Synthesis and Crystal Structures of $[\overline{C_6H_4SC(\cdots S)\cdots N}Na\cdot 3P(NMe_2)_3O\cdot Na\overline{N\cdots(S\cdots)CSC_6H_4}]$ and $[\overline{C_6H_4SC(\cdots S)\cdots N}Li\cdot pmdien]$ (pmdien = *N,N,N′,N″,N″*-Pentamethyldiethylenetriamine): Alkali-metal Amides from 2-Sulfanylbenzothiazole‡

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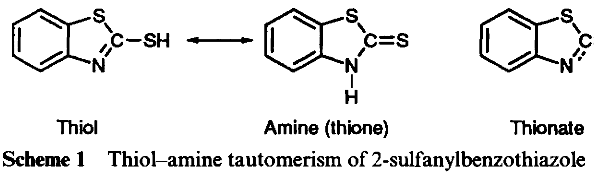
Reaction of 2-sulfanylbenzothiazole with MBu^n (M = Li or Na) in the presence of the Lewis-base donors $Me_2NCH_2CH_2NMeCH_2CH_2NMe_2$ (pmdien) and $P(NMe_2)_3O$ gave, respectively, the monomer $[\overline{C_6H_4SC(\cdots S)\cdots N}Li\cdot pmdien]$ and the dimer $[\overline{C_6H_4SC(\cdots S)\cdots N}Na\cdot 3P(NMe_2)_3O\cdot Na\overline{N\cdots(S\cdots)CSC_6H_4}]$, the structures of which have been determined by X-ray crystallography. In common with other structurally characterised sulfanylbenzothiazolate complexes, both the five-co-ordinate metal cations are involved in bridged bonding with the exocyclic S and the amido N. The amido $N^+{-}M^-$ is the formal bond making these two structures amide rather than thiolate complexes. In the sodium complex this is clear [N–Na 2.46(1) Å], however, in the lithium case the Li–N bond is exceptionally long [amido N–Li 2.14(1) Å] but an analysis of the bond lengths within the sulfanylbenzothiazolate moiety verifies its amido nature. The two complexes also show rare secondary bonding of the exocyclic S atoms by the alkali-metal cations, *exo*-S–Li 2.73(1) and *exo*-S–Na 2.995(1) and 2.951(7) Å.

The solid-state structures of the alkali-metal amido complexes of the important corrosion inhibitor benzotriazole $[\{\overline{C_6H_4N_3}K\cdot P(NMe_2)_3O\}_\infty]$[1] and $[(\overline{C_6H_4N_3}Li\cdot Me_2SO)_\infty]$[2] were recently reported. These revealed not only the versatility of the ligand itself, benzotriazole utilises all available N atoms to form the polymers with Li and K, but also highlighted the propensity of the alkali metals for forming 'internal' secondary bonds, even in the presence of competitive donor solvents [*e.g.* tetrahydrofuran (thf), $Me_2NCH_2CH_2NMe_2$ (tmen), $Me_2NCH_2CH_2NMeCH_2CH_2NMe_2$ (pmdien) or $P(NMe_2)_3O$]. For the heavier alkali metals Na, K, Rb and Cs the latter occurs more easily[3] due, in part, to their greater size and co-ordinative requirements. However, Li will also form such secondary or compensatory interactions in complexes in which it is in a low-co-ordinate environment.[4] This was exemplified by the report of a recent series of lithiated sulfanylamines.[5]

Another widespread and important corrosion inhibitor, particularly on copper surfaces, is 2-sulfanylbenzothiazole (Scheme 1). Attempts at modelling its action on a surface crystallographically have led to resolution of the solid-state structures of many complexes *e.g.* of Ru,[6] Mn,[7] Re,[7] Ni,[8] Cu,[9] Hg[10] and Cd,[11] either with the anion within an anionic moiety or as the direct counter ion to a metal cation. Corresponding solid-state structures of Group I or II complexes are unknown (Cambridge Crystallographic Database) despite their valuable use as precursors in organic and inorganic synthesis.



Scheme 1 Thiol–amine tautomerism of 2-sulfanylbenzothiazole

Organic corrosion inhibitors such as sulfanylbenzothiazole and benzotriazole often contain several heteroatoms which allow for flexibility in bonding with the metal atoms on a surface. A knowledge of the possible ligating modes is important in understanding their effectiveness, *e.g.* it is known that the exocyclic S atom in $C_7H_4NS_2$ allows it to be effective while benzothiazole is a poor inhibitor.[12] Moreover, such compounds are of great interest to alkali/alkaline-earth-metal chemists since any available 'internal' donor atoms can and have been used to stabilise complexes in which the metal is in, or might be in, an unfavourably low co-ordination environment. Such internal bonding can also reduce the need for the introduction of other donor solvents into the system.

Combining the multiheteroatomic compounds with the co-ordinative demands of alkali-metal cations can lead to complexes with a great deal of structural flexibility and diversity. The series of lithiated sulfanylamines mentioned above offer just such an example. 2-Sulfanylpyrimidine gave a polymer, $[\{\overline{N{=}CHCH{=}CH(N\cdots C}\cdots S)Li\cdot P(NMe_2)_3O\}_\infty]$, with Li bonded to terminal $P(NMe_2)_3O$, while 2-sulfanylbenzimidazole formed a dimer, $[\{\overline{C_6H_4[N\cdots C\cdots(S)\cdots N]}\}Li_2\cdot 3P(NMe_2)_3O]_2$, with terminal and bridging $P(NMe_2)_3O$. 2-Sulfanylthiazoline, with tmen, gave a dimer, $[\{\overline{SCH_2CH_2(N\cdots C}\cdots S)Li\cdot tmen\}_2]$, bonded through the exocyclic sulfur atom. For lithium amides, recent reviews[13] cover in-depth their synthesis, crystal structures and bonding patterns. However, there is still a dearth of such information on the organyls of the heavier alkali metals where the structures can become more unpredictable, particularly in the region of competition between 'external' and 'internal' secondary bonding. We have prepared,

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‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

isolated and characterised crystals of a lithium and a sodium derivative of 2-sulfanylbenzothiazole in the presence of pmdien and $P(NMe_2)_3O$ respectively. From X-ray diffraction studies we have found the sodium complex to exist as the bridged dimeric species $[\overline{C_6H_4SC(\overset{..}{-}S)\overset{..}{-}N}Na{\cdot}3P(NMe_2)_3O{\cdot}Na\overline{N\overset{..}{-}(S\overset{..}{-})CSC_6H_4}]$, **1** and the lithium complex to be the monomeric species $[\overline{C_6H_4SC(\overset{..}{-}S)\overset{..}{-}N}Li{\cdot}pmdien]$ **2**.

Results and Discussion

The pale yellow trigonal-bipyramidally shaped crystals of complex **1** were grown from a $P(NMe_2)_3O$–thf solution at 4 °C in relatively high yield (see Experimental section). Proton NMR studies in $[^2H_8]$thf and in C_6D_6 revealed there to be 1.5 $P(NMe_2)_3O$ units present per $[C_7H_4NS_2]^-$. This ratio was later confirmed by the crystal structure (Fig. 1). The colourless rhomboid crystals of **2** were grown from a hexane–toluene solvent mixture at −30 °C and although an excess of pmdien was added to the initial reaction mixture (1.5 equivalents) ^1H NMR studies revealed, as expected, only one co-ordinated pmdien molecule per $[C_7H_4NS_2]^-$ unit in the molecular structure. The crystal structure of the monomer is shown in Fig. 2.

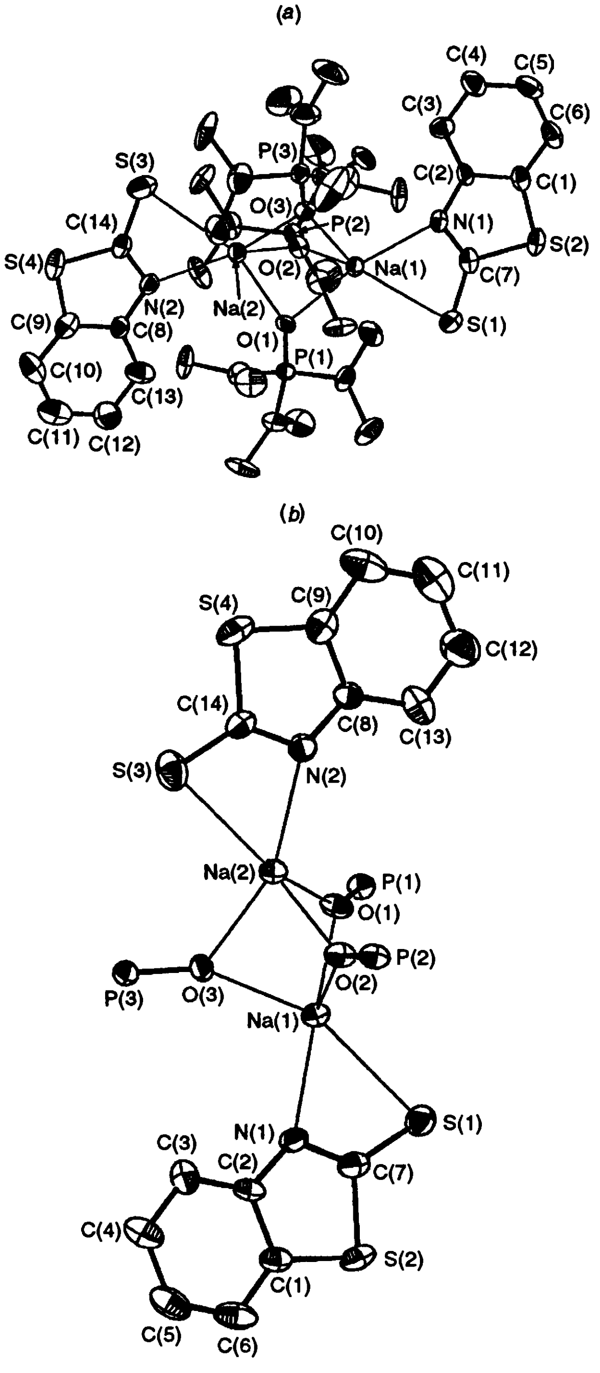


Fig. 1 (*a*) Crystal structure of $[\overline{C_6H_4SC(\overset{..}{-}S)\overset{..}{-}N}Na{\cdot}3P(NMe_2)_3O{\cdot}Na\overline{N\overset{..}{-}(S\overset{..}{-})CSC_6H_4}]$ **1**. Important angles and bond lengths given in Table 1. (*b*) The structure is devoid of all H atoms and the methyl groups on the $P(NMe_2)_3O$ ligands for clarification

These two structures present results which are interesting not only in their comparison with other structurally characterised complexes of Li and Na but also in the substantial differences they show in relation to other sulfanylbenzothiazolate complexes.

The structure of complex **1** is dimeric with the sulfanylbenzothiazolate groups *trans* both to the plane containing the three O atoms of the bridging $P(NMe_2)_3O$ ligands and to the line joining the two sodium ions. The main feature is the Na^+ cations, each of which is formally bonded to an amido nitrogen and forms a secondary interaction with the associated exocyclic sulfur atom. Although this mode of bonding is consistent with studies showing the amine (thione) form of the thiazole to be predominant in the solid state and to dominate the amine–thiol equilibrium in polar media,[14] it would appear to be a rare example of sulfanylbenzothiazole actually reacting, and remaining, in its amine form. An initial examination of the bond lengths in the monomeric structure of **2**, where the lithium cation again bonds in a bridging manner with N and the *exo*-S, would seem to suggest that this is not the case since both the amido N–Li and *exo*-S–Li bonds resemble co-ordinative rather than formal bonds. In comparison with the analogous bond in **1** the amido N–Li bond has lengthened to beyond the distance normally expected for a formal N^-–Li^+ interaction.

Almost all other solid-state transition- and main-group-metal sulfanylbenzothiazolate complexes are reported to have *exo*-S–M as their strongest bond. This arises from either the thiazole being in the thiol form on reacting or from a molecular transition taking place after it has reacted. However, since in most cases both the *exo*-S and the N are bound to the metal, usually in a bridging manner, it would appear to depend on the 'hard'/'soft' relationship between each heteroatom and metal as to which is the stronger of the two bonds formed. This relationship is dependent on many factors including the relative thermodynamic stabilities, as well as kinetic and solubility factors. Sulfanylbenzothiazolate complexes, though, with M–N as the strongest of the two bonds are rare but not unknown, *e.g.* $[Zn(C_7H_4NS_2)_3(OH_2)]^-$.[15]

However, in contrast, alkali-metal compounds are best described as being predominantly ionic and so an electrostatic interpretation is much more useful in understanding the

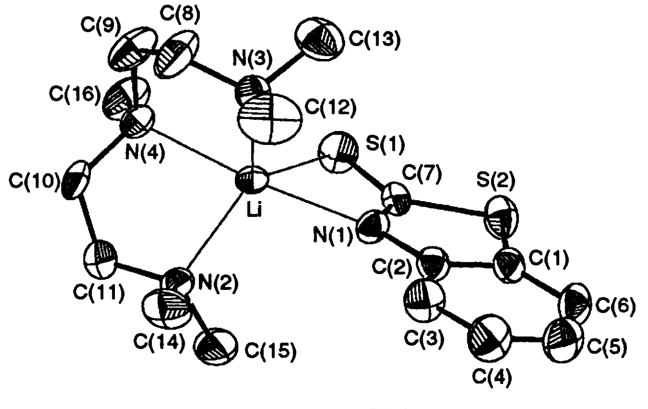


Fig. 2 Crystal structure of $[\overline{C_6H_4SC(\overset{..}{-}S)\overset{..}{-}N}Li{\cdot}pmdien]$ **2**. Important angles and bond lengths given in Table 2

Table 1 Selected bond lengths (Å) and angles (°) for complex 1

Na(1)–O(1)	2.41(1)	S(1)–C(7)	1.68(2)
Na(1)–O(2)	2.31(1)	N(2)–C(14)	1.31(2)
Na(1)–O(3)	2.34(1)	N(2)–C(8)	1.37(2)
Na(2)–O(1)	2.35(1)	N(1)–C(2)	1.38(2)
Na(2)–O(2)	2.34(1)	N(1)–C(7)	1.33(2)
Na(2)–O(3)	2.40(1)	S(2)–C(7)	1.78(2)
Na(1)–N(1)	2.47(1)	S(4)–C(14)	1.79(2)
Na(1)–S(1)	2.951(7)	O(1)–P(1)	1.47(1)
Na(2)–N(1)	2.46(1)	O(2)–P(2)	1.48(1)
Na(2)–S(3)	2.995(7)	O(3)–P(3)	1.47(1)
S(3)–C(14)	1.66(2)		
Na(1)–O(1)–Na(2)	77.7(3)	Na(2)–S(3)–C(14)	73.1(6)
Na(1)–O(2)–Na(2)	79.9(3)	Na(2)–N(2)–C(14)	100.0(1)
Na(1)–O(3)–Na(2)	78.0(3)	Na(1)–S(1)–C(7)	74.6(6)
O(1)–Na(1)–O(2)	85.1(4)	Na(1)–N(1)–C(7)	99(1)
O(1)–Na(1)–O(3)	80.1(4)	Na(2)–Na(1)–O(1)	50.2(2)
O(1)–Na(1)–N(1)	161.4(4)	Na(2)–Na(1)–O(2)	50.4(3)
O(1)–Na(1)–S(1)	111.2(3)	Na(2)–Na(1)–O(3)	51.8(3)
O(2)–Na(1)–O(3)	87.5(4)	Na(1)–Na(2)–O(1)	52.1(3)
O(2)–Na(1)–N(1)	113.3(4)	Na(1)–Na(2)–O(2)	49.6(3)
O(2)–Na(1)–S(1)	117.6(3)	Na(1)–Na(2)–O(3)	50.2(3)
O(3)–Na(1)–N(1)	102.5(4)	Na(1)–Na(2)–N(2)	150.4(4)
O(3)–Na(1)–S(1)	152.5(3)	Na(1)–Na(2)–S(3)	151.7(3)
O(1)–Na(2)–O(2)	85.9(4)	Na(2)–Na(1)–N(1)	144.4(4)
O(1)–Na(2)–O(3)	80.2(3)	Na(2)–Na(1)–S(1)	153.7(2)
O(1)–Na(2)–N(2)	106.0(4)	S(3)–Na(2)–N(2)	57.5(3)
O(1)–Na(2)–S(3)	147.7(3)	S(1)–Na(1)–N(1)	58.9(3)
O(2)–Na(2)–O(3)	85.6(4)	N(1)–C(7)–S(1)	128(1)
O(2)–Na(2)–N(2)	117.6(5)	N(2)–C(14)–S(3)	128(1)
O(2)–Na(2)–S(3)	126.0(3)	S(1)–C(7)–S(2)	121(1)
O(3)–Na(2)–N(2)	156.0(5)	S(3)–C(14)–S(4)	120.7(9)
O(3)–Na(2)–S(3)	105.0(3)		

Table 2 Selected bond lengths (Å) and angles (°) for complex 2

Li–N(1)	2.14(1)	N(1)–C(7)	1.325(9)
Li–N(2)	2.13(1)	S(2)–C(7)	1.781(8)
Li–N(3)	2.13(1)	S(2)–C(1)	1.731(10)
Li–N(4)	2.18(1)	N(1)–C(2)	1.378(10)
Li–S(1)	2.73(1)	C(2)–C(1)	1.41(1)
S(1)–C(7)	1.668(9)		
Li–S(1)–C(7)	69.5(4)	N(2)–Li–N(4)	83.7(5)
Li–N(1)–C(7)	97.4(6)	N(3)–Li–N(4)	83.1(5)
S(1)–Li–N(2)	118.5(6)	N(2)–Li–N(3)	121.7(7)
S(1)–Li–N(3)	119.6(6)	S(1)–C(7)–C(1)	127.1(7)
S(1)–Li–N(4)	99.7(5)	C(7)–S(2)–C(1)	91.8(5)
N(1)–Li–N(2)	102.6(6)	S(2)–C(1)–C(2)	108.3(9)
N(1)–Li–N(3)	104.0(6)	C(1)–C(2)–N(1)	114.9(9)
N(1)–Li–N(4)	165.4(7)	C(2)–N(1)–C(7)	114.4(8)

bonding in both **1** and **2**. From a simple comparison of the electronegativities of N and S it would be expected that the more ionic M^+–N^- bond would be formed in preference to the M^+–S^-. Indeed, although in both cases the negative charge contributes to delocalised bonding within the $N{\cdots}C{\cdots}S$ unit, thus both structures are formally thionates, in **1** the charge is centred predominantly on N while in **2** the extended nature of the Li–*exo*-S bond and the long amido Li–N bond suggest the charge is much more delocalised. The secondary Na–*exo*-S bond can be viewed as a typical co-ordinating dative bond from S to the highly positive metal centre, the sulfur atom therefore behaving as an internal donor. While this is also the case in **2** the amido N–Li bond is comparable in length with the co-ordinative (pmdien)N–Li bonds and so in contrast to **1** the amido nature of the complex is more ambiguous.

It is interesting that a sodium derivative of sulfanylbenzothiazolate has been found in synthesis to react in the thiolate (Na^+–*exo*-S^-) form.[16] Although the reported yield from this particular reaction is only 8% it nevertheless suggests that, in polar media at least, the thiolate species exists in equilibrium with the amine species. Within this equilibrium, though, it would be the amine species which would be more highly favoured.

The five-co-ordinate bonding environment of Na^+ is completed by three bridging $P(NMe_2)_3O$ molecules which connect the two $[C_7H_4NS_2]^-Na^+$ ion pairs. Such M–μ(O)P-$(NMe_2)_3$ bonding has become a common feature in the structures of lithium organyls. Examples for the heavier alkali metals are more scarce but can be found in some inorganic salts, *e.g.* $[\{[NaNCS\cdot P(NMe_2)_3O]_2\}_\infty]$, $[\{NaNCS\cdot 2P(NMe_2)_3O\}_2]$[17] and $[(KNCS)_3\cdot 5P(NMe_2)_3O]$.[18] However, the most salient comparison is with the sodium amide $[Ph(NH_4C_5)NNa\cdot 3P(NMe_2)_3O\cdot NaN(C_5H_4N)Ph]$[19] **3** which shares the common feature of having a secondary bond from Na^+ to the $N(C_5H_4N)$ and also of having its R groups *trans* to the plane containing the three $P(NMe_2)_3O$ oxygens.

The Na–N distances of 2.46(1) Å in complex **1** are slightly longer than those of 2.439(1) Å found in **3** but are normal within sodium amides for five-co-ordinate Na^+: in $[\{Ph(NH_4C_5)N\text{-}Na\cdot pmdien\}_2]$, where pmdien acts as a bi- and not a tri-dentate ligand, the amido N–Na distances are 2.449, 2.552 Å[19] and in the sodioindole complex, $[(C_8H_7NNa\cdot pmdien)_2]$, 2.474, 2.481 Å.[20] The Na–$OP(NMe_2)_3$ distances are surprisingly short, ranging between the shortest bond of 2.31(1) for Na(1)–O(2) and the longest of 2.41(1) for Na(1)–O(1). They are on average significantly shorter than the distances of 2.381, 2.436 and 2.437 Å found in **3**, even though Na^+ is five-co-ordinate in both complexes. In fact the bonds are closer in length to those in the thiocyanate complex $[\{NaNCS\cdot 2P(NMe_2)_3O\}_2]$ (average 2.336 Å) where the Na^+ is only four-co-ordinate. Normally, the expected consequence of increased co-ordination at a metal centre is an increase in the co-ordinative bond lengths.

One reason for the comparative shortness of the Na–OP-$(NMe_2)_3$ bond distances may be the relatively long and weak nature of the Na–S bonds. Sulfur is not normally considered to be as strong a donor towards alkali metals as is N or O.[21,22] Therefore comparisons for the secondary S(1)–Na(1) and S(3)–Na(2) bonds are rare. At 2.951(7) and 2.995(1) Å they are, as expected, longer than the direct Na–S bond distances of 2.895 Å found in $[\{[NaNCS\cdot P(NMe_2)_3O]_2\}_\infty]$ and of 2.838 and 2.835 Å in $[\{2,4,6\text{-}(F_3C)_3C_6H_2SNa\cdot 2thf\}_\infty]$.[23] However, they are also longer than two of the three neutral Na–S bonds found in $[V(C_6H_4NS)_4Na\cdot 2thf]$[24] (2.887, 2.951 Å), and only marginally shorter than the third (3.042 Å). All the neutral bonds in another mixed Na–V thiolato[25] complex are shorter (2.749–2.927 Å), implying that the Na–S bonds in **1** are relatively weak.

An almost analogous complex to **1** is $[\{\overline{C_6H_4OC({\cdots}S){\cdots}N}\text{-}Na\}_2\cdot 3P(NMe_2)_3O]$.[26] This complex, formed from 2-sulfanylbenzoxazole, highlights the extent to which the structures of these sodium complexes are dependent upon the fine interactions between the metal, ligand and any donor molecules present. One of the oxazole groups in the bridged dimer bonds to Na in the amine form (Na^+–N^-), however, there is no bond formed between the Na^+ and the associated *exo*-S. The other oxazole group bonds in the thiolate form (Na^+–S^-) but in this case with the sodium also bonded to the N atom. These unusual and unexpected differences in the solid-state structures of the two complexes may arise due to differing electronic environments induced by the endocyclic O and perhaps a differing solution behaviour of 2-sulfanylbenzoxazole compared with 2-sulfanylbenzothiazole. Importantly though, it highlights the weak nature of the *exo*-S–Na co-ordinative bonding and confirms that the thiolate derivative $[\{C_7H_4NS_2Na\cdot 3P(NMe_2)_3O\}_2]$ could, and probably does, exist as an equilibrium product in solution. Despite our attempts to isolate this product by altering the polarity and temperature of the reaction mixture only crystals of the amido complex, **1**, could be coaxed from solution, in varying yields.

If we now consider the structure of complex **2**, the lithium centre like that of Na^+ above is five-co-ordinate, bonding with the amido N and the exocyclic S of the thiazole anion and the

Table 3 Comparison of bond lengths (Å) and angles (°) in complexes **1** and **2** and the free thiazole [32]

	1	**2**	$C_7H_4NS_2H$
C(7)–N(1), C(14)–N(2)	1.320(20)	1.325(9)	1.340(3)
C(7)–S(1), C(14)–S(3)	1.670(20)	1.668(9)	1.657(3)
C(7)–S(2), C(14)–S(4)	1.785(20)	1.781(8)	1.746(3)
C(2)–N(1), C(8)–N(2)	1.375(20)	1.378(10)	1.388(4)
N(1)–C(7)–S(1), N(2)–C(14)–S(3)	128(1)	127.1(7)	127.8(2)

three N atoms of the pmdien molecule. For Li^+ a five-co-ordinate bonding environment is not rare but is far less common than four. What is striking in this case is that Li becomes five-co-ordinate by bonding with the *exo*-S and that the amido N–Li bond elongates to become comparable with any N–Li co-ordination bond. This is clearly supported by a comparison of the bond lengths within **2** itself and also with several other structures, mainly those of the lithiated 2-sulfanylbenzoxazoles $[\mathrm{C_6H_4OC(\overset{\cdot\cdot}{-}S)\overset{\cdot\cdot}{-}NLi{\cdot}tmen{\cdot}H_2O}]$ **4**,[27] $[\{\mathrm{C_6H_4OC(\overset{\cdot\cdot}{-}S)\overset{\cdot\cdot}{-}NLi{\cdot}P(NMe_2)_3O{\cdot}H_2O}\}_2]$ **5**, $[\{\mathrm{C_6H_4OC(\overset{\cdot\cdot}{-}S)\overset{\cdot\cdot}{-}NLi{\cdot}P(NMe_2)_3O}\}_2]{\cdot}\mathrm{H_2O}$ **6**,[28] which are unambiguously described as lithium amides.

The amido N(1)–Li bond distance of 2.14(1) Å in complex **2** is only shorter than one of the three pmdien (N)–Li bonds. The distances of 2.13(1), 2.13(1) and 2.18(1) Å for N(2)–Li, N(3)–Li and N(4)–Li, respectively, are common neutral N–Li bond distances. Here complex **4** is of great interest since the Li^+ is also co-ordinated by three 'external' donor atoms and has the opportunity to increase its co-ordination environment of four by also bonding with the *exo*-S. However, it does not do this. The amido N–Li bond length is 2.051(7) Å with Li^+ and S separated by 3.370(5) Å, clearly too long to represent any kind of bond. The S atom in **4** is bonded intramolecularly with co-ordinated H_2O. Reinforcing the apparent lack of attraction between the alkali metals and S, only in complex **6** is there an internal S–Li bond and then only one of a possible two in the dimer. Again the others preferentially form hydrogen bonds with the H_2O. In **5** the amido N–Li bond distances average 2.067(8) Å while in **6** the portion of the dimer which has N and S bridged by Li has (amide) N–Li 2.056(13) Å and *exo*-S–Li 2.757(12) Å. It could of course be argued that the amido N–Li distance is elongated in **2** because Li^+ is five- and not four-co-ordinate. However, in the absence of a direct comparison we can compare it with another complex in which Li is five-co-ordinate, namely the pmdien adduct $[\mathrm{(PhN\overset{\cdot\cdot}{-}C\overset{\cdot\cdot}{-}NPh)Li{\cdot}pmdien}]$.[29] Here Li bridges the two N atoms in the delocalised N–C–N unit with an amido N–Li distance of 2.076(6) Å and N–Li distance of 2.188(6) Å. Even taking into account the difference in size of S and N, the amido N–Li bond distance is very long for a formal N^-–Li^+ bond. However, it is not without precedent that the deprotonated N ion is not involved in the shortest, and by inference the strongest, M–N bond, especially when the metal ion is highly co-ordinated. In the potassium derivative of benzotriazole, $[\{\mathrm{C_6H_4N_3K{\cdot}P(NMe_2)_3O}\}_\infty]$, the variety in N–K bond lengths in the polymer makes it impossible to conclude which N atom was initially deprotonated.

Given the unusual and unexpectedly long N–Li bond it might have been surmised that the complex was thiolate in character, *i.e.* with S^-–Li^+ being the strongest bond. However, the *exo*-S–Li bond is also long, again associated more with simple co-ordinative bonding whether directly or in a bridging situation. Most formal S–Li bonds are approximately 2.4–2.5 Å in length, *e.g.* in $[\{\mathrm{PhC(O)SLi{\cdot}tmen}\}_2]$ S–Li is 2.478(4) Å,[30] and co-ordinate bonds can vary between 2.555(3) Å in $[\mathrm{(PhSCH_2Li{\cdot}tmen)_2}]$[31] and 2.804(5) Å as found in $[\{\mathrm{N{=}CHCH{=}CH(N\overset{\cdot\cdot}{-}C\overset{\cdot\cdot}{-}S)Li{\cdot}P(NMe_2)_3O}\}_\infty]$.[5] Therefore given that the *exo*-S(1)–Li bond in **2** is 2.73(1) Å a tentative assumption that it was thiolate in character would have been reasonable. However, we do not believe this is the case on analysis of the bond distances within the sulfanylbenzothiazolate moiety. Though it can also be said that the bonding within **2** is not nearly as clear a representation of an amide structure as is **1**.

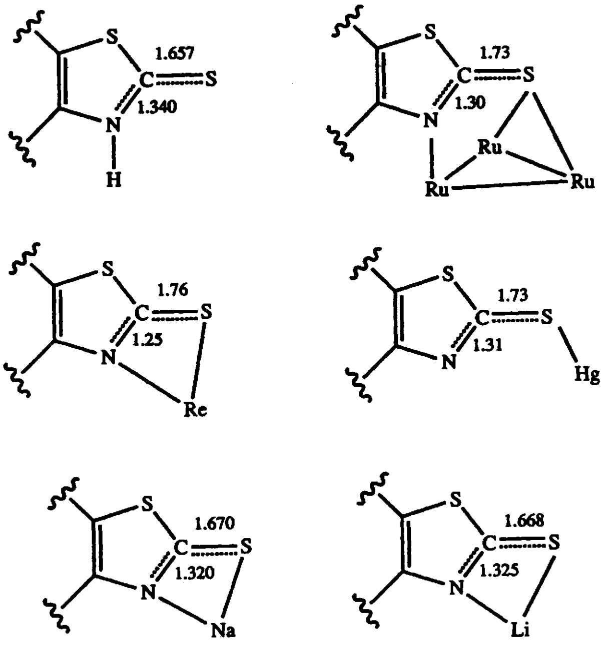
Due to the delocalised nature of the $\mathrm{N\overset{\cdot\cdot}{-}C\overset{\cdot\cdot}{-}S}$ unit in free sulfanylbenzothiazole, verified by its solid-state structure,[32] it is possible to make a direct comparison with the bonding in both complex **1** and **2** (Table 3). It is apparent that on metallation only a slight change occurs in the bond lengths within the $\mathrm{N\overset{\cdot\cdot}{-}C\overset{\cdot\cdot}{-}S}$ delocalised units. This is unexpected since the negative charge on N would increase significantly on replacement of $H^{\delta+}$ with M^+. Table 3 does confirm though that the benzothiazole reacts in its amine form with NaBu and also we assume therefore with LiBu. From the structure of **1** it is also apparent that there is very little interaction between the Na^+ and the delocalised $\mathrm{N\overset{\cdot\cdot}{-}C\overset{\cdot\cdot}{-}S}$ unit as a whole, in contrast to what might have been expected given the highly positive nature of the sodium cation. The $\mathrm{N\overset{\cdot\cdot}{-}C\overset{\cdot\cdot}{-}S}$ units are situated only 30° above and below the line which bisects the two sodium ions. It may be possible to conclude from this that direct bonding of the Na^+ with N^- is more favourable than is interaction with the complete $\mathrm{N\overset{\cdot\cdot}{-}C\overset{\cdot\cdot}{-}S}$ unit. This would explain why only a small perturbation in the bonding within the delocalised unit is found on changing from $H^{\delta+}$ to Na^+. The same argument can be extended to the lithium complex to explain why the bonds between the sulfanylbenzothiazolate moiety and the metal are so long. The lithium cation is again sited only slightly out of the rough plane containing the N–C–S unit and prior to complexation the amido N–Li would also be expected to be the main bond, resembling a common N^-–Li^+ formal bond. This bond lengthens dramatically on introduction of the pmdien due to the additional electron density given to the lithium cationic centre by the three donating N atoms. Given this and the relatively small size of Li^+ there is no electronic requirement for it to move into, or possibly even remain in, a bridging situation more directly above the $\mathrm{N\overset{\cdot\cdot}{-}C\overset{\cdot\cdot}{-}S}$ unit.

Although on metallation a shortening of the C(7)–N(1) bond is expected the change is only slight in both complexes and is not nearly as significant as it is in other sulfanylbenzothiazolate complexes. The C(7)–S(1) bonds in **1** and **2** remain almost as close in double-bond character as they are in the free benzothiazole. The other benzothiazolate complexes cited earlier all showed an elongation of the $\mathrm{C\overset{\cdot\cdot}{-}S}$ bond toward single-bond character with a concomitant reduction in the $\mathrm{C\overset{\cdot\cdot}{-}N}$ bond to almost double-bond character, see Scheme 2 for examples. The lithiated sulfanylamine complexes mentioned earlier also contain longer delocalised $\mathrm{C\overset{\cdot\cdot}{-}S}$ bonding, ranging from 1.700 to 1.735 Å, similar to the thiolate character of the other transition and main-group-metal sulfanylbenzothiazolate complexes above. Since this bond distance in **2** is only 1.668(9) Å it should rule out complex **2** being considered thiolate in character. However, the similarity in the delocalised bonding between 2-sulfanylbenzothiazole and **1** is not reflected in the IR spectrum which, while substantially different from that of the thiazole, is not wholly inconsistent with the solid-state structure of **1**. The NH peak disappears on reaction with the NaBu and there is no evidence of a strong absorption in the region 1550–1650 cm^{-1} (1604 for the thiazole) which could be assigned to the appearance of a stronger C=N bond. The sharp, medium–strong absorption at 1074 cm^{-1} (1080 for the thiazole) is in the region assigned for C–S bonds with high double-bond character,[33] however such assignment has been contested.[34]

A surprising aspect of the crystals of complex **1** was their apparent stability to atmospheric moisture and oxygen. This, however, was not the case with the crystals of **2** which are fully hydrolysed within 5 min of exposure. The IR studies confirm that although the crystals of **1** are highly hygroscopic, there is no evidence, after prolonged air exposure (30 s to 20 min), of NaOH formation. The characteristic peak of NaOH at *ca.* 3580

Table 4 Atomic coordinates for complex 1

Atom	*X/a*	*Y/b*	*Z/c*
Na(1)	0.8035(3)	0.5339(2)	0.1756(2)
Na(2)	0.7520(3)	0.4557(2)	0.3064(2)
P(1)	0.6817(3)	0.3924(1)	0.1230(2)
P(2)	0.6479(3)	0.6035(2)	0.3243(2)
P(3)	1.0311(3)	0.4579(2)	0.2700(2)
O(1)	0.7130(6)	0.4372(3)	0.1805(4)
O(2)	0.7069(6)	0.5563(3)	0.2819(4)
O(3)	0.9227(6)	0.4798(3)	0.2522(4)
N(1)	0.9151(9)	0.6188(4)	0.1314(5)
N(2)	0.6236(9)	0.3944(5)	0.3776(5)
S(1)	0.7491(3)	0.6004(2)	0.0376(2)
S(2)	0.9174(3)	0.6979(2)	0.0248(2)
S(3)	0.8054(3)	0.4035(2)	0.4568(2)
S(4)	0.6286(4)	0.3124(2)	0.4808(2)
C(1)	1.019(1)	0.7019(6)	0.0897(7)
C(2)	1.004(1)	0.6551(6)	0.1431(7)
C(3)	1.075(1)	0.6508(7)	0.2020(8)
C(4)	1.163(1)	0.6889(9)	0.2059(9)
C(5)	1.178(1)	0.7343(8)	0.153(1)
C(6)	1.104(2)	0.7408(7)	0.0963(9)
C(7)	0.860(1)	0.6340(5)	0.0713(7)
C(8)	0.530(1)	0.3610(6)	0.3728(7)
C(9)	0.517(1)	0.3136(7)	0.4234(7)
C(10)	0.426(2)	0.2762(8)	0.423(1)
C(11)	0.350(2)	0.288(1)	0.372(1)
C(12)	0.359(2)	0.334(1)	0.322(1)
C(13)	0.448(1)	0.3701(7)	0.3221(9)
C(14)	0.686(1)	0.3759(5)	0.4329(7)
N(11)	0.7440(9)	0.4070(5)	0.0438(5)
N(12)	0.7115(9)	0.3228(5)	0.1455(6)
N(13)	0.5528(8)	0.3938(5)	0.1074(6)
N(21)	0.5917(9)	0.5827(5)	0.4040(6)
N(22)	0.7287(9)	0.6572(5)	0.3504(6)
N(23)	0.5494(9)	0.6296(5)	0.2732(6)
N(31)	1.1042(9)	0.4491(7)	0.1963(7)
N(32)	1.092(1)	0.5038(6)	0.3248(7)
N(33)	1.030(1)	0.3909(7)	0.3114(8)
C(111)	0.855(1)	0.4264(7)	0.0450(8)
C(112)	0.692(1)	0.3988(9)	−0.0279(8)
C(121)	0.677(1)	0.2993(7)	0.2170(9)
C(122)	0.778(1)	0.2828(7)	0.1027(9)
C(131)	0.497(1)	0.4504(7)	0.105(1)
C(132)	0.488(1)	0.3410(7)	0.091(1)
C(211)	0.490(1)	0.5509(7)	0.4027(9)
C(212)	0.661(1)	0.5671(8)	0.4668(8)
C(221)	0.829(1)	0.6678(7)	0.3141(9)
C(222)	0.703(2)	0.7048(8)	0.404(1)
C(231)	0.483(2)	0.6796(8)	0.297(1)
C(232)	0.523(1)	0.6077(8)	0.202(1)
C(311)	1.104(1)	0.4937(8)	0.1381(9)
C(312)	1.162(2)	0.393(1)	0.179(1)
C(321)	1.213(1)	0.511(1)	0.324(1)
C(322)	1.034(2)	0.536(1)	0.3825(9)
C(331)	1.083(1)	0.381(1)	0.385(1)
C(332)	0.960(2)	0.3451(8)	0.285(1)



Scheme 2 Comparison of the different bonding distances (Å) within the N$\cdots$C$\cdots$S fragments of 2-sulfanylbenzothiazolate and the thiolate complexes [HgMe(S$_2$NC$_7$H$_4$)], [Ru$_3$H(CO)$_9$(S$_2$NC$_7$H$_4$)], [Re(CO)$_3$(S$_2$NC$_7$H$_4$)] with the amide complexes **1** and **2**. For aggregates the mean distances are given

Table 5 Atomic coordinates for complex 2

Atom	*x*	*y*	*z*
S(1)	−0.1794(2)	0.0070(3)	0.3257(2)
S(2)	−0.2694(2)	−0.1879(3)	0.1743(2)
N(1)	−0.1006(5)	−0.0487(8)	0.2095(5)
N(2)	0.1234(5)	0.0056(9)	0.3508(4)
N(3)	−0.0297(6)	0.3261(9)	0.2260(4)
N(4)	0.0408(6)	0.2797(9)	0.3983(4)
C(1)	−0.2041(8)	−0.214(1)	0.1083(6)
C(2)	−0.1143(8)	−0.128(1)	0.1381(6)
C(3)	−0.0484(8)	−0.133(1)	0.0960(7)
C(4)	−0.070(1)	−0.222(2)	0.0267(8)
C(5)	−0.157(1)	−0.306(2)	−0.0018(7)
C(6)	−0.2254(9)	−0.306(1)	0.0381(8)
C(7)	−0.1735(6)	−0.0671(10)	0.2393(5)
C(8)	0.019(1)	0.447(1)	0.2786(8)
C(9)	0.0231(9)	0.438(1)	0.3612(7)
C(10)	0.1460(8)	0.243(1)	0.4329(6)
C(11)	0.1653(7)	0.078(1)	0.4307(6)
C(12)	0.0088(9)	0.326(1)	0.1596(7)
C(13)	−0.1385(9)	0.348(1)	0.1914(7)
C(14)	0.1886(7)	0.026(1)	0.3029(7)
C(15)	0.1083(7)	−0.160(1)	0.3573(6)
C(16)	−0.0024(8)	0.269(1)	0.4629(5)
Li	−0.0166(9)	0.120(2)	0.2958(8)

cm^{-1}, which would confirm cleavage of the Na–N bonds, is absent, although after 20 min all the peaks are slightly broader and less detail is visible. The hydrolysis spectrum of **1** after 1 min remains almost superimposable upon that of the unexposed complex except for the appearance of the peak at 1638 cm^{-1}, which is absent from the spectrum of the sulfanylbenzothiazole. Confirmation of Na–N bond cleavage could also be obtained by the reappearance of the NH absorption, but this is masked by a strong broad peak caused by the absorbed water. The structure of this complex remains, as yet, elusive. The addition of equimolar amounts of water to a toluene solution of **1** leads to its complete hydrolysis and addition at an earlier stage leads to the formation of NaOH. However, the structural characterisation of $[\{\overline{C_6H_4OC(\cdots S)\cdots N}Li\cdot P(NMe_2)_3O\cdot H_2O\}_2]$ and $[\{\overline{C_6H_4OC(\cdots S)\cdots N}Li\cdot(PNMe_2)_3O\}_2]\cdot H_2O$[28] revealed that H$_2$O may act as a ligand and not as a reactant towards lithium organyls. The evidence above may hint towards the feasibility of such water complexes of the heavier alkali metals.

Conclusion

The sodium derivative of 2-sulfanylbenzothiazolate, **1**, is the first characterised solid-state complex of this thiazolate which is highly ionic and with a very clear and defined amido mode of bonding. This may prove important and useful in further synthetic procedures especially those involving transmetallation reactions with other main-group or transition metals. Any further reaction of **1** has a very high possibility of occurring specifically at the N^- with a greater degree of certainty than if only the thiazole or the lithiated thiazolate was employed. The weak nature of the Na–*exo*-S bond may also allow for the possibility of further direct sulfur co-ordination independent of any interaction with the N. The mode of bonding in the lithium derivative **2** is much less definable. Although it would also be expected that the complex is highly ionic and that after deprotonation the formal bond would be the N–Li bond, with the bridging initially being completed by the *exo*-S, the amido N–Li becomes so elongated on co-ordination with pmdien that it resembles a dative bond. The bonding of the metal to S is within calculated and experimental values for bridging and co-ordinated S–Li bonds. The amido N–Li bond, however, is weak and this is probably reflected in the ease with which complex **2** hydrolyses in comparison with the sodium complex.

That it is the co-ordinative demands of the metal which is the main driving force behind the adopted structures is reinforced by the formation of the relatively unfavourable Na–*exo*-S bonds in the absence of more likely donating atoms or solvents. As in previous sulfanylbenzothiazolate structures the exocyclic S atom is important in stabilising the structure. However, the endocyclic S atom takes no part in bonding. In forming the bridged dimer the Na^+ achieves a higher co-ordination environment than if it were in the monomeric (*i.e.* five and four respectively) state where only two $P(NMe_2)_3O$ units would be available per metal centre. The steric bulk of $P(NMe_2)_3O$ probably precludes the formation of the higher six-co-ordinate dimer, which might have been possible given that two equivalents of $P(NMe_2)_3O$ were available to each Na^+. Lithium also gains a co-ordination environment of five by the unexpected interaction with the *exo*-S. Co-ordination of $[(C_7H_4NS_2{\cdot}Li)_n]$ with pmdien is not sufficient to break the *exo*-S–Li bond. This supports the ionic model for organolithium compounds since the lithium cation attempts to, and will, form as many bonds as possible until this is precluded by steric factors.

Experimental

All reagents were obtained from Aldrich Chemical Co. The synthesis and characterisation of complexes **1** and **2** was carried out under dried argon gas using standard inert-atmosphere Schlenk techniques. Hexane was dried by reflux over Na–K amalgam and thf was refluxed initially over sodium wire in the presence of benzophenone and then over Na–K amalgam. The $P(NMe_2)_3O$ and pmdien were distilled from small pieces of sodium and stored over molecular sieve 4 Å under argon. 2-Sulfanylbenzothiazole was heated and vacuum dried over 4 h before storage in a dry-box. Butylsodium, $(NaBu^n)_n$, which is a cream coloured highly pyrophoric solid, was prepared from the reaction of commercially obtained $(LiBu^n)_6$ with Na(O–Bu^t) in pre-dried degassed hexane and stored in a dry-box prior to use.

Synthesis of Complex **1**.—Pale yellow 2-sulfanylbenzothiazole powder (1.73 g, 10 mmol) was added to a stirred, cooled (−30 °C) suspension of $(NaBu^n)_n$ (0.80 g, 10 mmol) in hexane (5 cm^3). The hexane suspension had been immersed in an ultrasonic bath for 30 min to ensure that it was as fine as possible. The reaction mixture was allowed to stir and warm slowly to room temperature at which point it was stirred for 2 h. Two equivalents of $P(NMe_2)_3O$ (3.48 cm^3, 20 mmol) were added to the yellow suspension resulting in the formation of a two-layer heterogeneous solution. The hexane was removed *in vacuo* and thf (2 cm^3) added giving a light yellow homogeneous solution. Cooling this solution to 4 °C for 24 h resulted in a crop of pale yellow trigonal-bipyramidal crystals (yield 73%, from the mother-liquor). They were washed with cold thf–toluene (20:80), dried *in vacuo* and stored in a dry-box. The crystals were identified as $[\overline{C_6H_4SC(\overset{\cdot\cdot}{-}S)\overset{\cdot\cdot}{-}N}Na\cdot 3P(NMe_2)_3O\cdot Na\text{-}\overline{N\overset{\cdot\cdot}{-}(S\overset{\cdot\cdot}{-})CSC}_6H_4]$ **1**, m.p. 122–122.5 °C. NMR (C_6D_6, 25 °C): ^{1}H, δ 7.60 (d, H), 7.34 (d, H), 7.17 (t, H), 6.99 (t, H), 2.35, 2.37 [d, 18 H, $P(NMe_2)_3O$]; ^{13}C, δ 189.6 (C), 156.1 (C), 139.1 (C), 124.7 (CH), 121.5 (CH), 120.5 (CH), 117.9 (CH), 37.1 [6CH$_3$ of $P(NMe_2)_3O$] (Found: C, 50.5; H, 6.4; N, 16.1. Calc.: C, 49.1; H, 6.8; N, 16.8%). Infrared spectra: (Nujol mull) 1618w, 1584w, 1509w, 1300s, 1245m, 1195s, 1168s, 1126m, 1100w, 1074m-s, 1021m (sh), 995s (br), 858w, 800w, 745s, 729s and 642s; on exposure to air for 1 min 3377m (br), 1638w (br), 1585w, 1509w, 1299s, 1245m, 1198m, 1168m, 1126m (sh), 1088m-w, 985s, 858w, 747m-s, 728m-s and 641m cm^{-1}.

Synthesis of Complex **2**.—Pale yellow 2-sulfanylbenzothiazolate powder (0.69 g, 4.1 mmol) was dissolved in thf (15 cm^3) and cooled to 0 °C. The compound $(LiBu^n)_6$ in hexane (4.2 mmol, 2.6 cm^3, 1.6 mol dm^{-3}) was added dropwise *via* a syringe giving an immediate red colouration which dissipated. A light yellow oil was obtained on warming to ambient temperature and removing the volatile components under high vacuum. It was diluted with toluene (5 cm^3) and hexane (5 cm^3) and filtered. The addition of pmdien (1.5 equivalents) and cooling to −30 °C overnight resulted in pale yellow crystals (1.16 g, yield 81%, in two crops). The yield was not optimised. The crystals were washed with cold hexane, dried *in vacuo* and stored in a dry-box. The crystals were identified as $[\overline{C_6H_4SC(\overset{\cdot\cdot}{-}S)\overset{\cdot\cdot}{-}N}Li\cdot pmdien]$ **2**, m.p. > 150 °C (decomp.). NMR (C_6D_6, 25 °C): ^{2}H, δ 7.37–6.91 (4 H, m, C_6H_4), 2.10 (s, NCH_2) and 1.98 (s, 15 H, NCH_3); ^{13}C, δ 190.2 (C), 155.0 (C), 138.2 (C), 125.0 (CH), 121.5 (CH), 120.6 (CH), 116.7 (CH), 56.8 (NCH_2), 53.8 (NCH_2), 45.3 (NMe_2) and 44.8 (NMe) (Found: C, 55.90; H, 7.60; N, 16.30. Calc.: C, 55.45; H, 7.85; N, 16.15%). Infrared spectrum (Nujol Mull) (s, strong; m, medium; w, weak): 1289m, 1260m, 1154w, 1111w, 1060w, 1021w, 989s, 938w, 901w, 793m, 753s, 725s, 654w, 604w and 568w cm^{-1}.

Crystal Structure Analyses.—*Complex* **1**. Single crystal mounted and sealed in capillary.

Crystal data. $C_{32}H_{62}N_{11}Na_2O_3P_3S_4$, $M_r = 916$, monoclinic, space group $P2_1/a$, $a = 12.436(2)$, $b = 22.028(2)$, $c = 17.906(3)$ Å, $\beta = 90.31(1)°$, $V = 4905.3(1)$ Å^3, $D_c = 1.240$ g cm^{-3}, $F(000) = 1944$, Mo-Kα radiation, $\lambda = 0.710\,69$ Å, $\mu = 0.35$ mm^{-1}, crystal dimensions 0.2 × 0.2 × 0.2 mm.

The structure was determined by direct methods (XTAL 3.2)[35] and refined from 8606 observed and 2410 unique reflections on an Enraf-Nonius CAD4 diffractometer, $2\theta_{max} = 50°$, 25 °C, $R = 0.056$, $R' = 0.060$ [unit weights, $I > 2.5\sigma(I)$]. All hydrogen atoms calculated (C–H 0.95 Å). Non-hydrogen atoms refined with anisotropic thermal parameters. Atomic coordinates (non-H atoms) are given in Table 4.

Complex **2**. Single crystal mounted and sealed in capillary.

Crystal data. $C_{16}H_{27}LiN_4S_2$, $M_r = 346.28$, monoclinic, space group $P2_1/a$, $a = 14.269(4)$, $b = 8.593(2)$, $c = 17.502(4)$ Å, $\beta = 110.16(2)°$, $V = 2014.7(9)$ Å^3, $D_c = 1.142$ g cm^{-3}, $F(000) = 744.00$, Mo-Kα radiation, $\mu = 2.67$ cm^{-1}, crystal dimensions 0.50 × 0.50 × 0.25 mm.

The structure was determined by direct methods (SIR 92)[36] and refined from 3967 observed and 3805 unique reflections using TEXSAN[37] collected on a Rigaku AFC7R diffractometer, $2\theta_{max} = 50°$, 22 ± 1 °C, $R = 0.061$, $R' = 0.052$ [$w = (\sigma^2F_o)^{-1}$, $I > 3.0\sigma(I)$]. All hydrogen atoms calculated. Non-hydrogen atoms were refined with anisotropic thermal parameters. Atomic coordinates (non-H atoms) are given in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the Australian Research Council and the Royal Society (P. C. A.) for financial support and also Karl Byriel and Colin Kennard for some data collection.

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Received 25*th May* 1995; *Paper* 5/03375F