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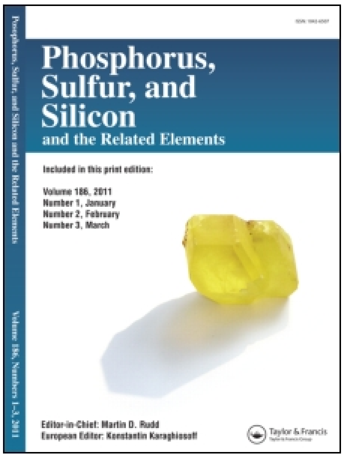

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SELF-ASSEMBLY OF QUATERNARY (LiOSN) CLUSTERS

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The reaction of RNSO with $LiNH^tBu$ produces the hexamers $\{Li_2[SO(N^tBu)(NR)]\}_6$. These thirty-six atom ($Li_{12}S_6O_6N_{12}$) clusters adopt novel structural arrangements derived from (a) the aggregation of three $Li_4S_2O_2N_4$ hexagonal prisms via their Li_2O_2 faces (R = ^tBu) or (b) the dimerization of two $Li_6S_3O_3N_6$ eighteen atom cages *via* their Li_3O_3 faces (R = $SiMe_3$).

Keywords: clusters; self-assembly; diazasulfites

INTRODUCTION

Cluster compounds have played an important role in the development of main group element chemistry.[1] The imido (NR) ligand is a versatile cornerstone for the construction of cluster molecules as exemplified by the series of binary clusters $(RAlNR')_n$, where n may be 4 (cubane), 6 (hexagonal prism) (See Fig. 1), 7 or 8 depending on the steric requirements of the R and R′ groups.[2] The NR ligand is also a well established feature of group 14 clusters, notably those of the type $(MN^tBu)_4$ (M = Ge, Sn, Pb) with a cubane structure.[3]

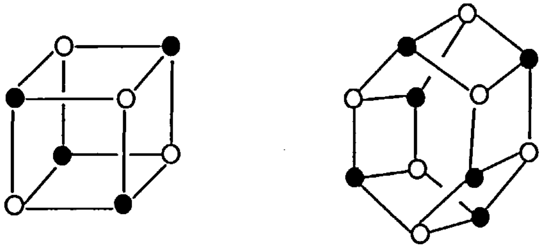


FIGURE 1 (a) Cubane and (b) Hexagonal Prism
(● = AlR, ○ = NR)

The oxo ligand (O) is isoelectronic with an NR group, but the lack of a bulky group on this cluster atom can result in significant structural differences. For example, alumoxanes $(^tBuAlO)_n$ adopt an eighteen atom cage structure (Fig. 2), in addition to the well known hexagonal prism (n = 6).[4] Like iminoalanes $(RAlNR')_n$, there is spectroscopic evidence for higher oligomers (n > 9), but structural characterization is not available.

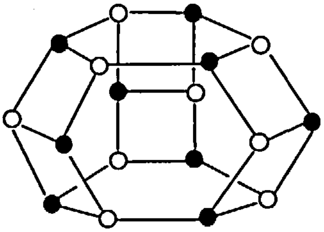
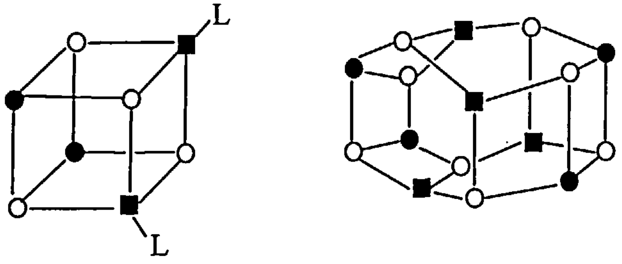


FIGURE 2 Eighteen atom cage of $(^tBuAlO)_9$
(● = Al^tBu, ○ = O)

Recently, attention has been focused on homoleptic polyimido anions of the p-block elements, $E(NR)_x^{y-}$, which are most commonly obtained as lithium derivatives.[5-7] In some cases these ternary clusters adopt unique structures based on the well known building blocks of binary clusters. For example, the unsolvated dimer $\{Li_2Sb_2(NCy)_4\}_2$ may be viewed to result from face-to-face dimerization of two cubes (see Fig. 3). By contrast, the solvation of each Li atom by a THF molecule in the bismuth analogue $[Li_2Bi_2(N^tBu)_4]\cdot 2THF$ precludes the self-aggregation of the simple cubane structure.[7]

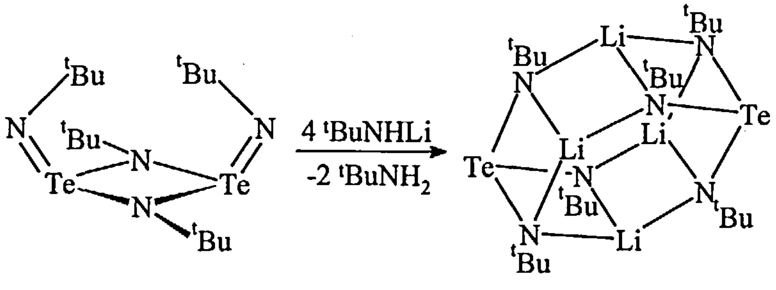


(a) (b)

FIGURE 3 Schematic structures of
(a) $Li_2Bi_2(N^tBu)_4\cdot 2THF$ and
(b) $[Li_2Sb_2(NCy)_4]_2$
(● = Bi/Sb, ○ = NR, ■ = Li, L = THF)

THE HEXAGONAL PRISMS $\{Li_2[E(N^tBu)_3]\}_2$ (E = Te, Se, S)

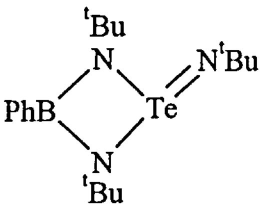
Two years ago we described the synthesis and structure of the ternary cluster $\{Li_2[Te(N^tBu)_3]\}_2$ (**1a**) according to Eq. (1).[8] Crystals of the unsolvated cluster were obtained from toluene.



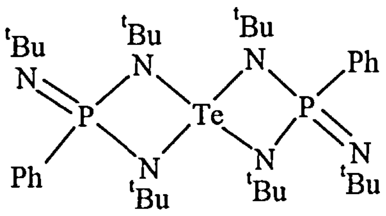
(1)

1a

The cluster **1a** contains the novel polyimido anion $[Te(N^tBu)_3]^{2-}$, a potentially versatile ligand for the incorporation of other main group elements or transition metals into Te-N ring systems. For example, the reactions of **1a** with $PhBCl_2$ or $PhPCl_2$ produce the four-membered BN_2Te ring **2** or the spirocyclic Te(IV) system **3**, respectively.[8]



2



3

Subsequent to the discovery of **1a**, the sulfur and selenium analogues (**1b** and **1c**) have been obtained in a similar manner [Eq. (2)].[9,10]

$$2\ {}^tBuN = E = N^tBu \xrightarrow[-2\ {}^tBuNH_2]{4\ {}^tBuNHLi} \{Li_2[E(N^tBu)_3]\}_2 \quad (2)$$

1b (E = S), **1c** (E = Se)

The structures of **1a-c** can be viewed as cyclic, six-runged ladders by analogy with the proposed aggregation of lithium anilide, $(PhNHLi)_6$.[11] Alternatively, the novel cluster molecules **1a-c** may be depicted as distorted hexagonal prisms in which the pyramidal $[E(N^tBu)_3]^{2-}$ ions are linked by four Li ions. Hexagonal prismatic structures based on A_6X_6 clusters (where X = NR) include $(RAlNR')_6$[2] and $[(thf)MgNPh]_6$.[12] The clusters **1a-c** are the first examples of hexagonal prisms with an $A_4B_2X_6$ core.

THE HEXAMERS $\{Li_2[S(O)(NR)(NR')]\}_6$

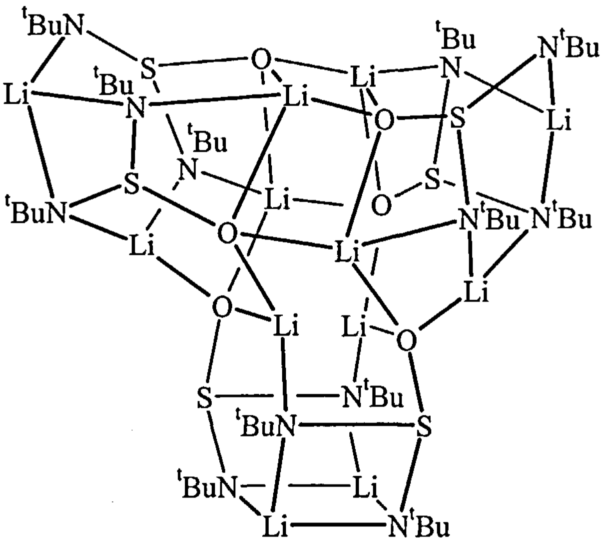
In order to determine the structural consequences of replacing bulky N^{t}Bu groups in **1b** by oxygen atoms, we have investigated the reaction of thionylamines, RNSO (R = ^{t}Bu, SiMe$_3$), with two molar equivalents of ^{t}BuNHLi in toluene [(Eq. 3)]. These reactions provide excellent yields of the novel cluster compounds **4a** and **4b**, which contain the pyramidal $[S(O)(NR)(NR')]^{2-}$ anions, i.e. di-aza derivatives of sulfite, SO_3^{2-}.[13]

$$RNSO + 2\,R'NHLi \rightarrow 1/6\ \{Li_2[S(O)(NR)(NR')]\}_6 \qquad (3)$$

4a, R = R′ = ^{t}Bu

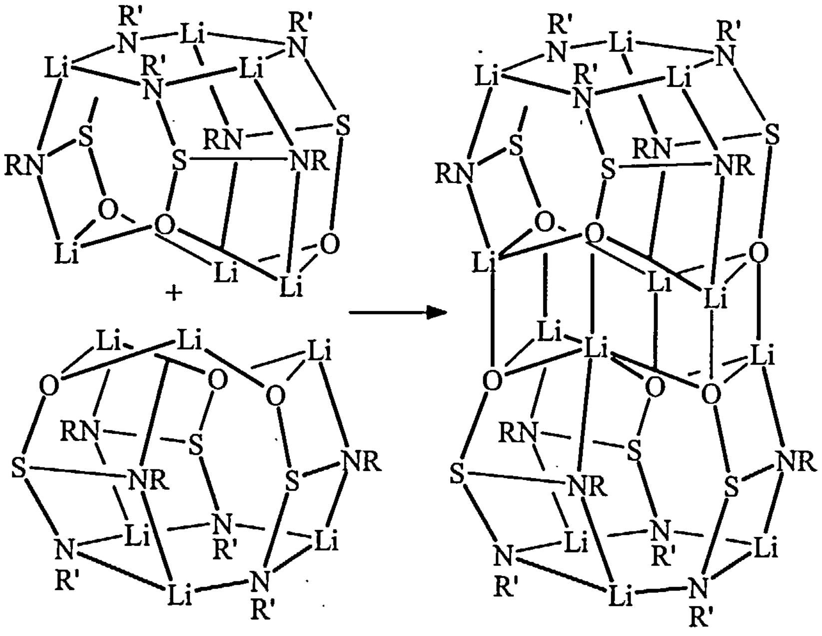
4b, R = ^{t}Bu, R′ = SiMe$_3$

An X-ray structural determination of **4a** revealed a remarkable thirty-six atom cluster with the composition $Li_{12}S_6O_6N_{12}$. The formation of this hexamer involves the self-assembly of three $Li_4S_2O_2N_4$ hexagonal prisms *via* their Li_2O_2 faces.



4a

The derivative **4b** was also shown to be a hexamer by X-ray crystallography but, in this case, the unique thirty-six atom cluster results from the **dimerization** of two $Li_6S_3O_3N_6$ cages (see Fig. 4). The crystal structure exhibited disorder in which N-bonded silicon and carbon atoms were scrambled over all positions. However, the ^{7}Li NMR spectrum of **4b** in C_7D_8 at 23°C shows four well resolved resonances of approximately equal intensity and the ^{1}H NMR spectrum shows two equally intense resonances for the ^{t}Bu as well as for the $SiMe_3$ groups. In view of the S_6 symmetry of this $Li_{12}S_6O_6N_{12}$ cluster, the NMR data indicate the presence of two isomers **4b′** and **4b″** in solution in approximately equal amounts.



4b', (R = ^{t}Bu, R' = $SiMe_3$)
4b", (R = $SiMe_3$, R' = ^{t}Bu)

FIGURE 4 Schematic representation of the dimerization of $Li_6S_3O_3N_6$ cages to form **4b**.

SUMMARY

The dilithium derivatives of the novel diazasulfite ions $[OS(N^tBu)(NR)]^{2-}$ (R = ^{t}Bu, $SiMe_3$) are hexameric and represent the first examples of main group element clusters formed by the aggregation of either hexagonal prisms (R = ^{t}Bu) or eighteen atom cages (R = $SiMe_3$). The self-assembly of these hexamers is envisaged to occur through the aggregation of smaller clusters via

their Li_xO_x faces (x = 2 or 3, respectively). Consequently, the replacement of two NR groups in $[S(NR)_3]^{2-}$ by two oxygen atoms is likely to produce more highly associated clusters.

Acknowledgements

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