Preparation and Crystal Structure of a Novel Lithium Thiolate Cluster: $[Li_{14}(SCH_2Ph)_{12}S(TMEDA)_6]$ (TMEDA = tetramethylethylenediamine)

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The title compound, simply prepared from benzyl mercaptan, n-butyl-lithium, and TMEDA in toluene (TMEDA = tetramethylethylenediamine), crystallises as an unusual type of cluster, in which a central S atom is surrounded by a distorted cube of Li atoms, each edge of which is bridged by a benzyl thiolate group such that the twelve S atoms form a cubo-octahedron; a further six Li atoms form a large outer octahedron, each one sitting above an S–S edge, with tetrahedral co-ordination completed by a TMEDA molecule.

Organolithium compounds have been used as *in situ* reagents for organic synthesis and recently, as an aid to a better understanding of the nature of these reactions, many lithium structures have been examined, particularly those containing Li–C, Li–N, and Li–O bonds.[1] Investigations of Li–S compounds have been more limited[2,3] and reported structures have often been dimeric. We recently[2] reported the structures of three aryl thiolates in which a minor modification in the aryl composition (CH_2 insertion) caused major structural change. In the presence of pyridine, the *o*-thiocresol derivative $[o\text{-}MeC_6H_4SLi{\cdot}(NC_5H_5)_3]$ (**1**) crystallises as a monomer, but removal of the *ortho*-methyl group allows growth to an infinite chain $[PhSLi{\cdot}(NC_5H_5)_2]_\infty$ (**2**). The even less hindered benzyl compound $[PhCH_2SLi{\cdot}NC_5H_5]_\infty$ (**3**), crystallises as an unusual folded ladder.

Organolithium compounds often show enhanced reactivity when used in tetramethylethylenediamine (TMEDA).[4] We have investigated the reaction of benzyl mercaptan and n-butyl-lithium in the presence of TMEDA, particularly when the molar ratio TMEDA : Li is 1 : 2 (*i.e.* two NC_5H_5 ligands in the compounds previously investigated replaced by TMEDA). Since in the ladder polymer (**3**), pyridine molecules co-ordinate alternately on opposite sides of the ladder, we hoped to modify or restrict the oligomerisation. We now report the preparation and *X*-ray crystal structure of the complex $[Li_{14}(SCH_2Ph)_{12}S(TMEDA)_6]$ (**4**), formed from benzyl mercaptan and n-butyl-lithium using TMEDA as a co-ordinating ligand.

Addition of n-butyl-lithium to $PhCH_2SH$ and TMEDA (molar ratio Bu^nLi : TMEDA 2 : 1) in toluene, produces a deep orange colour at the point of addition. This colour is probably due to the dilithiation of $PhCH_2SH$ and disappears

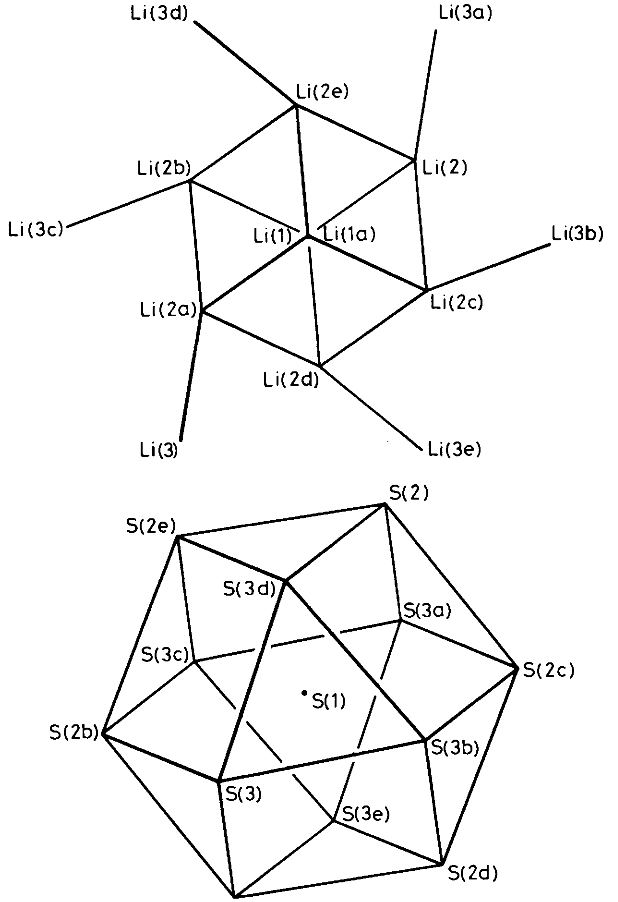

Figure 1. The arrangements of the lithium atoms and of the sulphur atoms in the molecule of (**4**); both are shown in projection along the S_6 ($\bar{3}$) axis. Lines drawn between atoms indicate the shapes of the polyhedra, and do not imply direct bonding.

on stirring. It becomes permanent only on adding Bu^{n}Li beyond equimolar proportions (with respect to thiol). As expected, addition in the reverse order (PhCH$_2$SH to Bu^{n}Li) produces an orange colour with the first drop of thiol; this deepens with further addition and disappears on adding the final drops. Complex (**4**) was prepared by dropwise addition of benzyl mercaptan (10 mmol) to a chilled (−20 °C) solution of TMEDA (5 mmol) and Bu^{n}Li (11 mmol) in toluene (10 cm^3). Warming slowly to room temperature precipitated an orange solid which failed to dissolve in excess of toluene. On filtering, the colour disappeared leaving a white solid and a pale straw coloured filtrate, which, on cooling, deposited small colourless crystals of (**4**), m.p. 180—182 °C. Further preliminary experiments [following the structure determination of (**4**)] suggested that the small (10%) excess of Bu^{n}Li caused the formation of a small amount of an unstable dilithiated product, probably PhCHSLi$_2$ (orange), which decomposed during reaction and filtration to give Li$_2$S. The latter provides sulphur for the centre of the cluster (**4**), which can also be expressed as [(PhCH$_2$SLi)$_{12}$(Li$_2$S)(TMEDA)$_6$]. To date, the orange compound, prepared by addition of benzyl mercaptan (5 mmol) to Bu^{n}Li (10 mmol), and TMEDA (2.5 mmol) in toluene, has proved too unstable to isolate.

^{7}Li High field n.m.r. spectra at 20 °C in [^{2}H$_8$]toluene solutions show two peaks, indicating the presence of two types of lithium environment. It seems likely, therefore, that the cluster retains its integrity in solution.

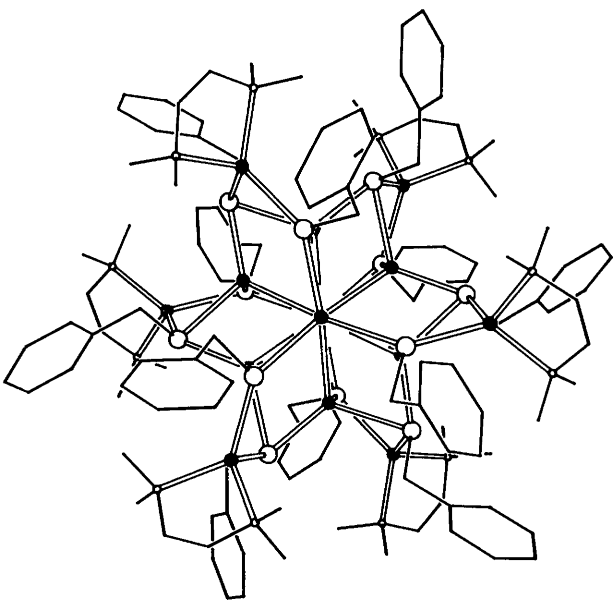

Figure 2. The molecular structure of (**4**) seen along the S_6 axis: ● Li atoms, ○ S atoms, ∘ N atoms, double lines indicate bonds to Li, H atoms omitted.

An *X*-ray crystal structure determination† showed that (**4**) is a hitherto unknown type of Li–S cluster with a single S atom at the centre of a distorted cube of lithium atoms, each of the 12 edges of the cube bridged by a SCH$_2$Ph unit such that these 12 S atoms form a cubo-octahedron. The 12 sulphur atoms are bridged in pairs by an Li–TMEDA unit, these six Li atoms forming an outer octahedron. Figure 1 shows the lithium and sulphur atom arrangements, and Figure 2, the complete molecular structure. The central cluster can alternatively be described as a fragment of a cubic close packed array of 13 sulphur atoms with 8 lithium atoms in the tetrahedral interstices. This is equivalent to the arrangement of lithium and sulphur atoms in the antifluorite structure of Li$_2$S, where there is an approximately cubic close packed array of S^{2-} ions with Li$^+$ ions in the tetrahedral holes.[5]

The Li–S bond lengths between the central S atom and the cube Li atoms are 2 × 2.50(2) and 6 × 2.55(2) Å (av. 2.54 Å), while those from the cube Li atoms to the thiolate S atoms in the cubo-octahedron are 4 × 2.52(1), 4 × 2.46(1), 4 × 2.47(1), and 4 × 2.44(1) Å (av. 2.47 Å). The overall average (2.49 Å) is close to the Li–S distance (2.47 Å) in Li$_2$S.[6] These values are also similar to those found in other Li–S compounds [av. 2.49, 2.48 Å in compounds (**2**) and (**3**), respectively].[2] All the Li atoms have a slightly distorted tetrahedral environment, the Li atoms in the cube being surrounded by four S atoms, while the outer Li atoms co-ordinate to two S atoms in addition to the two N atoms of the TMEDA ligand.

The structure of the title compound can be compared with some octanuclear copper and silver complexes,[7] particularly those where a halide ion is surrounded by a Cu$^{\text{I}}_8$S$_{12}$Cu$^{\text{II}}_6$ structure.

To our knowledge there is no precedent for this type of structure in alkali metal chemistry. An (Li$_8$)$_2$ double cluster

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† *Crystal data* for (**4**): rhombohedral, $a = 26.853(2)$, $c = 16.595(1)$ Å (hexagonal axes), space group $R\bar{3}$, $Z = 3$. $R = 0.083$, $R_w = 0.057$ for 1751 reflections with $F > 4\sigma(F)$ and $2\theta \leq 45°$ (Mo-K_α radiation, $\lambda = 0.71073$ Å). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

has been reported for the compound $\{Li_8[Me_3COS(N)F]_4F_2\}$-$\{Li_4(OCMe_3)_5\}_2\cdot 4C_5H_{12}$,[8] but this is a mixed Li, N, F, O polyhedron.

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