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Copper and Silver Triimidosulfites: $S(N^tBu)_3{}^{2-}$-Bicapped M_3-Triangles Connected via Lithium Halide Ladders or Fragments Thereof

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Starting from the dilithium triimidosulfite dimer $[Li_4\{(N^tBu)_3S\}_2]$, only three of the four lithium cations can be replaced by copper(I) cations in $[(thf)_2Cu_3Li_2I\{(N^tBu)_3S\}_2]$ (**1**). In the isomorphous silver complex $[(thf)_2Ag_3Li_2Br\{(N^tBu)_3S\}_2]$ (**2**), the cations are arranged in a triangle. Each metal is linearly coordinated by two imido nitrogen atoms, resulting in relatively short Cu···Cu (251.41 pm) and Ag···Ag (278.60 pm) distances. Two lithium cations are additionally coordinated to each $S(N^tBu)_3{}^{2-}$ cap. They pincer a single halide anion. $[(thf)Ag_3Li_2Br\{(N^tBu)_3S\}_2]_2$ (**3**) and $[(thf)_2Ag_3Li_3Br_2\{(N^tBu)_3S\}_2]_2$ (**4**) show an increasing content of lithium bromide. In **3** a two-rung and in **4** a four-rung LiBr ladder is terminated by a $LiM_3\{(N^tBu)_3S\}_2$ unit. In $[(thf)_2Li_3Cl\{(N^tBu)_3S\}]_2$ (**5**), no LiCl ladder extension is observed presumably because the $Li_2(N^tBu)_3S$ terminating moiety meets the requirements of the cubic LiCl solid-state lattice.

Introduction

Isoelectronic replacement of the oxygen atoms in the simple p-block element oxoanions by a NR imido group is currently a flourishing area of main group chemistry.[1] These species are soluble even in nonpolar organic solvents because unlike the simple oxoanions they form contact ion pairs in cage complexes surrounded by a lipophilic layer rather than infinite solid-state lattices by multiple oxygen/cation contacts. The cap-shaped geometry together with the steric demand of the nitrogen-bonded substituents should enable homoleptic metal complexes. So far we employed metal amides of alkaline earth metals (Mg, Ca, Ba) and tin[2] in deprotonation reactions. Different types of complexes are obtained in the reactions with $[thf_2M\{N(SiMe_3)_2\}_2]$ (M = Ca, Ba). While two lithium atoms are still present in the calcium derivative (eq 1), only one remains in the barium complex (eq 2). Hence, they exhibit different levels of transmetalation. In the calcium complex only half the equivalent of the present lithium cations is replaced by calcium dications, whereas 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 (Scheme 1).

$$[Li_4\{(N^tBu)_3S\}_2] + [thf_2Ca\{N(SiMe_3)_2\}_2] \xrightarrow{thf} 2\,LiN(SiMe_3)_2 + [(thf)_2CaLi_2\{(N^tBu)_3S\}_2] \quad (1)$$

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

The monomeric tin derivative is obtained in the analogous reaction of triimidosulfite with $[Sn\{N(SiMe_3)_2\}_2]$ (eq 3).

$$[Li_4\{(N^tBu)_3S\}_2] + [Sn\{N(SiMe_3)_2\}_2] \xrightarrow{thf} [(thf)LiSn\{N(SiMe_3)_2\}\{(N^tBu)_3S\}] \quad (3)$$

Results and Discussion

Preparation of the Copper and Silver Complexes 1−4. The structure of the triimidosulfite $[Li_4\{(N^tBu)_3S\}_2]$ and in particular the thf-coordinated $[(thf)Li_4\{(N^tBu)_3S\}_2]$ suggest that there is not quite enough space for the four lithium cations. The monovalent coinage metal cations should therefore give rise to different coordination polyhedra. In contrast to lithium they prefer linear 2-fold coordination. They should force the alkyl groups at nitrogen to be arranged in an eclipsed conformation rather than in a staggered one found in the lithium complexes. Coinage metal halides undergo transmetalation reactions with dilithium triimidosulfite. Although 4 equiv of copper iodide were used for complete transmetalation, only three of the four present lithium metal centers in the dimer of the starting material are replaced by copper (Scheme 2). In addition, 1 equiv of the eliminated lithium halide is cocoordinated to the periphery of the complex $[(thf)_2Cu_3Li_2I\{(N^tBu)_3S\}_2]$ (**1**) (Scheme 2).

Similar to the reaction of triimidosulfite with copper iodide, only three lithium cations in the dimer are

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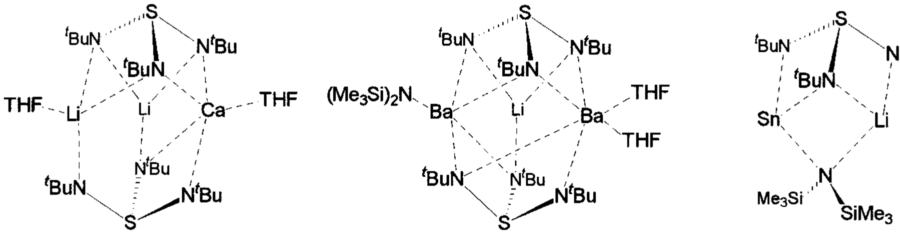
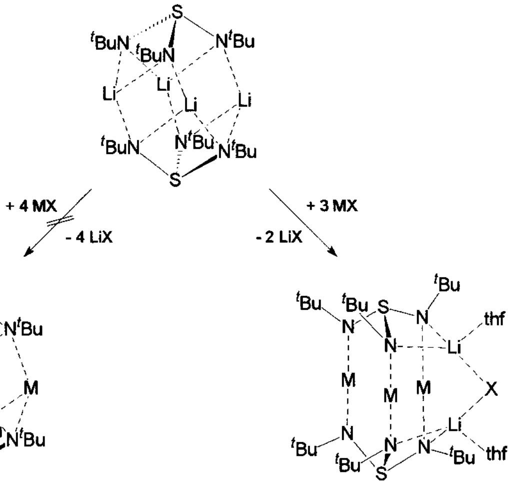
Scheme 1. Structures of the Transmetalation Products with M{N(SiMe$_3$)$_2$}$_2$ (M = Ca, Ba, Sn)

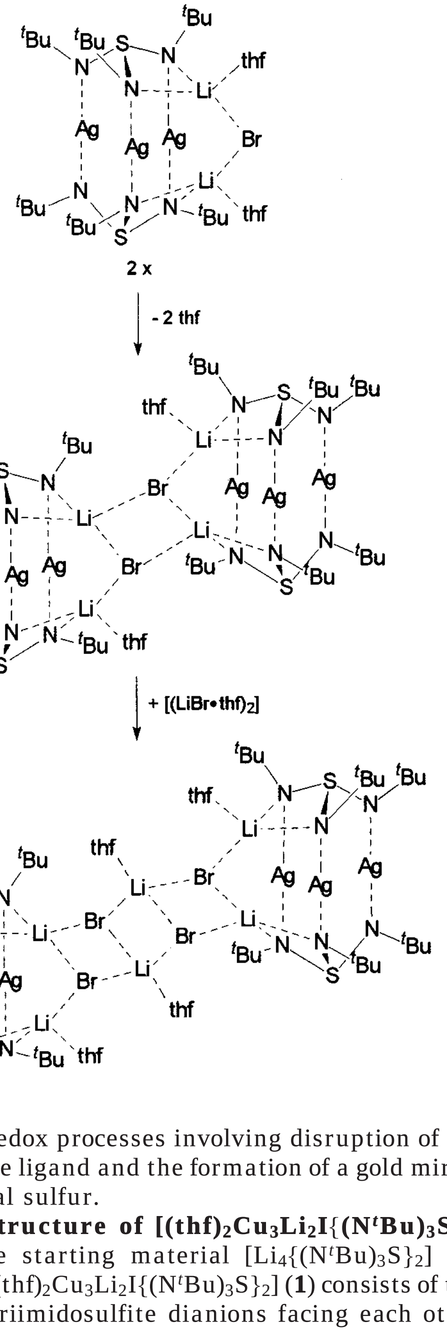


Scheme 2. Transmetalation of Triimidosulfite with CuI and AgBr



M = Cu (**1**), Ag (**2-4**); X = Br (**2-4**), I (**1**).

Scheme 3. Dimerization of 2 via a Li$_2$Br$_2$ Square and Insertion of [(thf·LiBr)$_2$]in 3



2

3

4

replaced by silver atoms in the reaction with silver bromide. The obtained silver complex [(thf)$_2$Ag$_3$Li$_2$Br{(N^{t}Bu)$_3$S}$_2$] (**2**) is isomorphous but not isostructural to **1**. However, **2** is by no means the only product from that reaction. LiBr, the product of the salt elimination, is reasonably well soluble in thf to give various [(thf·LiBr)$_n$] complexes.[3] To recover the silver complex from the reaction solution and to suppress formation of soluble lithium bromide, the thf has to be removed in a vacuum and to be replaced by a nondonating solvent like hexane. In correlation with the time and, hence, to the amount of soluble LiBr formed, different silver triimidosulfites co-complexed with lithium bromide are obtained. The longer the complex **2** is exposed to the mother liquor, the bigger the co-complexed LiBr moieties are. So far we retrieved three different silver triimidosulfites with increasing content of LiBr, and there is no obvious reason why there are not more present. While the monomeric complex **2** is isomorphous to **1**, [(thf)Ag$_3$Li$_2$Br{(N^{t}Bu)$_3$S}$_2$]$_2$ (**3**) can be rationalized as dimerized **2** by removing one donor base and switching the Li−thf contact to a Li−Br contact (Scheme 3). A central Li$_2$Br$_2$ four-membered ring is formed. Insertion of a [(thf·LiBr)$_2$] unit in the Li−Br bond of that four-membered ring gives [(thf)$_2$Ag$_3$Li$_3$Br$_2${(N^{t}Bu)$_3$S}$_2$] (**4**).

Unfortunately, the successful synthesis and isolation of the related gold compound has been precluded to date by complex redox processes involving disruption of the triimidosulfite ligand and the formation of a gold mirror and elemental sulfur.

Crystal Structure of [(thf)$_2$Cu$_3$Li$_2$I{(N^{t}Bu)$_3$S}$_2$] (1). Like the starting material [Li$_4${(N^{t}Bu)$_3$S}$_2$] the structure of [(thf)$_2$Cu$_3$Li$_2$I{(N^{t}Bu)$_3$S}$_2$] (**1**) consists of two cap-shaped triimidosulfite dianions facing each other with their concave site (Figure 1). The ^{t}BuN groups are eclipsed with respect to each other. The six nitrogen atoms complex three copper atoms. Each copper atom is coordinated linearly to two nitrogen atoms of opposite caps, as one would anticipate from the favored coordination of Cu(I). The additional η^2 coordination of a lithium cation to each cap forces the involved nitrogen atoms

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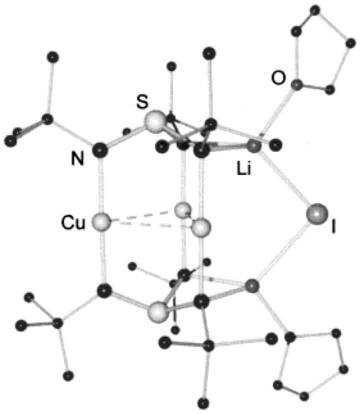

Figure 1. Crystal structure of $[(thf)_2Cu_3Li_2I\{(N^tBu)_3S\}_2]$ (**1**).

in closer proximity. The persistent linear N−Cu−N coordination enforces a relatively short distance between Cu2 and Cu3 (251.41(10) pm) compared to the average distance of 269.67(12) pm between the other copper atoms. The short distance is in the range of Cu⋯Cu distances caused by other A-frame ligands,[4] but considerably longer than η^2-bridged Cu⋯Cu distances.[5] As each copper atom is slightly pushed away from the others and the N−Cu−N angle of 177.8(2)° indicates electrostatic repulsion rather than metal $d^{10}-d^{10}$ closed shell attraction, this distance in **1** is not regarded a bond.[6]

The peripheral co-complexation of lithium cations induces severe asymmetries in the charge distribution of the triimidosulfite dianion. The S−N bonds coordinated by both metals are elongated because of the competition of both metals with the sulfur atom (av S−N(Cu,Li) 167.6(5) and av S−N(Cu) 160.7(5) pm). The same is valid for the copper−nitrogen distances. Additional lithium coordination causes them to elongate by 5 pm from av 187.6(5) pm in the Cu−N bonds to 192.6(6) pm in the Cu−N(Li) bonds. The longer distances almost exactly match those in the dinuclear copper organyl complex $[CuC(SiMe_3)_2C_5H_4N)]_2$ (191.0-(3) pm).[7] The shorter distances match those found in $[\{^tBuNTe(\mu\text{-}N^tBu)_2Te(\mu\text{-}O)\}_2\{Cu(H_2N^tBu)\}_2\{O_3SCF_3\}]$ (av 186.8(9) pm).[8] To maintain charge balance, both lithium atoms pincer a single iodide anion. A single donating thf molecule is coordinated to each lithium cation to give the preferred 4-fold coordination.

Crystal Structure of $[(thf)_2Ag_3Li_2Br\{(N^tBu)_3S\}_2]$ (2). The complex cores $[M_3\{(N^tBu)_3S\}_2]$ with M = Cu in **1** and M = Ag in $[(thf)_2Ag_3Li_2Br\{(N^tBu)_3S\}_2]$ (**2**) are very similar (Figure 2). Again, the eclipsed ^tBuN groups cause a linear coordination of each silver atom and forces them into a Ag_3 triangular arrangement with relatively short Ag⋯Ag distances. (N,N) chelation of a lithium cation to each cap forces the involved nitrogen atoms in closer contact and generates even shorter Ag⋯Ag distances (Ag2⋯Ag3 278.60(7) in comparison to 287.28(7) pm). While the difference between the short and long metal−metal distances is remarkable, 18 pm in **1**, it is only 9 pm on average in all silver complexes. However, both distances are in the range where $d^{10}-d^{10}$ interactions in silver complexes are regarded to be important. Like in **2** these close contacts are mainly supported by A-frame ligands like in $[Ag_2\{(Py)C(SiMe_3)_2\}_2]$ (265.4 pm),[9] $[Ag_2\{(Me_3Si)NC(Ph)N(SiMe_3)\}_2]$ (265.5 pm),[10] $[Ag_2\{PhNNNPh\}_2]$ (266.9 pm),[11] $[Ag_2\{(Pyz)_3BH\}_2]$ (279.6 pm),[12] and $[Ag_2\{(O_2)CPh\}_2]$ (290.2 pm).[13] Due to the bigger radius, the N−Ag−N angle of 171.83-(12)° in **2** is sharper than the related angle in **1**. Hence, each silver atom is even more buckled from the center of the Ag_3 triangle.

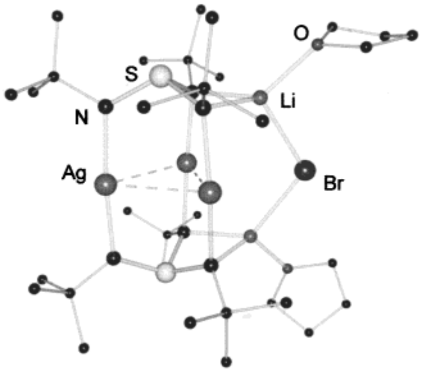

Figure 2. Crystal structure of $[(thf)_2Ag_3Li_2Br\{(N^tBu)_3S\}_2]$ (**2**).

Like in **1**, peripheral (N,N) chelation of lithium cations induces asymmetries in the charge distribution of the triimidosulfite dianion. While the difference in the S−N bond lengths of **2** is only 4.9 pm (6.3 pm in **1**), the divergence in the Ag−N distances of 8.4 pm is much more pronounced than that in **1** (5.0 pm). The softer silver cation tends not to polarize the dianion as much as the harder copper cation.

Aggregates $[(thf)Ag_3Li_2Br\{(N^tBu)_3S\}_2]_2$ (3) and $[(thf)_2Ag_3Li_3Br_2\{(N^tBu)_3S\}_2]_2$ (4). The molecular structure of $[(thf)Ag_3Li_2Br\{(N^tBu)_3S\}_2]_2$ (**3**) consists of a dimer around a Li_2Br_2 four-membered ring (Figure 3). Two $[Ag_3Li\{(N^tBu)_3S\}_2]$ subunits are connected by opposite sides of that square. The formation of lithium halide squares from in situ generated salts is quite common.[14] In thf, lithium bromide forms an infinite ladder. Depending on the nature of donating solvent the Li−X (X = F, Cl, Br, I) bonds from the infinite solid-state structures are broken. In a deintegration process, reminiscent of the interconversion process known from

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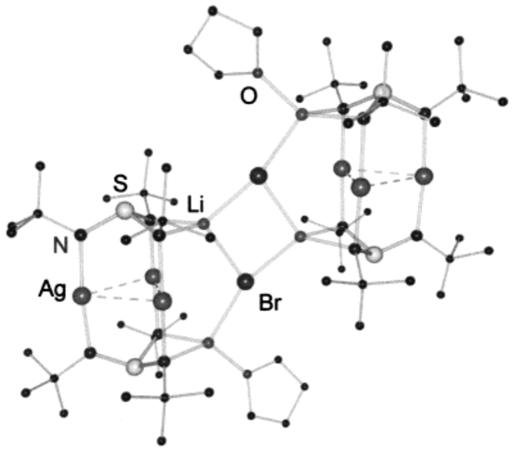

Figure 3. Crystal structure of $[(\text{thf})\text{Ag}_3\text{Li}_2\text{Br}\{(\text{N}^t\text{Bu})_3\text{S}\}_2]_2$ (**3**).

the ring stacking and laddering principle of lithium amides,[15] isolated squares or cubic structures of LiX are assembled.[16] The geometrical features of the $[\text{Ag}_3\text{Li}\{(\text{N}^t\text{Bu})_3\text{S}\}_2]$ cages are virtually the same in **2** and **3**. The Ag2···Ag3 distance in **3** in comparison to the other Ag···Ag distances is shortened by 8.8 pm to 278.60(7) pm and the (Li)N−Ag distances are on average 8.4 pm longer than those to the nonmetal-bridged nitrogen atoms. For further bond lengths and angles see Table 1.

The crystal structure of $[(\text{thf})_2\text{Ag}_3\text{Li}_3\text{Br}_2\{(\text{N}^t\text{Bu})_3\text{S}\}_2]_2$ (**4**) (Figure 4) can be rationalized to be an extension of **3**. A single insertion of a $[(\text{thf}\cdot\text{LiBr})_2]$ square in the Li−Br bond of the four-membered ring in **3** gives **4**. Hence, the Li_6Br_4 four-rung ladder is terminated by the $[\text{Ag}_3\{(\text{N}^t\text{Bu})_3\text{S}\}_2]^-$ anionic cages spanning the Li···Li diagonal of the terminal Li_2Br_2 squares. As the central lithium atoms Li3 and Li3a are not linearly coordinated by the two bromide atoms along the ladder spars and are additionally coordinated by a thf molecule each, the ladder is folded by an angle of 45.2° (angle between the Li3, Br2, Li3a, Br2a best plane and the Li1, Br1, Li3a, Br2a best plane). Of course, this ladder extension and shift of the silver triimido sulfite moieties has no effect on the geometrical parameters of the cages. The structural features are the same as above. For bond lengths and angles see Table 1.

Lithium Chloride Adduct $[(\text{thf})_2\text{Li}_3\text{Cl}\{(\text{N}^t\text{Bu})_3\text{S}\}]_2$ (5). From our work the dilithium triimidosulfite is known to be capable of co-coordinating various salts such as LiHal in $[(\text{thf})_3\text{Li}_3\text{I}\{(\text{N}^t\text{Bu})_3\text{S}\}]_2$[17] and $[(\text{thf})_3\text{Li}_3\text{Br}\{(\text{N}^t\text{Bu})_3\text{S}\}]_2$,[17] LiN_3 in $[(\text{thf})_3\text{Li}_3\text{N}_3\{(\text{N}^t\text{Bu})_3\text{S}\}]_\infty$,[18] or KO^tBu in $[(\text{thf})_2\text{Li}_2\text{K}(\text{O}^t\text{Bu})\{(\text{N}^t\text{Bu})_3\text{S}\}]_2$.[19] The Li···Li distances in this cap-shaped $\text{Li}_3(\text{N}^t\text{Bu})_3\text{S}^+$ cation are quite variable and depend on the radius of the coordinated anion (275 (S^{2-}),[20] 285 (N^{3-}),[18] 293 (Br^-),[17] 300 pm (I^-)[17]). The dilithium triimidoselenite $[\text{Li}_2\{(\text{N}t\text{Bu})_3\text{Se}\}]_2$[21] shows a similar property to co-coordinate lithium halides.[22]

The bromide and iodide adducts were isolated as intermediates in the oxidation reactions of triimidosulfite with bromine or iodine. In both cases the halide anion is η^3 coordinated to the three lithium atoms. The coordination sphere of the lithium atoms is completed by the η^2 coordination of the triimidosulfite dianion and one thf. Since the oxidation reaction with chlorine could not be controlled, the chloride adduct was not identified. Hence another synthetic route was adopted. The synthesis of triimidosulfite from sulfur diimide with 2 equiv of lithium *tert*-butylamide was attempted in the presence of *tert*-butylammonium chloride.

$$\text{S(N}^t\text{Bu)}_2 + 3\ {}^t\text{BuNHLi} \xrightarrow{{}^t\text{BuNH}_3\text{Cl/thf}} \underset{\mathbf{5}}{[(\text{thf})_2\text{Li}_3\text{Cl}\{(\text{N}^t\text{Bu})_3\text{S}\}]_2} + 2\ {}^t\text{BuNH}_2 \quad (4)$$

Storing of the reaction solution for several days at −36 °C affords colorless crystals of **5** suitable for X-ray structure determination. In contrast to the bromide or iodide adduct, the crystal structure shows a dimerization via a distorted Li_2Cl_2 square (Figure 5). Like for the heavier congeners the lithium atoms are η^2 coordinated by the triimidosulfite dianion, but only two lithium cations are coordinated to a thf molecule each, whereas the third lithium cation provides the link to a second chloride anion in the dimer. This coordination mode is known from the N_3^- adduct.[18] Consequently, the coordination sphere of Li1 and Li2 is tetrahedral, while Li3 is almost located in the base of a trigonal pyramid together with N2, N3, and Cl1A. Cl1 is the apex of that pyramid.

Thus formation of a dimeric structure in **5** is not an unusual feature. In comparison to its heavier homologues the chloride anion is a stronger Lewis base and prefers a coordination of four lithium cations.

Conclusion

The triimidosulfite dianion is electronically a very flexible ligand. It responds by shifting charge density in the SN_3 backbone to the different requirements induced by hard or soft metals.[23] (**A**) The electron density is delocalized equally over all three SN bonds in $[\text{Li}_2\{(\text{N}^t\text{Bu})_3\text{S}\}]_2$. (**B**) One formal double bond and two amidic nitrogen atoms could be found in **1**−**4**, $[(\text{thf})\text{LiSn}\{\text{N}(\text{SiMe}_3)_2\}\{(\text{N}^t\text{Bu})_3\text{S}\}]$, and $[(\text{thf})_2\text{CaLi}_2\{(\text{N}^t\text{Bu})_3\text{S}\}_2]$.[2]

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Table 1. Selected Bond Lengths (pm) and Angles (deg) for 1−4[a]

M = Cu, Ag	**1**	**2**	**3**	**4**
S−N(M)	160.8(5)	162.5(6)	160.7(8)	162.6(9)
S−N(M,Li)	167.6(6)	167,8(6)	166.9(8)	168.7(9)
(N)M−M(N,Li)	269.75(12)	287.28(7)	286.55(12)	289.25(11)
(N,Li)M−M(N,Li)	251.41(10)	278.60(7)	277.42(11)	279.92(10)
(M)N−M(N)	187.6(5)	209.7(5)	210.8(8)	210.6(8)
(M,Li)N−M(N,Li)	192.6(6)	218.1(6)	214.6(7)	218.3(8)
Li−N(M,Li)	208.0(10)	207.9(13)	206.2(19)	206.4(18)
N−M−N	177.8(2)	171.83(12)	171.9(3)	171.5(3)
(M)N−S−N(M,Li)	109.4(3)	109.9(3)	110.0(5)	110.3(4)
(M,Li)N−S−N(M,Li)	93.0(3)	94.2(3)	94.1(4)	93.5(4)
(N)M−M(N,Li)−M(N,Li)	62.22(3)	61.021(18)	60.99(6)	61.02(3)
(N,Li)M−M(N)−M(N,Li)	55.56(3)	58.010(17)	58.02(3)	57.87(3)

[a] Bond lengths and angles of chemically identical subgroups are averaged.

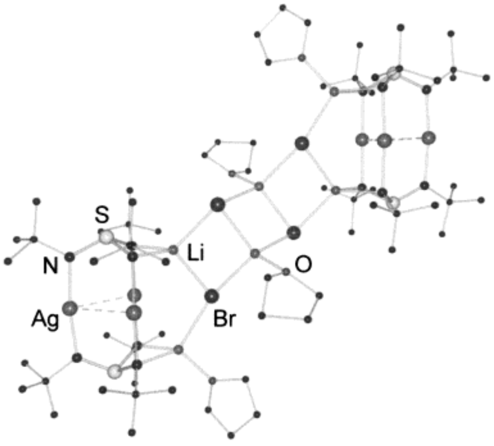

Figure 4. Crystal structure of [(thf)$_2$Ag$_3$Li$_3$Br$_2${(N^{t}Bu)$_3$S}$_2$]$_2$ (**4**).

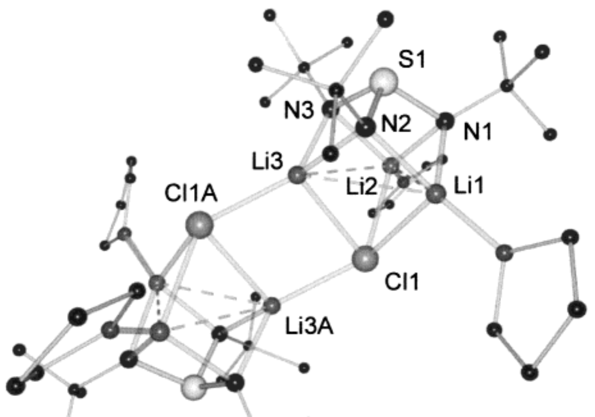

Figure 5. Crystal structure of [(thf)$_2$Li$_3$Cl{(N^{t}Bu)$_3$S}]$_2$ (**5**).

(**C**) An examples with one long and two short SN distances is [(thf)$_2$Ba$_2$Li{N(SiMe$_3$)$_2$}{(N^{t}Bu)$_3$S}$_2$] (Chart 1).[2]

The coordination of the triimidosulfite ligand is mainly dominated by the metals. With main group metal cations, which might be described as point charges, the imido substituent tends to coordinate μ_2. With coinage metal a linear orbital controlled coordination is observed.

In compounds with two triimidosulfite dianions the relative position to each other depends nearly on the amount of metals, coordinated between the two ligands. With three cations they are eclipsed and with four they are staggered to each other (Scheme 4).

In all known complexes of this type the anion is η^3 coordinated by three lithium cations. In the azide and the chloride adduct further dimerization (Cl$^-$) or polymerization (N$_3$$^-$) is observed.

The Li···Li distances in the cap-shaped [Li$_3$(N^{t}Bu)$_3$S]$^+$ cation are quite variable and depend on the radius of the coordinated anion (263 (H$_3$C$^-$),[24] 265 (H$_2$CCHO$^-$),[25] 275 (S^{2-}),[20] 285 (N^{3-}),[18] 292 (Cl$^-$) **5**, 293 (Br$^-$),[17] 300 pm (I$^-$)[17]). This flexibility demonstrates the impressive application of the cationic ligand.

In **3**, **4**, and **5** lithium halide ladders of various extensions are formed. The (LiCl)$_2$ subunit in **5** is terminated by a neutral Li$_2$(N^{t}Bu)$_3$S moiety at opposite sites. In **3** and **4** the terminating group is a LiM$_3${(N^{t}Bu)$_3$S}$_2$ unit. The first suits the requirements of the cubic LiCl solid-state lattice quite well by forming a cubic SN$_3$Li$_3$Cl terminating group, while the S-bicapped trigonal prismatic coinage metal complex in **3** and **4** is inappropriate to mimic the LiBr solid-state structure. This might be the reason why LiBr ladder extension is observed while LiCl laddering is precluded (Scheme 5).

Experimental Section

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.

NMR data were obtained from Bruker AMX 400 and Bruker AMX 300 instruments in the FT mode in C$_6$D$_6$ solvent. Elemental analyses were performed by the Mikroanalytisches Labor der Universität Würzburg.

[(thf)$_2$Cu$_3$Li$_2$I{(N^{t}Bu)$_3$S}$_2$] (1). To a suspension of 1 g (5.25 mmol) of CuI in 15 mL of thf was added dropwise a solution of (1.31 mmol, 0.78 g) [(thf)Li$_2${(N^{t}Bu)$_3$S}]$_2$ in 20 mL of thf and stirred for 1 h. Thf was removed in a vacuum, and the resulting white precipitate was dissolved in cold hexane. The remaining white precipitate (LiI) was removed by filtration. Storage of the clear solution at −36 °C for 3 days affords colorless crystals of **1**, which were suitable for X-ray structure determination (0.8 g, 63%). ^{1}H NMR (300.4 MHz, C$_6$D$_6$): δ 1.24 (m, 8 H, thf), 1.43,1.48 (2 s, 54 H, C(CH$_3$)), 3.70 (m, 8 H, thf). ^{13}C NMR (100 MHz, C$_6$D$_6$): δ 26.09, 69.46 (thf), 35.30, 35.98 (C(CH$_3$)$_3$), 57.05, 57.74 (C(CH$_3$)$_3$). ^{7}Li NMR (155.5 MHz, ext. sat. LiCl solution): δ 1.16. Anal. Calcd (%): C 39.77, H 7.30, N 8.70, S 6.63. Found: C 40.12, H 7.18, N 8.55, S 6.38.

[(thf)$_2$Ag$_3$Li$_2$Br{(N^{t}Bu)$_3$S}$_2$] (2), [(thf)Ag$_3$Li$_2$Br{(N^{t}Bu)$_3$S}$_2$]$_2$ (3), and [(thf)$_2$Ag$_3$Li$_3$Br$_2${(N^{t}Bu)$_3$S}$_2$]$_2$ (4). To

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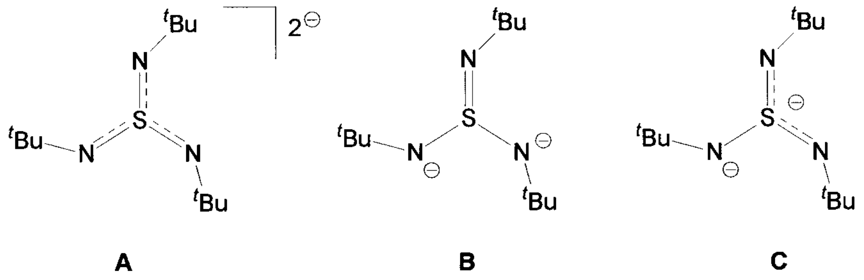
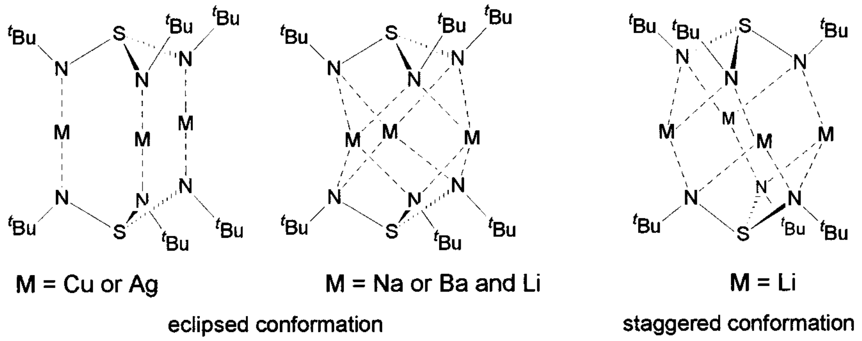
Table 2. Selected Bond Length (pm) and Angles (deg) of [(thf)$_2$Li$_3$Cl{(N^{t}Bu)$_3$S}]$_2$ (5)

S1−N1	166.4(2)	S1−N2	165.5(2)	S1−N3	165.8(2)
N1−Li1	200.7(5)	N1−Li2	207.3(5)	N2−Li1	208.4(6)
N2−Li3	199.1(5)	N3−Li3	210.0(5)	N3−Li2	199.1(5)
Li1−Cl1	248.4(5)	Li2−Cl1	253.2(5)	Li3−Cl1	253.2(5)
Li3−Cl1A	235.5(5)				
N1−S1−N2	100.76(12)	N2−S1−N3	100.55(12)	N3−S1−N1	99.49(11)
Cl1A-Li3−Cl1	101.45(17)	Li3−Cl1−Li3A	78.55(18)		

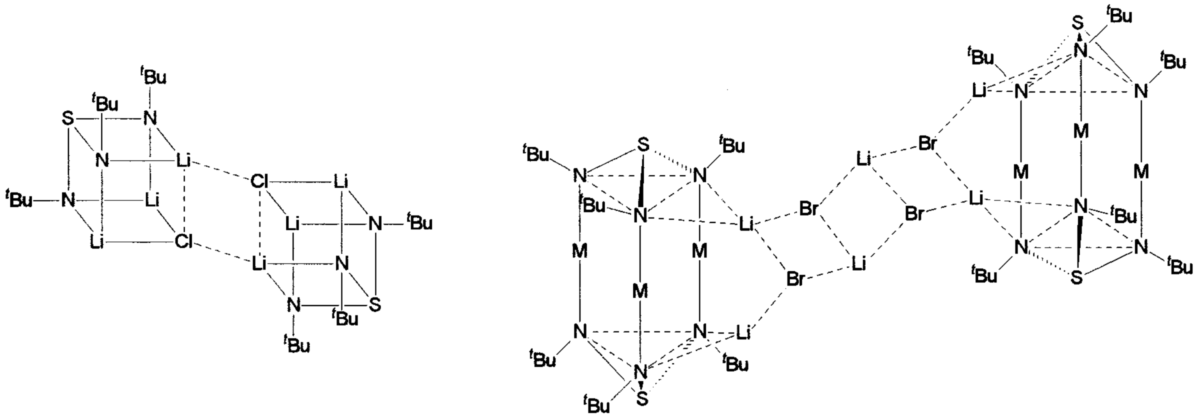
Chart 1



Scheme 4. Relative Position of Two Triimidosulfite Dianions Depending on the Number and Nature of Coordinated Metal Cations between the Two Ligands



Scheme 5. Terminating Groups for Lithium Halide Ladders



a suspension of 1 g (5.33 mmol) of AgBr in 15 mL of thf was added dropwise a solution of (1.33 mmol, 0.78 g) [(thf)Li$_2$-{(N^{t}Bu)$_3$S}]$_2$ in 20 mL of thf and stirred for 1 h. Thf was removed in a vacuum, and the white precipitate was resolved in cold hexane. The remaining white precipitate (LiBr) was removed by filtration. Storage of the solution at −36 °C for 3 days affords colorless crystals of **2**. After some time crystals of **3** and **4** with identical morphology to those of **2** were recovered from the same flask. The NMR spectra of the bulk material afford the same chemical shifts for all compounds present in the flask. Apparently the increasing content of LiBr in the compounds **2**−**4** has no impact on the chemical shifts of the organic periphery. The integration of the ^{1}H NMR spectrum of the bulk material indicates a ratio of thf to ^{t}Bu of 1:4. ^{1}H NMR (300.4 MHz, C$_6$D$_6$): δ 1.39 (m, 8H, thf), 1.58, 1.60 (2 s, 54 H, C(CH_3)), 3.67 (m, 8 H, thf). ^{13}C NMR (100 MHz, C$_6$D$_6$): δ 25.65, 68.25 (thf), 35.54, 35.61 (C(CH$_3$)$_3$), 55.96, 56.97 (C(CH$_3$)$_3$).

[(thf)$_2$Li$_3$Cl{(N^{t}Bu)$_3$S}]$_2$ (5). To a solution of (17.20 mmol, 3.0 g) S(N^{t}Bu)$_2$ and (17.20 mmol, 1,88 g) ^{t}BuNH$_3$Cl in 20 mL of thf was added dropwise a solution of (34.40 mmol, 2.68 g) ^{t}BuNHLi in thf at −78 °C. Half of the thf was removed in a vacuum. Storage of the solution at −36 °C for several days affords colorless crystals (1.5 g, 44%) which were suitable for X-ray structure determination. ^{1}H NMR (300.4 MHz, C$_6$D$_6$): δ 1.37 (m, 12H, thf), 1.57 (s, 54H, C(CH_3)), 3.72 (m, 12 H, thf). ^{13}C NMR (100 MHz, C$_6$D$_6$): δ 25.47, 68.39 (thf), 34.45 (C(CH$_3$)$_3$), 53.24 (C(CH$_3$)$_3$). ^{7}Li NMR (155.5 MHz, ext. sat. LiCl solution): δ 1.80. Anal. Calcd (%): C 53.87, H 9.72, N 9.43, S 7.19. Found: C 53.67, H 9.89, N 9.04, S 7.08.

Crystal Structure Determinations. Crystal data for the structures **1**−**5** are presented in Table 3. Data for structures

Table 3. Crystal Data and Structure Refinement for Complexes 1−5 at $T = 173(2)$ K

	1	**2**	**3**	**4**	**5**
empirical formula	$C_{32}H_{70}Cu_3ILi_2N_6O_2S_2$	$C_{32}H_{70}Ag_3BrLi_2N_6O_2S_2$	$C_{60}H_{132}Ag_6Br_2Li_4N_{12}O_3S_4$	$C_{32}H_{70}Ag_3Br_2Li_2N_6O_2S_2$	$C_{23}H_{50}ClLi_3N_3O_2S$
M	966.46	1052.46	2032.82	1139.31	488.99
CCDC no.	176 505	176 506	176 507	176 508	176 509
cryst syst	orthorhombic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	*Pbcn*	$P2_1/c$	$Pca2_1$	$P2_1/c$	$P2_1/n$
a (pm)	4030.5(8)	1885.62(18)	2232.2(5)	1226.60(9)	1037.54(10)
b (pm)	1241.4(3)	1880.56(17)	1954.7(4)	1073.36(8)	17.3973(16)
c (pm)	1777.2(4)	1279.31(12)	1963.4(4)	3652.9(3)	17.1851(16)
β (deg)	90	99.559(2)	90	94.352(3)	91.152(2)
V (nm^3), Z	8892(3)	4473.5(7)	8567(3)	4795(6)	3101.4(5)
D_c (Mg m^{-3})	1.444	1.565	1.576	1.578	1.074
μ (mm^{-1})	2.243	2.320	2.419	2.998	0.211
$F(000)$	3984	2136	4112	2288	1068
cryst size (mm)	0.4 × 0.3 × 0.2	0.4 × 0.3 × 0.3	0.4 × 0.4 × 0.3	0.4 × 0.4 × 0.3	0.4 × 0.4 × 0.3
θ range (deg)	2.23−24.12	1.54−26.58	2.10−24.74	1.12−24.71	1.67−26.48
no. of reflns collected	37 894	11 563	56 554	11 253	33 463
no. of ind reflns	7074	11 563	7539	7338	6359
R(int)	0.0983	0.0362	0.1166	0.0966	0.0587
no. of data/restraints/ params	7074/370/553	11595/252/521	7539/608/951	7338/115/473	5310/382/400
goodness of fit on F^2	0.808	0.941	1.032	1.047	1.150
R1 [$I > 2\sigma(I)$]	0.0478	0.0438	0.0416	0.0721	0.0764
wR2 (all data)	0.1183	0.1183	0.1063	0.2047	0.1875
Flack x[29]			0.37(4)		
g1, g2	0.0671/0.0000	0.0629/0.0000	0.0840/0.0000	0.1312/8.4046	0.1000
largest diff peak and hole (e nm^{-3})	608/−896	994/−710	1139/−1278	2003/1252	587/−27

1 and **3** were collected on a Stoe IPDS and for **2**, **4**, and **5** on a Bruker Smart Apex with a D8 goniometer at low temperature using oil-coated shock-cooled crystals[26] using Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS 97.[27] The structures were refined by full-matrix least-squares procedures on F^2, using SHELXL 97.[28] 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: $R1 = \sum||F_o| - |F_c|/\sum|F_o|$ and $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = 1/\{\sigma^2(F_o^2) + (g_1P)^2 + g_2P\}$; $P = (F_o^2 + 2F_c^2)/3$.

In complex **1** the disordered iodine atom was refined with distance restraints to a split occupancy of 0.60/0.40. The disordered thf molecules in **1** coordinated to Li1 and Li2 were refined using distance and adp restraints to split occupancies of 0.34/0.66 and 0.69/0.31. Compound **2** crystallized as a second-order partial merohedral twin. The two domains were determined via RLATT and integrated separately. The disordered thf molecules coordinated to Li1 and Li2 were refined using distance and adp restraints to split occupancies of 0.68/0.32 and 0.51/0.49, respectively. The disordered thf molecules in **3** coordinated to Li2 and Li4 were refined using distance and adp restraints to split occupancies of 0.71/0.29 and 0.75/0.25, respectively. The disordered thf molecule in **4** coordinated to Li3 was refined with distance and adp restraints to split occupancies of 0.26/0.47/0.27. The disordered thf molecules in **5** coordinated to Li1 and Li2 were refined using distance and adp restraints to split occupancies of 0.75/0.25 and 0.43/0.57, respectively. Other crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication (CCDC numbers see Table 3). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) + 44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk].

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Supporting Information Available: Five X-ray crystallographic files are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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