2 + 4LiHN^tBu \xrightarrow{\text{thf}} [(thf)Li_4\{(N^tBu)_3S\}_2] + 2H_2N^tBu. \qquad (2)$$

In both $S(N^tBu)_3^{2-}$ dianions the central sulphur atom shows pyramidal environment and holds a stereochemical active lone pair on top of a N-centred tripod. Two of the cap-shaped dianions face each other with their concave side and accommodate four lithium cations through N coordination. The six *t*-butyl groups are arranged in a staggered orientation to minimize sterical strain and to cover the Li_4 core with a hydrocarbon layer to provide solubility in non-polar solvents (figure 1a).

Even synthesized and crystallized from donating thf solution the solid state structure is only coordinated by one single thf molecule (figure 1b). The lower $S(N^tBu)_3^{2-}$ dianion is almost C_3 symmetrically coordinated by three lithium cations. Different to the donor-free product, only three lithium atoms are located between the staggered ^tBuN groups. The fourth, Li4 (figure 1b), is only coordinated to two nitrogen atoms (N2 and N3) of the cap dianion and to the thf molecule. While the nitrogen atoms N2 to N6 are coordinated to two lithium atoms each, N1 is exclusively coordinated to Li1.

Pure dilithium triazasulphite is a white pyrophoric solid. Handled in an inert gas atmosphere (Ar 5·0) without an additional oxygen absorber, the solid as well as its solution instantaneously turns dark blue. Using an oxygen absorber, both can be handled for a short time with Schlenk techniques. This phenomenon suggests that in the reaction with oxygen a radical is formed. Even at room temperature a dark blue solution of oxidized dilithium triazasulphite in hexane shows an ESR signal. The ESR-spectrum of the radical in hexane solution displays a signal even at room temperature. The hyperfine splitting of the signal, to give a septet ($a = 5·75$ G, intensity ratio 1:3:6:7:6:3:1), confirms that the single electron interacts with three equivalent ^{14}N nuclei ($I = 1$) (figure 2a). An additional hyperfine splitting (decet with $a = 0·87$ G) has to be assigned to an interaction with three equivalent ^7Li nuclei ($I = 3/2$). Line shape analysis and simulation of the spectrum confirms this assignment (figure 2b). The structure therefore can be deduced from the ESR spectrum. In the dimer of the radical monoanion $S(N^tBu)_3^{\bullet-}$ and the
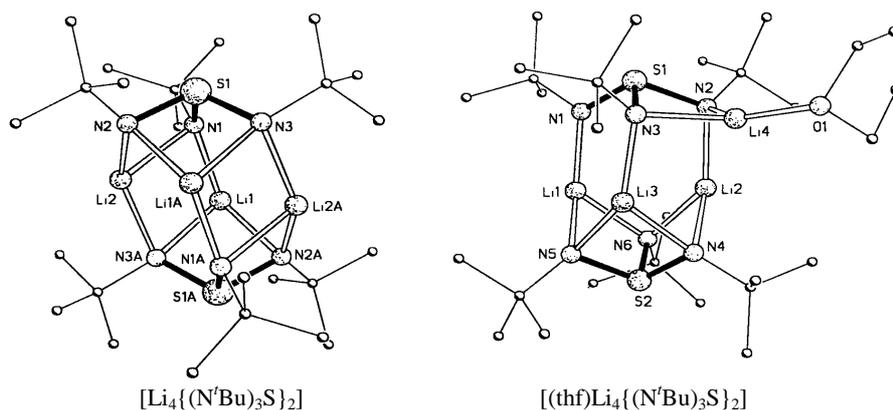

[Li$_4$\{(N^{t}Bu)$_3$S\}$_2$]   [(thf)Li$_4$\{(N^{t}Bu)$_3$S\}$_2$]

Figure 1. Solid state structures of the donor-free dilithium triazasulphite [Li$_4$\{(N^{t}Bu)$_3$S\}$_2$] and the thf coordinated [(thf)Li$_4$\{(N^{t}Bu)$_3$S\}$_2$] derivative.
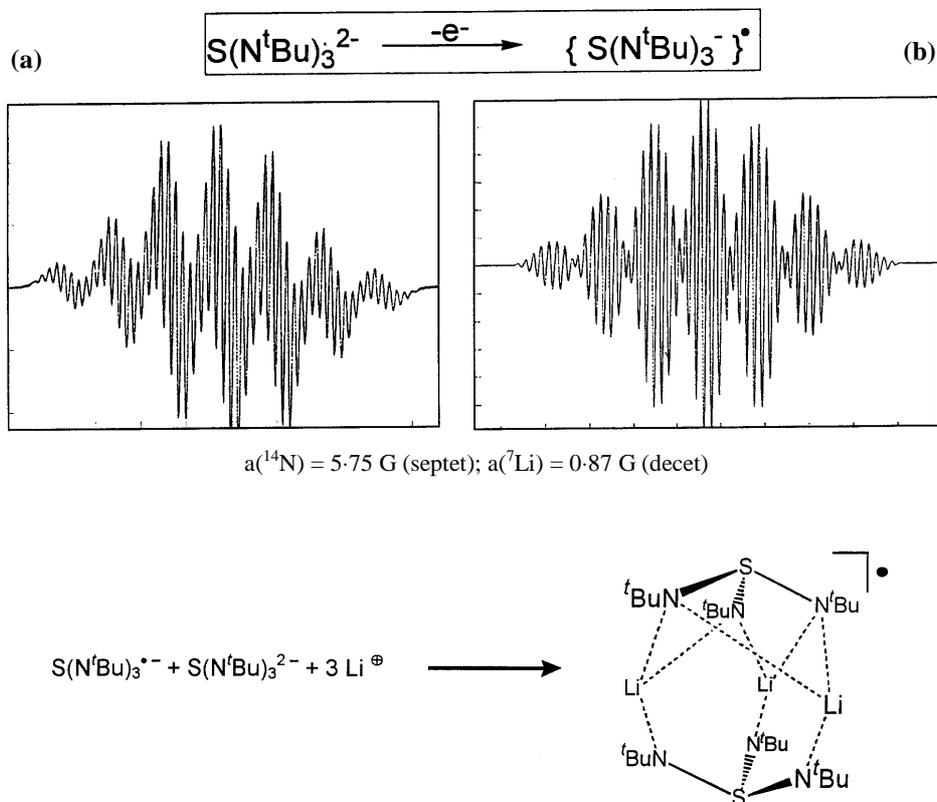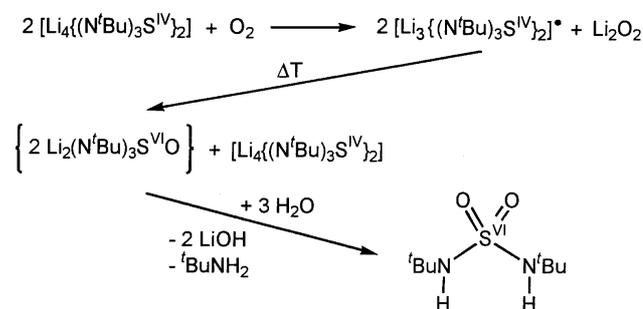
$$S(N^tBu)_3{}^{2-} \xrightarrow{\;-e^-\;} \{ S(N^tBu)_3{}^- \}^\bullet$$

(a)   (b)

$$a(^{14}N) = 5 \cdot 75 \text{ G (septet)}; \; a(^7Li) = 0 \cdot 87 \text{ G (decet)}$$

$$S(N^tBu)_3{}^{\bullet -} + S(N^tBu)_3{}^{2-} + 3\,Li^\oplus \longrightarrow$$

Figure 2. Experimental (**a**) and calculated (**b**) ESR spectra of the radical $[Li_3\{(N^tBu)_3S\}_2]^\bullet$.

dianionic $S(N^tBu)_3{}^{2-}$ three lithium cations are located between the cap shaped ligands (figure 2, scheme)[9]. Later this arrangement was confirmed by Chivers *et al*[10].

The formation of the $[Li_3\{(N^tBu)_3S\}_2]^\bullet$ radical is already suggested by the structure of $[(thf)Li_4\{(N^tBu)_3S\}_2]$ (figure 2) in which one lithium is about to leave the area between the cap shaped dianions. When dry oxygen is bubbled through a solution of dilithium triazasulphite 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 it becomes colourless again. Unfortunately, no defined product could be isolated and purified neither by distillation, nor by crystallisation. Only after hydrolysis could $O_2S(^tBuNH)_2$ be isolated and characterised. The reaction sequence of this oxidation is shown in scheme 1.

3. The sulphurtriimide

Two products can be isolated when chlorine, bromine or iodine is used in the oxidation of $[Li_4\{(N^tBu)_3S\}_2]$. Dependent on the stochiometry, a lithium halide adduct of monomeric $[Li_3X(N^tBu)_3S]$ (figure 3) and the sulphurtriimide $S(N^tBu)_3$ can be isolated in variable yields. Right after the addition of halogen to a solution of $[Li_4\{(N^tBu)_3S\}_2]$ in thf/hexane,

$$2\,[Li_4\{(N^tBu)_3S^{IV}\}_2] \; + \; O_2 \longrightarrow \; 2\,[Li_3\{(N^tBu)_3S^{IV}\}_2]^{\bullet} \; + \; Li_2O_2$$

$$\Delta T \downarrow$$

$$\left\{ 2\,Li_2(N^tBu)_3S^{VI}O \right\} \; + \; [Li_4\{(N^tBu)_3S^{IV}\}_2]$$

$$\xrightarrow[\substack{-\,2\,LiOH \\ -\,^tBuNH_2}]{+\,3\,H_2O}$$

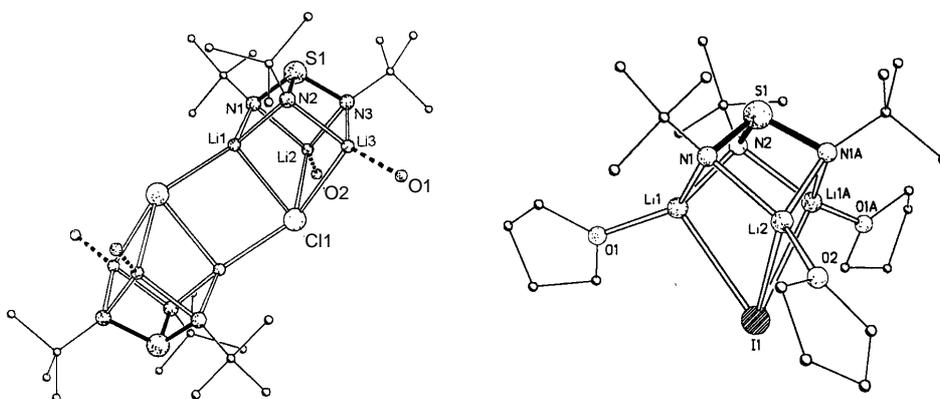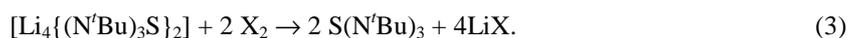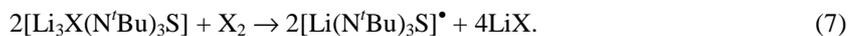**Scheme 1.** Oxidation of dilithium triazasulphite via oxygen.

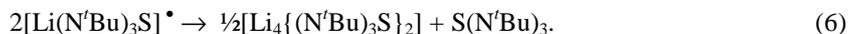**Figure 3.** Oxidation of dilithium triazasulphite via halogens (X = Cl, Br, I); equation (3) is the overall reaction while equations (4) to (7) are the reaction pathway; the reaction intermediates [(thf)$_2$Li$_3$Cl(N^{t}Bu)$_3$S] [11] and [(thf)$_3$Li$_3$X(N^{t}Bu)$_3$S] [10] (X = Br, I) could be isolated.

the mixture instantaneously turns dark blue similar to 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 but not until two equivalents are added at the end of the oxidation. The final product of this oxidation reaction is the tri(*tert*-butyl)sulphurtriimide. Hence, the reaction of [Li$_4${(N^{t}Bu)$_3$S}$_2$] with two equivalents of halogens provides easy access to sulphurtriimides (3) [9].

$$[Li_4\{(N^tBu)_3S\}_2] + 2\,X_2 \rightarrow 2\,S(N^tBu)_3 + 4LiX. \tag{3}$$

$$2[Li_4\{(N^tBu)_3S\}_2] + X_2 \rightarrow 2\,[Li_3\{(N^tBu)_3S\}_2]^{\bullet} + 2LiX. \tag{4}$$

$$2[\text{Li}_3\{(\text{N}^t\text{Bu})_3\text{S}\}_2]^\bullet + 2\text{LiX} \rightarrow 2[\text{Li}_3\text{X}(\text{N}^t\text{Bu})_3\text{S}] + 2[\text{Li}(\text{N}^t\text{Bu})_3\text{S}]^\bullet. \tag{5}$$

$$2[\text{Li}(\text{N}^t\text{Bu})_3\text{S}]^\bullet \rightarrow \tfrac{1}{2}[\text{Li}_4\{(\text{N}^t\text{Bu})_3\text{S}\}_2] + \text{S}(\text{N}^t\text{Bu})_3. \tag{6}$$

$$2[\text{Li}_3\text{X}(\text{N}^t\text{Bu})_3\text{S}] + \text{X}_2 \rightarrow 2[\text{Li}(\text{N}^t\text{Bu})_3\text{S}]^\bullet + 4\text{LiX}. \tag{7}$$

Until this route was discovered, only two methods were known to give sulphurtriimides, using either NSF_3 [12] or OSF_4 [13]. The first is quite hazardous, because the starting material is S_4N_4, which tends to explode very easily and the second is limited to the *tris*(trimethylsilyl)sulphurtriimide $S(NSiMe_3)_3$. Both routes gave unsatisfactory yields ($\leq 23\%$).

When discovered first, the sulphurtriimide causes considerable attention because it was considered the first example of valence expansion at sulphur. Bonding between S and N was interpreted as three covalent double bonds. The Raman bands at ≈ 1200 cm^{-1} were assigned to the SN stretching frequencies and witnessed that fact [14]. Recent Raman spectroscopic experiments and the assignment of the SN vibrations to much smaller wave numbers (641 and 918 cm^{-1}) suggest mainly electrostatic contribution in a $>\text{S}^+-\text{N}^-$ bond of sulphur [15]. The hypothesis of valence expansion at sulphur to three covalent double bonds ($S(=NR)_3$) seems no longer valid. Unequivocally the bands at 1200 cm^{-1} previously reported to be the SN stretching frequencies have to be assigned to CN stretching and CH_3 rocking vibrations (figure 4).

A charge density distribution from a multipole refinement based on high resolution X-ray diffraction data favours the electrostatic bonding rather than covalent double bonds.
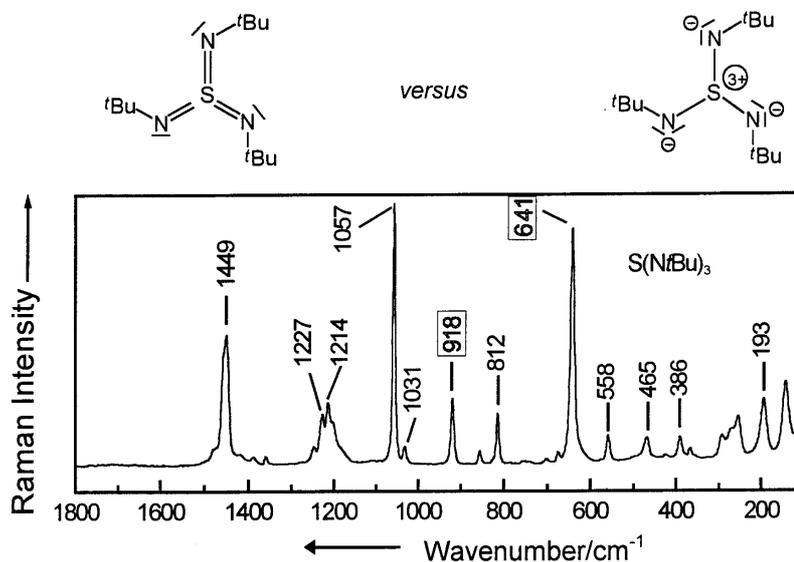

Figure 4. Raman spectrum of $S(N^t\text{Bu})_3$ and DFT (*BPW*91/6-31 + *G**) assignment; SN (sym./asym.) stretching vibrations at 642 and 918 cm^{-1}; the bands at 1227 and 1214 cm^{-1} are caused by CN stretching and CH_3 rocking vibrations.

4. Transmetallation of triazasulphite

It is an obvious course to employ the tripodal triazasulphite in metal coordination. While various monoanionic (e.g. tripyrazolylborate) and trianionic (e.g. triamidomethane and –silane) tripodal ligand systems are known, the triazasulphite anion is the first dianionic system. Their coordination chemistry is unique among the chelating nitrogen ligands due to the two negative charges and its cap shaped geometry. In contrast to the S(NR)$_3^{2-}$ dianion, the analogous carbon compounds (guanidines C(NR)$_3^{2-}$) are planar[16]. The cap shaped geometry together with the steric demand of the nitrogen bonded substituents should enable homoleptic metal(II) complexes

4.1 *Transmetallation via main group amides*

Although metal amides are predominantly used in deprotonation reactions, we endeavoured transmetallation of the triazasulphite with secondary amides of certain alkaline earth metals (Mg, Ca, Ba) and Sn[17]. Different to the alkaline earth metal halides which are nearly inert and insoluble, the related metal amides provide excellent solubility and sufficient reactivity. Different types of complexes are obtained in the reactions with [thf$_2$M{N(SiMe$_3$)$_2$}$_2$] (M = Ca, Ba). While two lithium atoms are still present in the calcium derivative (8) only one remains in the barium complex (9). Hence, they exhibit different levels of transmetallation. In the calcium complex only half the equivalent of the present lithium cations are replaced by calcium dications, while in the barium complex three out of four lithium cations are exchanged by two barium dications. The *bis*(trimethylsilyl)amide group found in the barium complex provides charge balance. In both compounds the dimeric structure of two cap shaped ligands facing each other with their concave sides is retained (figure 5).
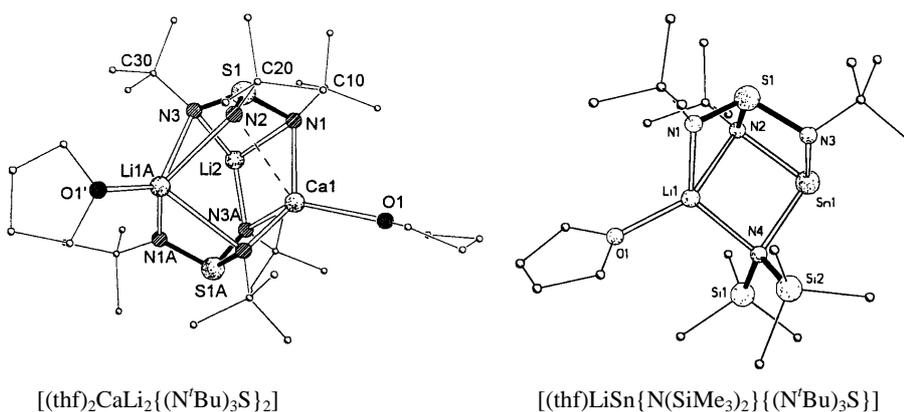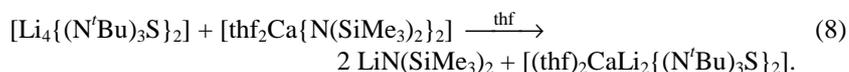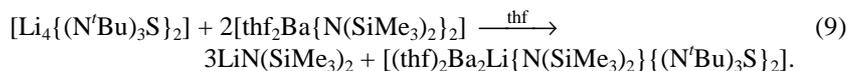
$$[\text{Li}_4\{(\text{N}^t\text{Bu})_3\text{S}\}_2] + [\text{thf}_2\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2] \xrightarrow{\text{thf}} \quad (8)$$
$$2\,\text{LiN}(\text{SiMe}_3)_2 + [(\text{thf})_2\text{CaLi}_2\{(\text{N}^t\text{Bu})_3\text{S}\}_2].$$

[(thf)$_2$CaLi$_2${(N^{t}Bu)$_3$S}$_2$]   [(thf)LiSn{N(SiMe$_3$)$_2$}{(N^{t}Bu)$_3$S}]

Figure 5. Solid state structures of the transmetallation products [(thf)$_2$CaLi$_2${(N^{t}Bu)$_3$S}$_2$] and [(thf)LiSn{N(SiMe$_3$)$_2$}{(N^{t}Bu)$_3$S}].

$$[Li_4\{(N^tBu)_3S\}_2] + 2[thf_2Ba\{N(SiMe_3)_2\}_2] \xrightarrow{\ thf\ } \qquad\qquad (9)$$
$$3LiN(SiMe_3)_2 + [(thf)_2Ba_2Li\{N(SiMe_3)_2\}\{(N^tBu)_3S\}_2].$$

The monomeric tin derivative is obtained in the analogue reaction of triazasulphite with $[Sn\{N(SiMe_3)_2\}_2]$ (10)[17].

$$[Li_4\{(N^tBu)_3S\}_2] + [Sn\{N(SiMe_3)_2\}_2] \xrightarrow{\ thf\ } [(thf)LiSn\{N(SiMe_3)_2\}\{(N^tBu)_3S\}]. \quad (10)$$
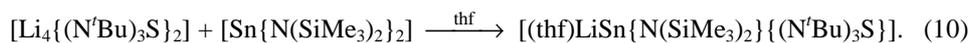
Depending on the electronic requirements, different resonance forms of the ligand can be utilized by which the charges of the coordinated cations are stabilized. The electronic requirements of different cations can also be satisfied simultaneously. Therefore, mixed metal complexes are quite common in the coordination chemistry of this ligand.

4.2 *Transmetallation via coinage metal halides*

The structure of the triazasulphite $[Li_4\{(N^tBu)_3S\}_2]$ and particularly the thf coordinated $[(thf)Li_4\{(N^tBu)_3S\}_2]$ suggested that there is not quite enough room for the four lithium cations. The monovalent coinage metal cations should therefore give rise to different coordination polyhedra because unlike lithium they prefer a linear two-fold coordination. They should cause the alkyl groups at nitrogen to be arranged in an ecliptic conformation rather than in a staggered one in the lithium complexes. Coinage metal halides react with dilithium triazasulphite in a transmetallation reaction[18]. Only three of the four present lithium metal centres in the dimer of the starting material are replaced by copper or silver. In addition, one equivalent of the eliminated lithium halide is co-coordinated in the periphery of the complex. The degree of aggregation is apparently dependent on the size of the halide anion. The products from copper and silver bromide give dimers (figure 6), while copper iodide gives a monomer (11).
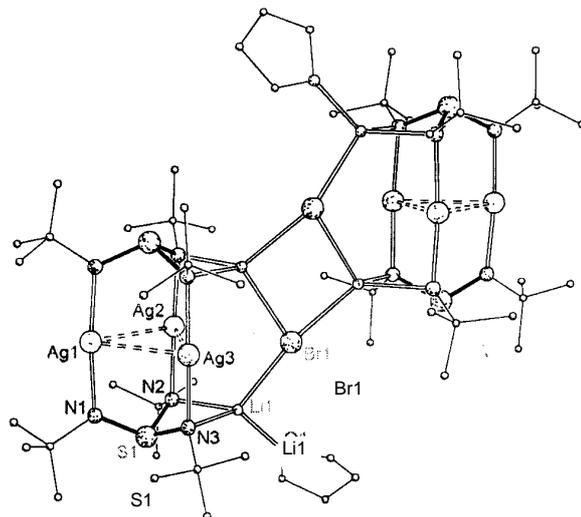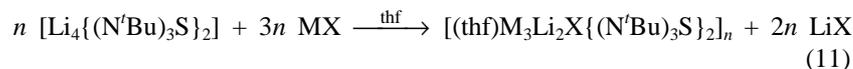

Figure 6. Solid state structure of the transmetallation product $[(thf)Li_2Ag_3Br\{(N^tBu)_3S\}_2]_2$[18].

$$n \ [\text{Li}_4\{(\text{N}^t\text{Bu})_3\text{S}\}_2] \ + \ 3n \ \text{MX} \ \xrightarrow{\text{thf}} \ [(\text{thf})\text{M}_3\text{Li}_2\text{X}\{(\text{N}^t\text{Bu})_3\text{S}\}_2]_n \ + \ 2n \ \text{LiX}$$

$$(11)$$

$$n = 1: \text{M} = \text{Cu}; \text{X} = \text{I}$$
$$n = 2: \text{M} = \text{Cu}, \text{Ag}; \text{X} = \text{Br}$$

5. Salt co-complexation of triazasulphite

Polyimido polyanions containing *p*-block element bridgeheads like [RSi(NsiMe$_3$)$_3$]$_2^{3-}$ [19], RE(E′R′$_2$NR″)$_3^{3-}$ (R, R′ = H, alkyl; R″ = alkyl, aryl; E, E′ = C, Si) [20], [Sb(NR)$_3$]$^{3-}$ [21], [Sb$_2$(NR)$_4$]}$^{2-}$ [21], and [E(N^{t}Bu)$_3$]$^{2-}$ (E = Se, Te) [22] furnish a new family of ligand systems to construct macromolecular architectures of mixed metal cages and clusters [23]. 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 the triazasulphite anion, i.e. the ability to localise or delocalize the charge in the anion core backbone, should provide the opportunity to complex neutral metal salts.
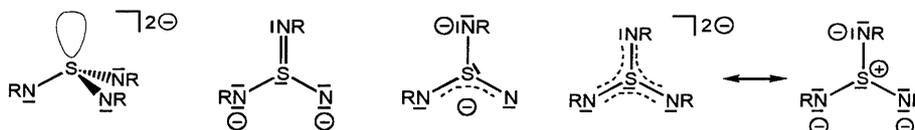
5.1 *Co-complexation of lithium sulphide*

In the reduction reaction of S(N^{t}Bu)$_2$ and lithium or sodium metal in thf [thf$_6$M$_6$(m$_3$S){(N^{t}Bu)$_3$S}$_2$] (M = Li, Na) is obtained as the final product, even with excess of active metal (12) [24].

$$3 \ \text{S}(\text{N}^t\text{Bu})_2 + 6 \ \text{M} \ \xrightarrow{\text{thf}} \ [(\text{thf})_6\text{M}_6(\text{m}_3\text{S})\{(\text{N}^t\text{Bu})_3\text{S}\}_2]; \text{M} = \text{Li}; \text{Na}. \qquad (12)$$

Formally, these compounds are M$_2$S adducts of [M$_4${(N^{t}Bu)$_3$S}$_2$]. A similar reaction with potassium metal gives [thf$_3$K$_3${(N^{t}Bu)$_3$S}$_2$]$^•$ and no incorporation of metal sulphide was observed.

[thf$_6$Li$_6$(m$_3$S){(N^{t}Bu)$_3$S}$_2$] crystallizes in the rhombohedral space group R$\bar{3}$, with all sulphur atoms on the threefold axis. In addition, S2 is located on a centre of inversion. The same is valid for the isotype structure of [thf$_6$Na$_6$(m$_3$S){(N^{t}Bu)$_3$S}$_2$] in the cubic space group Pa3. Thus complete delocalization of the negative charges within the SN$_3$ backbone in both ligands is imposed by crystallographic threefold symmetry. Each alkali metal atom m$_2$-bridges two nitrogen atoms of one ligand and is coordinated to the central S^{2-} ion. An additional thf donor molecule completes the coordination sphere to give the coordination number four at each alkali metal centre (figure 7).

5.2 *Co-complexation of alkali metal alkoxides*

While the heavier alkali metal diaminosulphinates are accessible either by deprotonation reactions of RS(NHR)NR with MH or addition of the secondary metal amides MNR$_2$; (M = Na, K, Rb, Cs) to S(NR)$_2$, direct syntheses of the heavier alkali metal triazasulphites

is humped by the difficult syntheses of the required primary metal amides MN(H)R in preparative yields. However, initiated by the fundamental work by Lochmann and Schlosser in the late 60s on the so-called super-basic mixtures, we embarked on transmetallation via the heavier alkali metal alkoxides MOR[25]. Donor-free $[Li_4\{(N\text{-}t\text{-}Bu)_3S\}_2]$ was reacted with the heavy alkali metal *tert*-butylalkoxides MO^{t}Bu (M = Na, K) to see whether this reaction pathway is governed by transmetallation (13) or co-complexation (14).

$$[Li_4\{(N^tBu)_3S\}_2] + 4\,Mo^tBu \;\;\nrightarrow\;\; [M_4\{(N^tBu)_3S\}_2] + 4\,LiO^tBu \qquad (13)$$
$$M = Na,\, K.$$
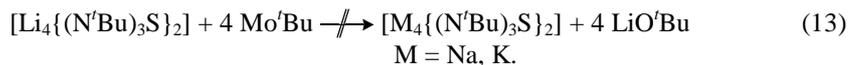
The energetically very attractive Li-O interaction in the formed lithium *tert*-butylalkoxide is often regarded to be the driving force in metal metathesis reactions. In the reactions of triazasulphite $[Li_4\{(N^tBu)_3S\}_2]$ with sodium and potassium *tert*-butylalkoxides transmetallation does not occur and formation of LiO^{t}Bu is not observed. Instead two equivalents of *tert*-butylalkoxide are incorporated into the complex structure (14).

$$[Li_4\{(N^tBu)_3S\}_2] + 2\,Mo^tBu \rightarrow [(thf)_2Li_4M_2(O^tBu)_2\{(N^tBu)_3S\}_2]. \qquad (14)$$
$$M = Na,\, K$$
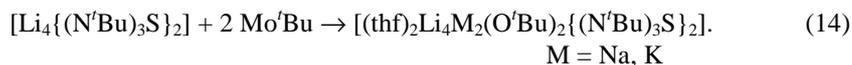
In the structure the heavier alkali metals occupy different coordination sites. While one adopts a square planar pyramidal environment with four nitrogen atoms in the basal positions and the oxygen atom of a donating thf molecule at the apical position, the other adopts a trigonal planar geometry, being complexed by the two O atoms of the ^{t}BuO$^-$ groups and one thf donor molecule.

The structural motif of two triazasulphite caps facing each other with their concave sides is flexible enough to suit the different requirements in mixed metal cage compounds.
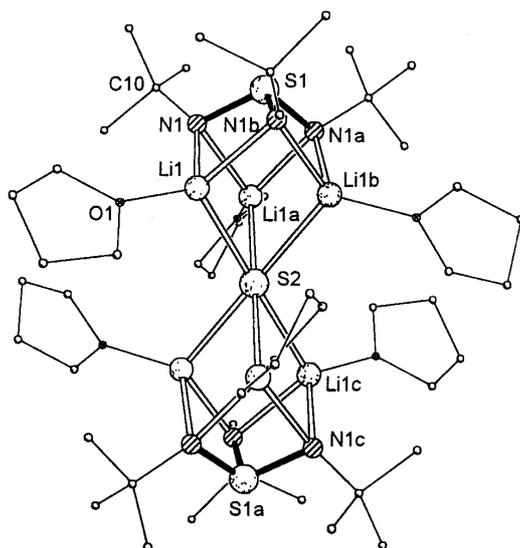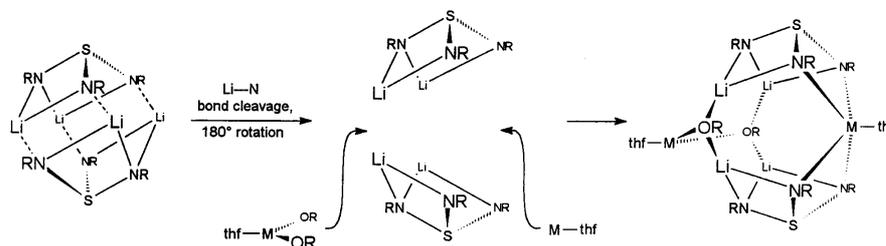

Figure 7. Solid state structures of the alkali metal sulphide adduct $[thf_6Li_6(\mu_6S)\{(N^tBu)_3S\}_2]$.

Scheme 2. Rearrangement of the dilithium triazasulphite dimer and co-complexation of two equivalents of alkali metal *tert*-butylalkoxide to give [(thf)$_2$Li$_4$M$_2$(O^{t}Bu)$_2${(N^{t}Bu)$_3$S}$_2$]; M = Na, K[25].
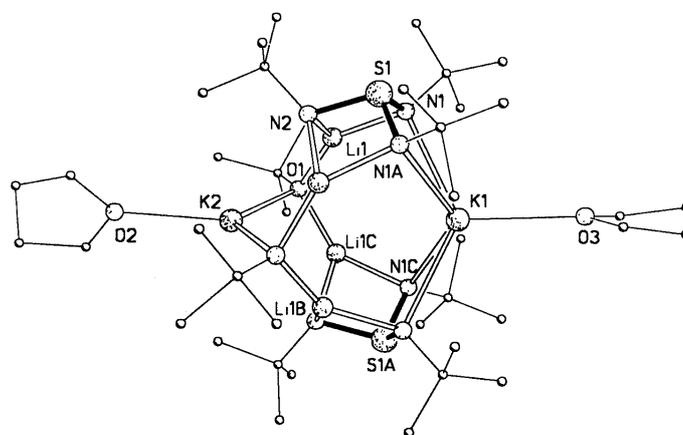
Figure 8. Solid state structures of the *tert*-butylalkoxide adduct [(thf)$_2$Li$_4$M$_2$(O^{t}Bu)$_2${(N^{t}Bu)$_3$S}$_2$]; M = Na, K.

The S···S distance is indicative of the different arrangements (table 1). The small and hard metals Li and Ca/Li prefer as many metal-nitrogen contacts as possible. This forces the caps in close contact and the ^{t}BuN-groups in a staggered conformation. The ^{t}Bu-groups are interlocked like the parts of a universal joint to coat the electropositive cage core with a hydrocarbon layer. The S···S distance ranges from 460 to 490 pm. The larger and softer metal Ba allows the caps to get further apart (S···S distance > 490 pm) and to arrange the ^{t}BuN-groups in an ecliptic conformation. The linear N-M-N coordinated coinage metals Cu and Ag force the caps in an ecliptic conformation as well. Their S···S distance ranges from 514 to 557 pm. Salt co-complexation of alkali metal *tert*-butylalkoxide furnishes even larger S···S distances with eclipsed ^{t}BuN-groups (584 and 610 pm).

6. Sulphur(VI) nitrogen compounds

By analogy to the reactions of sulphurdiimides, addition of nucleophils to the double bond of sulphurtriimides provides access to anionic S^{VI}–N species. Although most reactions of sulphurdiimides are applicable to sulphurtriimides as well, only little is known of the anionic S^{VI}–N species. This is due to the lack of easy synthetic access to sulphurtriimides.

Table 1. Orientation of NR groups and S…S non-bonded distances in cage molecules with two triazasulphite, $S(N^tBu)_3^{2-}$, caps.

| Compounds	NR orientation	$d(S{\cdots}S)$ [pm]	Lit.
$[Li_4\{(N^tBu)_3S\}_2]$	Staggered	459·5	8
$[(thf)Li_4\{(N^tBu)_3S\}_2]$	Staggered	473·1	8
$[(thf)_2Li_2Ca\{(N^tBu)_3S\}_2]$	Staggered	480·5	17
$[(thf)_2LiBa_2\{N(SiMe_3)_2\}\{(N^tBu)_3S\}_2]$	Eclipsed	497·9	17
$[(tBuNH_2)Li_2Cu_3Br\{(N^tBu)_3S\}_2]_2$	Eclipsed	514·2	18
$[(thf)_2Li_2Cu_3I\{(N^tBu)_3S\}_2]$	Eclipsed	517·1	18
$[(thf)Li_2Ag_3Br\{(N^tBu)_3S\}_2]_2$	Eclipsed	556·9	18
$[(thf)_2Li_4Na_2(OtBu)_2\{(N^tBu)_3S\}_2]$	Eclipsed	584·0	25
$[(thf)_2Li_4K_2(O^tBu)_2\{(N^tBu)_3S\}_2]$	Eclipsed	610·1	25

6.1 *The tetrazasulphate dianion*

The first fully structurally characterized example of this species is the dilithium tetrazasulphate $[thf_4Li_2(N^tBu)_4S]$ which can easily be synthesized by addition of lithium *tert*-butylamide to sulphurtriimide (15)[26]. The resulting lithium complex $[thf_4Li_2(N^tBu)_4S]$ is sensitive to oxygen.

$$S(N^tBu)_3 + 2\ LiHN^tBu \xrightarrow{\ thf\ } [(thf)_4Li_2(N^tBu)_4S] + H_2N^tBu. \qquad (15)$$

The crystal structure analysis proves $[(thf)_4Li_2(N^tBu)_4S]$ to be a molecular structure (figure 9) rather than an infinite solid state structure like lithium sulphate. Thf solvation of the lithium cations prevents further aggregation. Each lithium metal is coordinated by two thf molecules and μ_2-bridges two ^tBuN groups. The central sulphur atom is tetrahedrally coordinated by the four ^tBuN groups. Two opposite edges of the resulting SN_4 tetrahedron are bridged by the two lithium cations. The four crystallographically independent S–N-bond lengths (av. 160·1 pm) do not differ significantly. Thus the negative charge is completely delocalized over the $S(N^tBu)_4$ moiety. Owing to the lithium bridging the average N–S–N angle within the LiN_2S kite shaped rings is about 23° more acute (94·7°) than the other four (117·4°).

6.2 *The triazasulphonate anion*

Unlike the S-alkyl diazasulphinates $RS(NR')_2^-$, S-alkyl triazasulphinates $RS(NR')_3^-$ are relatively rare and only little structural information on these species is available. They can be obtained by the addition of lithium organics to sulphurtriimides (16)[15,26].

$$S(N^tBu)_3 + 2\ MeLi \xrightarrow{\ thf\ } [(thf)_2Li_2\{(N^tBu)_3SMe\}_2]. \qquad (16)$$
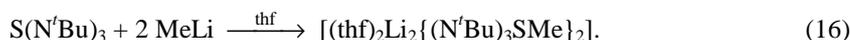
The solid state structure of $[(thf)_2Li_2\{(N^tBu)_3SMe\}_2]$ is very intriguing. In the dimeric molecule one $MeS(N^tBu)_3^-$ anion is coordinated to both lithium cations while the other is coordinated to only one lithium atom. The first lithium atom is tetrahedrally coordinated by two of the three nitrogen atoms bound to S1 and to two thf molecules. The second lithium atom is trigonal planar coordinated by the third nitrogen atom at S1 and two nitrogen atoms of the second $MeS(N^tBu)_3^-$ moiety. This leaves only one nitrogen atom not coordinated to any lithium.
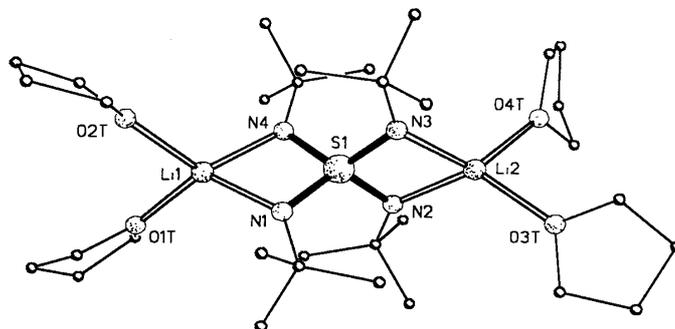
Figure 9. Solid state structure of the dilithium tetrazasulphate [(thf)$_4$Li$_2$(N^{t}Bu)$_4$S] [26].
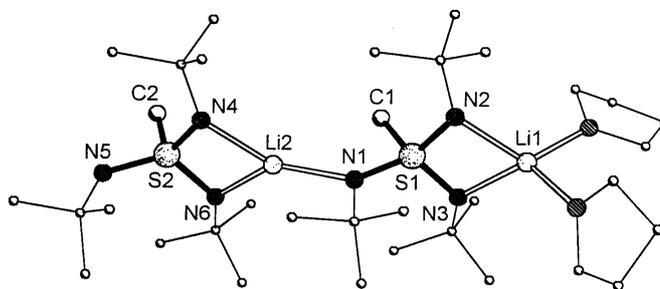
Figure 10. Solid state structure of the dimeric lithium methyltriazasulphonate [(thf)$_2$Li$_2${(N^{t}Bu)$_3$SMe}$_2$].

In an acid base reaction of [(thf)$_2$Li$_2${(N^{t}Bu)$_3$SMe}$_2$] and ^{t}BuNH$_3$Cl, the methyltriazasulphonic acid MeS(N^{t}Bu)$_3$H is obtained (17) [27].

$$[(thf)_2Li_2\{(N^tBu)_3SMe\}_2] + 2\ ^tBuNH_3Cl \xrightarrow{\ thf\ } \qquad\qquad (17)$$
$$2\ MeS(N^tBu)_3H + 2\ ^tBuNH_2 + 2\ LiCl.$$
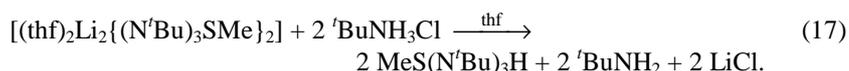
In the structure of MeS(N^{t}Bu)$_3$H the formal single S–N(H)^{t}Bu bond length of 164·7 pm is considerably longer than the two formal S = N^{t}Bu double bonds (av. 151·7 pm).

In general, deprotonation of acidic NH functions with strong bases like the alkaline earth metal *bis*{*bis*(trimethylsilyl)amides} provides easy access to alkaline earth metal complexes. The reaction of MeS(N^{t}Bu)$_3$H with [thf$_2$Ba{N(SiMe$_3$)$_2$}$_2$] yields the barium complex of the MeS(NtBu)$_3^-$ monoanion (18) [15].

$$2MeS(N^tBu)_3H + [thf_2Ba\{N(SiMe_3)_2\}_2] \xrightarrow{\ thf\ } \qquad\qquad (18)$$
$$2\ HN(SiMe_3)_2 + [thf_2Ba\{(N^tBu)_3SMe\}_2].$$
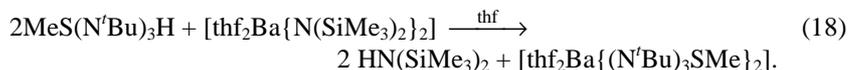
Tripodal coordination could not be observed in any triazasulphonate complex. In the S(N^{t}Bu)$_3^{2-}$ dianion, tripodal coordination is facilitated by all *tert*-butyl groups pointing towards the lone pair of the sulphur atom, leaving all lone pairs of the nitrogen atoms pointing towards the opposite direction. The structure of [Li$_6${(N^{t}Bu)$_3$SiMe}$_2$] published by Veith *et al* [28] shows almost rhombohedral D$_{3d}$ symmetry with the 3 axis along the Si–C
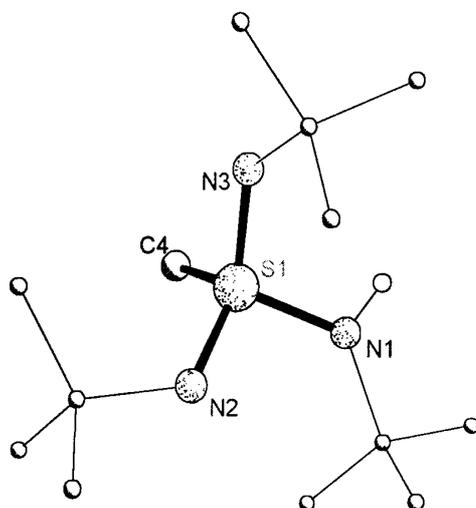
Figure 11. Solid state structure of the methyltriazasulphonic acid MeS(N^{t}Bu)$_3$H.

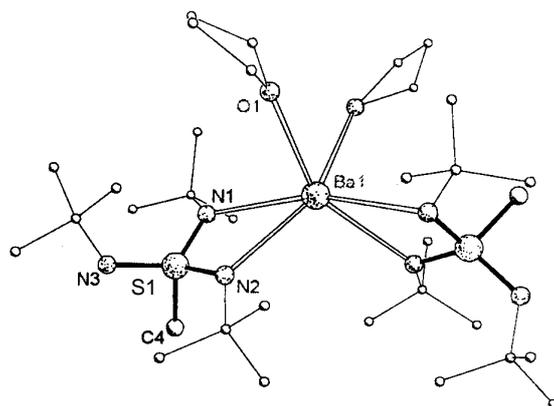**Figure 12.** Solid state structure of the barium di(methyltriazasulphonate) [(thf)$_2$Ba{(N^{t}Bu)$_3$SMe}$_2$].

bond. All *tert*-butyl groups are oriented towards the methyl group at the silicon atom. Hence all nitrogen atoms of the MeSi(N^{t}Bu)$_3^{3-}$ anion are exposed to lithium coordination. This arrangement is suitable because the Si–N bonds are considerably longer (174 pm) than the S–N bonds in the systems reported here (157 pm). Furthermore, the Si–N–C angles are wider (av. 130°) than the S–N–C angles in MeS(N^{t}Bu)$_3^{2-}$ (120–125°). This gives the methyl group at the central silicon atom sufficient room. The repulsion to the *tert*-butyl groups is only marginal and can by compensated by appropriate orientation of the hydrogen atoms at the methyl group. They slot into the gaps left by the *tert*-butyl groups. Such a hypothetical orientation of the *tert*-butyl groups in MeS(N^{t}Bu)$_3^{2-}$ is not possible due to steric crowding. The repulsion is much more pronounced than in the former example and the methyl group would not find any suitable orientation. The anion minimizes steric strain by turning one *tert*-butyl group away from the methyl group.

7. Objectives

The RS(NR)$_3^-$, S(NR)$_3^{2-}$ and S(NR)$_4^{2-}$ anions provide a vast variety of chemical opportunities in many fields of chemistry. In a sequence of an amide addition reaction followed by a halogen oxidation, all S(NR)$_n^{m-}$ species (i.e. S(NR)$_3^{2-}$, S(NR)$_3$ and S(NR)$_4^{2-}$) can be synthesized. Due to the easy oxidizability of even the S(NR)$_4^{2-}$ containing radical species, synthesis of the SO$_4$ analogue S(NR)$_4$ seems feasible. The dianions are tripodal ligands with tunable electronic and steric properties via the organic substituent periphery. Electron releasing substituents like Me$_3$Si-groups at the three nitrogen atoms at the basal plane of the SN$_3$ trigonal pyramid will increase the Lewis basicity of the central sulphur atom, whereas electron withdrawing groups like (substituted) aryls will couple to the nitrogen atom and decrease the electron density at sulphur. This allows to tune the coordination site selectivity of the dianion. The 'hard' N$_3$ site is adjustable to the requirements of even 'soft' metals by employing electron withdrawing substituents and the S-Lewis base centre can be made more attractive to 'hard' centres (e.g. early transition metal) by employing electron releasing substituents. The organic substituents need not only provide the appropriate steric bulk but could also participate in metal coordination ('side arm donation'; pioneered by Klumpp, van Koten, Corriu and others). By choice of the suitable primary amide the passive protecting hydrocarbon layer of the dianion can easily be converted into an active donating ligand periphery. Connection of two dianions will give rise to (RN)$_2$SN(CH$_2$)$_n$NS(NR)$_2^{4-}$ ions which make *ansa*-metallocene like residues feasible. Possibly this provides access to macromolecular architectures consisting of metal cation layers separated by connected SN$_3$ moieties. Linkage of all six nitrogen atoms in two dianions facing each other by their concave side gives rise to structural motifs known from cryptants. Simple access to asymmetrically substituted sulphur triimides S(NR^{1,2,3})$_3$ opens the door to chiral RS(NR^{1,2,3})$_3^-$ and S(NR^{1,2,3,4})$_4^{2-}$ species. Like the well-known chiral phosphanes (DIPAMP, BINAP, CHIRAPHOS, etc.) in transition metal based catalytic processes they might find an application as chiral auxiliaries in asymmetric synthesis and catalysis.

These opportunities might indicate that we have only recently entered a field where there is yet plenty to be discovered.

Acknowledgments

References

1. (a) Roesky H W 1979 *Adv. Inorg. Chem. Radiochem.* **22** 239 (b) Roesky H W 1979 *Angew. Chem.* **91** 112; 1979 *Angew. Chem., Int. Ed. Engl.* **18** 91 (c) Chivers T 1985 *Chem. Rev.* **85** 341 (d) Chivers T and Edelmann F T 1986 *Polyhedron* **5** 1986 (e) Scherer O and Schmitt R 1969 *J. Organomet. Chem.* **16** 11 (f) Mews R, Watson P J and Lork E 1996 *Coord. Chem. Rev.* **158** 233 (g) Fleischer R and Stalke D 1998 *Coord. Chem. Rev.* **176** 431
2. Goehring M and Weis G 1956 *Angew. Chem.* **68** 678

3. (a) Cramer R 1961 *J. Org. Chem.* **26** 3476 (b) Cohen B and MacDiarmid A G 1963 *Angew. Chem.* **75** 207 (c) Cohen B and MacDiarmid A G 1966 *J. Am. Chem. Soc.* 1780 (d) Kuyper J and Vrieze K 1974 *J. Organomet. Chem.* **74** 289

4. (a) Appel R and Kohnke J 1970 *Chem. Ber.* **103** 2152 (b) Appel R and Kohnke J 1971 *Chem. Ber.* **104** 2648

5. (a) Wannagat U and Kuckertz H 1962 *Angew. Chem.* **74** 117 (b) Scherer O J and Wies R 1970 *Z. Naturforsch.* **B25** 1486 (c) Ruppert I, Bastian V and Appel R 1975 *Chem. Ber.* **108** 2329 (d) Kuyper J and Street G B 1977 *J. Am. Chem. Soc.* **99** 7848 (e) Haubold W, Fehlinger H G and Frey G 1981 *Z. Naturforsch.* **B36** 157

6. (a) Pauer F and Stalke D 1991 *J. Organomet. Chem.* **418** 127 (b) Pauer F, Rocha J and Stalke D 1991 *J. Chem. Soc., Chem. Commun.* 1477 (c) Edelmann F T, Knösel F, Pauer F, Stalke D and Bauer W 1992 *J. Organomet. Chem.* **438** 1 (d) Freitag S, Kolodziejski W, Pauer F and Stalke D 1993 *J. Chem. Soc., Dalton Trans.* 3479

7. Fleischer R and Stalke D 1998 *J. Organomet. Chem.* **550** 173

8. Fleischer R, Freitag S, Pauer F and Stalke D 1996 *Angew. Chem.* **108** 208; 1996 *Angew. Chem., Int. Ed. Engl.* **35** 204

9. Fleischer R, Freitag S and Stalke D 1998 *J. Chem. Soc., Dalton Trans.* 193

10. Brask J K, Chivers T, McGarvey B, Schatte G, Sung R and Boere R T 1998 *Inorg. Chem.* **37** 4633

11. Walfort B and Stalke D (unpublished results)

12. (a) Glemser O and Wegener J 1970 *Angew. Chem.* **82** 324; 1970 *Angew. Chem., Int. Ed. Engl.* **9** 309 (b) Glemser O, Pohl S, Tesky F M and Mews R 1977 *Angew. Chem.* **89** 829; 1977 *Angew. Chem., Int. Ed. Engl.* **16** 789

13. Lidy W, Sundermeyer W and Verbeek W 1974 *Z. Anorg. Allg. Chem.* **406** 228

14. (a) Herbrechtsmeier A, Schnepel F-M and Glemser O 1978 *J. Mol. Struct.* **50** 43 (b) Meij R, Oskam A and Stufkens D J 1979 *J. Mol. Struct.* **51** 37 (c) Markowskii L N, Tovstenko V I, Pashinnik V E, Mel'nichuk E A, Makarenko A G and Shermolovich Yu G 1991 *Zh. Org. Khim.* **27** 769 (transl.)

15. Fleischer R, Walfort B, Gbureck A, Scholz P, Kiefer W and Stalke D 1998 *Chem. Eur. J.* **4** 2266

16. Chivers T, Parvez M and Schatte G 1998 *J. Organomet. Chem.* **550** 213

17. Fleischer R and Stalke D 1998 *Organometallics* **17** 832

18. Walfort B and Stalke D (unpublished results)

19. (a) Brauer D J, Bürger H, Liewald G R and Wilke J 1986 *J. Organomet. Chem.* **305** 119 (b) Kosse P, Popowski E, Veith M and Huch V 1994 *Chem. Ber.* **127** 2103 (c) Hemme I, Klingebiel U, Freitag S and Stalke D 1995 *Z. Anorg. Allg. Chem.* **621** 2093

20. (a) Bürger H, Mellies R and Wiegel K 1977 *J. Organomet. Chem.* **142** 55 (b) Friedrich S, Gade L H, Edwards A J and McPartlin M 1993 *Chem. Ber.* **126** 1797 (c) Hellmann K W, Gade L H, Steiner A, Stalke D and Möller F 1997 *Angew. Chem.* **109** 99; 1997 *Angew. Chem., Int. Ed. Engl.* **36** 160 (d) Hellmann K W, Gade L H, Fleischer R and Stalke D 1997 *J. Chem. Soc., Chem. Commun.* 527

21. Beswick M A and Wright D S 1998 *Coord. Chem. Rev.* **176** 373

22. (a) Bremer N J, Cutcliffe A B, Farona M F and Kofron W G 1971 *J. Chem. Soc.* 3264 (b) Björgvinsson M, Roesky H W, Pauer F and Sheldrick G M 1992 *Chem. Ber.* **125** 767 (c) Chivers T, Gao X and Parvez M 1995 *Angew. Chem.* **107** 2756; 1995 *Angew. Chem., Int. Ed. Engl.* **34** 2549 (d) Chivers T, Parvez M and Schatte G 1996 *Inorg. Chem.* **35** 4094

23. (a) Hellmann K W, Gade L H, Fleischer R and Kottke T 1997 *Chem. Eur. J.* **3** 1801 (b) Brask J K, Chivers T, Parvez M and Schatte G 1997 *Angew. Chem.* **109** 2075; 1997 *Angew. Chem., Int. Ed. Engl.* **36** 1986

24. Fleischer R, Hofmann C, Ilge D, Walfort B and Stalke D (unpublished results)

25. Ilge D, Wright D S and Stalke D 1998 *Chem. Eur. J.* **4** 2275

26. Fleischer R, Rothenberger A and Stalke D 1997 *Angew. Chem.* **109** 1140; 1997 *Angew. Chem., Int. Ed. Engl.* **36** 1105

27. Walfort B and Stalke D (unpublished results)

28. Veith M, Spaniol A, Pöhlmann J, Gross F and Huch V 1993 *Chem. Ber.* **126** 2625