Unusual Routes to Complexes of Binary Alkali Metal–Non-metal Compounds:† Preparations and Crystal and Solution Structures of Li_2S_6·(tmeda)$_2$ (tmeda = tetramethylethylenediamine), and Synthetic Extensions of the Routes

Arthur J. Banister,[a] Donald Barr,[b] Alan T. Brooker,[b] William Clegg,[c] Malcolm J. Cunnington,[a] Michael J. Doyle,[b] Simon R. Drake,[b] Wendy R. Gill,[a] Kenneth Manning,[a] Paul R. Raithby,[b] Ronald Snaith,*[b] Kenneth Wade,*[a] and Dominic S. Wright[b]

[a] *Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, U.K.*
[b] *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.*
[c] *Department of Chemistry, The University, Newcastle upon Tyne NE1 7RU, U.K.*

The complex Li_2S_6·(tmeda)$_2$ (tmeda = tetramethylethylenediamine) was obtained by reactions of Bu^{n}Li solution or Li metal or LiH solid with S powder suspended in toluene containing tmeda, or by tmeda/toluene extraction of the product from reaction of $LiBH_4$ and S (1 : 3 molar ratio) in tetrahydrofuran (thf): its crystal structure contains a central Li_2S_2 ring and there are alternating types of bond in the S_6^{2-} residue; in donor solvents, this dianion cleaves to give the bright blue $S_3^{\cdot -}$ radical anion; several other complexes of type $(MX_y{\cdot}xL)_n$ have been prepared from reactions of alkali metals (M = Li, Na, K) with non-metals (X = S, Se, Te, P, As) in toluene containing stoicheiometric amounts of donors [L = hexamethylphosphoramide (hmpa), tmeda, pentamethyldiethylenetriamine (pmdeta)].

The title complex Li_2S_6·(tmeda)$_2$, (**1**) [tmeda = $Me_2N(CH_2)_2NMe_2$], arose from two independent investigations. Recent work in Cambridge had established a novel route to alkali metal complexes $(MX{\cdot}xL)_n$ with M = Li, Na, and K, X = Cl, Br, I, and SCN, and L (Lewis base) = hmpa [$O{=}P(NMe_2)_3$], tmeda, and pmdeta [$MeN(CH_2CH_2NMe_2)_2$]. This route involves reacting solid ammonium salts NH_4X with metal sources (Bu^{n}Li solution, MH or M solids) in toluene containing stoicheiometric molar amounts (x) of the donor, L.[1] Such reactions proceed at or below room temperature and, during their course, unusual colour changes occur; when X = SCN, radical intermediates have been detected.[1c] These results implied that under mild solution/suspension conditions, simple metal sources might also transfer electrons to solid non- and semi-metallic later Main Group elements (X = P, As, Sb, Bi, S, Se, Te), thereby affording new materials of type $(MX_y{\cdot}xL)_n$. Furthermore, it was felt that initial complexation of these binary compounds could afford crystalline, organically-soluble materials amenable to structural (*X*-ray, NMR) study, though donors might be subsequently removable *in vacuo*. To first test these ideas, sulphur was chosen as the non-metal, X: it forms many radical species and there is considerable interest in alkali metal sulphides as battery components.[2] In fact, Bu^{n}Li solution reacts readily with S powder suspended in a tmeda/arene solvent mix to give $(LiS_3{\cdot}tmeda)_n$, (**1**), and several other complexes of binary alkali metal–non-metal compounds can be synthesised by analogous routes (Table 1).

The Durham group, having interests in various aspects of lithium co-ordination chemistry, including lithium–sulphur[3–5] and lithium borohydride chemistry,[6] isolated (**1**) during a study of a lithium borohydride–sulphur system. Reactions between alkali metal borohydrides, MBH_4, and sulphur in the B : S ratio 1 : 3 reportedly afford the products MBH_2S_3 thought to have four-membered B–S–S–S rings. Lalancette and co-workers demonstrated that these products have distinctive reducing properties, and an intimate mixture of $NaBH_4$ and 3/8 S_8 is marketed as 'Lalancette's reagent.'[7,8] However, these 'sulphurated borohydride' reagents have not been structurally characterised. Accordingly, a crystalline boron–sulphur complex soluble in organic solvents was sought by treatment of the lithium equivalent of Lalancette's reagent with donors (tmeda, pmdeta, or pyridine). In fact, such treatment with tmeda in toluene led instead to the isolation of the boron-free compound, (**1**).

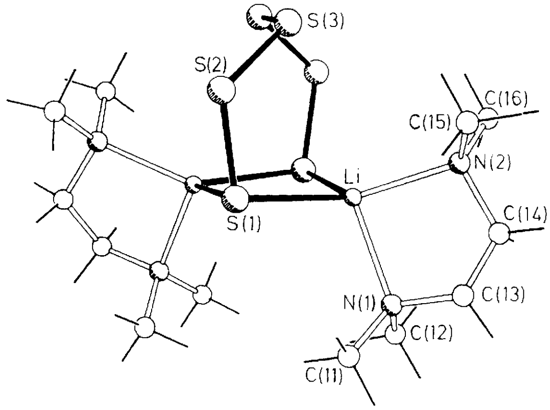

Figure 1. Molecular structure of (**1**) with independent non-hydrogen atoms labelled, and with only one disorder component shown. Key dimensions: Li-S(1) 2.499(11), Li-S(1') 2.501(8), S(1)-S(2) 2.000(3), S(2)-S(3) 1.945(7), S(2)-S(4) 1.892(8), S(3)-S(3') 2.097(10), S(4)-S(4') 2.053(18), Li-N(1) 2.138(9), Li-N(2) 2.124(8) Å; S(1)-Li-S(1') 98.1(2), Li-S(1)-Li' 81.5(2), Li-S(1)-S(2) 103.9(3), Li'-S(1)-S(2) 99.2(2), S(1)-S(2)-S(3) 113.7(3), S(1)-S(2)-S(4) 115.5(3), S(2)-S(3)-S(3') 112.6(2), S(2)-S(4)-S(4') 116.5(3)°.

Addition of Bu^{n}Li solution (in hexane; 10 mmol) to a frozen suspension of S powder (1.28g, 40 mmol) in toluene (10 ml) containing tmeda (2.32g, 20 mmol) initiated a vigorous exothermic reaction. In <1 min all the yellow powder had reacted to leave an orange solution which, at room temperature, precipitated an orange solid. This dissolved in warm benzene (20 ml), refrigeration then giving a mass of orange crystals identified as $(LiS_3{\cdot}tmeda)_n$, (**1**).§ This product is in fact obtained, in 80%+ yield, from 1:2 Bu^{n}Li : tmeda reactions with S over 3:8 ratios. It is also produced, in similarly high yields, from reactions in toluene of S and tmeda (4:2 ratio) with one molar proportion of Li metal or of LiH solid; however, these reactions require heating, at 40 °C for 3 min and at 80 °C for 5 h, respectively. Furthermore, reactions of Bu^{n}Li with S in toluene containing alternative donors, L =

---

† The alkali metal–non-metal route and its extensions were developed in Cambridge (A. T. B., S. R. D., R. S., and D. S. W.) and are the subjects of a U.K. patent application (8911600.8) filed by the Associated Octel Co. Ltd., U.K.

§ For $(LiS_3{\cdot}tmeda)_n$, (**1**): m.p., 158 °C (decomp.); ^1H NMR spectrum (80 MHz, [$^2H_6$]benzene, 25 °C), tmeda resonances at δ 2.14 (s, 12H) and 1.85 (s, 4H). Satisfactory analyses (C, H, N, S, Li) were obtained.

Table 1. Other [excluding (**1**)] complexes of binary alkali metal–non-metal compounds synthesised.

Product[a]	Reagents[b] (molar ratios)	Conditions[c] and observations	Product descriptions	Yields, first batch/%	Melting points/°C
Li_2S_6·2hmpa	BuLi : S : hmpa (1 : 4 : 2)	Dark red solution after <5 min at room temp.; layered with hexane, refrigerated	Pink crystals	62	145—149
Li_2S_6·2pmdeta	BuLi : S : pmdeta (1 : 4 : 2)	Orange solution after <1 min at room temp.; solution refrigerated	Orange needles	67	117—119
Na_2S_6·2pmdeta	Na : S : pmdeta (1 : 4 : 2)	Red solution after reflux for 3 min; refrigerated	Red crystals	84	131—134
K_2S_6·hmpa	K : S : hmpa (1 : 4 : 2)	Product precipitated after heating at 80 °C for 1 h. Dissolved in excess hmpa, then solution cooled	Red–orange crystals	46	214—217
K_2Se_6·hmpa	K : Se : hmpa (1 : 2 : 4)	Most solids dissolved after 2.5 h at 100 °C. Filtration, then refrigeration of dark green solution	Deep green crystals	40	185 (decomp.)
Na_2Te_4·2hmpa	Na : Te : hmpa (1 : 1 : 3)	Deep purple solution after 4 h at 100 °C; filtered then refrigerated	Purple–black crystals	43	225 (decomp.)
LiP_4·2tmeda	BuLi : white P : tmeda (1 : 4 : 1)	Yellow precipitate at room temp. Dissolved on warming, solution refrigerated	Yellow crystals	33	250 (decomp.)
KAs·hmpa	K : As : hmpa (1 : 1 : 2)	Red–orange solution after ultrasonication for 1 h, then reflux for 3 h; solution cooled	Orange crystals	10	292—294

[a] Satisfactory analyses were obtained for all products. [b] All reactions were carried out in toluene solvent. [c] All reactants were brought together in toluene chilled by liquid nitrogen.

hmpa, pmdeta, also work (see Table 1). Such processes, each giving a high yield of a single and pure crystalline material, rapidly and under mild conditions, may be contrasted with previous known routes to alkali metal sulphides; notably M + S reactions in boiling toluene (M = Na, K, giving mixed products, *e.g.*, $Na_2S_{3.3}$, $Na_2S_{3.5}$[9a]), electrochemical reactions [*e.g.*, of S and Na in dimethyl sulphoxide (dmso), giving Na_2S_n, n = 4,6,8[9b]], treatment of M in EtOH by H_2S/further S (*e.g.*, giving K_2S_3/K_2S_5[9c] or K_2S_5[9d]) and reactions of the elements in liquid NH_3 (*e.g.*, M = Li giving, in solution, S_4N^-, S_3^-, S_4^-, S_6^{2-} species[9e]).

In the alternative synthesis of (**1**), dry powdered sulphur (30 mmol) was added slowly to a solution of $LiBH_4$ (10 mmol) in tetrahydrofuran (thf) (20 ml), causing mildly exothermic evolution of hydrogen (n.b. addition of thf to a powdered mixture of $LiBH_4$ and S gives a violent reaction). Removal of solvent from the resulting yellow solution left a sticky green–yellow residue. This was extracted with a solution of tmeda (20 mmol) in toluene (30 ml) to give a solution from which orange crystals of (**1**) could be grown at −10 °C. Elemental analysis of the product left after extraction gives an approximate composition $LiB_3S_6H_2$·tmeda, appropriate for a lithium thioborate.

The crystal structure of (**1**) was determined by *X*-ray diffraction (by W. C. at Newcastle[‡] and by M. J. D. and P. R. R. in Cambridge). Complex (**1**) is dimeric (n = 2), Li_2S_6·2tmeda (Figure 1). It has exact crystallographic two fold symmetry and contains a near-planar Li_2S_2 ring in which each tetrahedrally co-ordinated metal atom bears a chelating tmeda ligand. The two pyramidally co-ordinated S atoms are linked to each other through a buckled S_4 chain, in which the central two S atoms are disordered. The bond between these two atoms [S(3) and S(3′) or S(4) and S(4′); these are alternative positions with site occupation factors of approximately 0.6 and 0.4 respectively] is an appropriate length for an S–S single bond (2.05 or 2.10 Å). The other four S–S bonds are all shorter than this (terminal 2.00 Å, others 1.95 or 1.89 Å), indicating possible delocalisation of the anionic charge in the chain. This alternation of S–S bond lengths differs from that in the caesium salt Cs_2S_6, in which S_6^{2-} anions have terminal and middle S–S bonds of length 2.02 Å, the other two bonds being longer at 2.11 Å.[13] The Li–S distances in (**1**) (*ca.* 2.50 Å) are typical of lithium–sulphur compounds in general.[3—5] Although S_6^{2-} has been detected in solutions of lithium polysulphides in liquid ammonia, DMSO, and dimethylformamide,[9e,14,15] the present studies have produced the first solid-state structure determination of any lithium sulphide above the disulphide Li_2S_2.[16] In fact, Li_2S_2 itself is produced on heating (130 °C) (**1**) *in vacuo*, tmeda and β-sulphur (which sublimes out) being lost.

Complex (**1**) dissolves in donor solvents (acetone, dmso, hmpa) to give bright blue solutions. (The initial product from the $LiBH_4$/S/thf reaction also gave blue solutions on treatment with donor solvents, consistent with Lalancette's report that 'sulphurated borohydrides' are soluble in hmpa to give blue solutions.[7]) The slightest cooling of the acetone solution deposits orange (**1**), but in dmso the colour persists from 298 to 258 K; over this temperature range, an ESR spectrum can be recorded as a broad singlet, g value 2.026. The blue species is thus shown to be $S_3^{\cdot -}$ (lit. g value 2.028[17]), as is found in lapis lazuli and ultramarine, and in some S-doped borate glasses.[9e,14,15] This radical anion has been detected before, by Raman[18,19] and electronic[20] spectroscopy, in donor solutions of alkali polysulphides. A recent report[9e] of Li_xS_y species (including y = 6) in liquid NH_3 noted in dilute solution a blue

---

[‡] *Crystal data* for (**1**): $C_{12}H_{32}Li_2N_4S_6$, M = 438.7, monoclinic, a = 22.823(3), b = 9.176(2), c = 15.041(2) Å, β = 129.784(7)°, U = 2420.6 Å^3, Z = 4, D_c = 1.203 g cm^{-3}, $F(000)$ = 936, μ = 0.55 mm^{-1} for Mo-K_α radiation (λ = 0.71073 Å), T = 295 K, space group $C2/c$. The structure was determined by direct methods[10] and refined to a minimum of $\Sigma w\Delta^2$ [$\Delta = |F_o| - |F_c|$; $w^{-1} = \sigma_c^2(F) + 4 + 25G - G^2 - 4H + 3H^2 - 50GH$; $G = F_o/F_{max.}$, $H = \sin\theta/\sin\theta_{max.}$][11] from 1252 reflections with $2\theta < 50°$ and $F > 4\sigma_c(F)$ (σ_c from counting statistics only) measured with a Stoe-Siemens diffractometer and on-line profile fitting.[12] Final R = 0.061, $R_W = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$ = 0.064 for 131 parameters including anisotropic thermal parameters and constrained hydrogen atoms. 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.

colour at room temperature but a red one in concentrated solution, attributed to $S_6^{2-} \rightleftharpoons S_3^{\cdot-}$ equilibria. In hmpa solutions of (**1**), partial dissociation of S_6^{2-} into $S_3^{\cdot-}$ is irreversible over 298—77 K; at 77 K the ESR spectrum resolves into three *g* tensors, $g_3 = 2.003$, $g_2 = 2.033$, and $g_1 = 2.047$, so $g_{av} = 2.028$.

The study to date on the $LiBH_4$/S/thf system suggests that the initial reaction product contains both thioborates and polysulphides in proportions that reflect the borohydride/sulphur ratio.

Regarding the metal–non-metal synthetic strategy outlined above for Li_2S_6 complexes, this seems widely applicable. Brief details of these synthetic extensions are given in Table 1. First, other alkali metals (Na, K) react with S powder suspended in toluene/L media to give crystalline products, though the conditions required become noticeably more stringent (*cf.* the Na system with the K one). Second, alkali metals (M = Na, K) react with the heavier non-metals from Group 6 (X = Se, Te) in toluene containing hmpa; crystalline products of form $M_2X_y \cdot x$hmpa (X = Se, $y = 6$, $x = 1$; X = Te, $y = 4$, $x = 2$) can be isolated. Finally, the route can be applied to Group 5 non-metals (X = P, As) *via* reactions in toluene of white P with Bu^{n}Li and tmeda and of As powder with K and hmpa.

We thank the S.E.R.C. (D. B., A. T. B., W. C., W. R. G., R. S., D. S. W.), the Associated Octel Co. Ltd. (M. J. C., R. S., D. S. W.), and St. John's College, Cambridge (S. R. D.) for financial support.

Received, 27th July 1989;¶ Com. 9/03189H

References

1 (a) D. Barr, R. Snaith, D. S. Wright, R. E. Mulvey, and K. Wade, *J. Am. Chem. Soc.*, 1987, **109**, 7891; (b) D. Barr, M. J. Doyle, R. E. Mulvey, P. R. Raithby, R. Snaith, and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1988, 145; (c) D. Barr, M. J. Doyle, S. R. Drake, P. R. Raithby, R. Snaith, and D. S. Wright, *ibid.*, 1988, 415; (d) D. Barr, M. J. Doyle, P. R. Raithby, R. Snaith, D. S. Wright, R. E. Mulvey, and D. Reed, *ibid.*, 1989, 318; (e) D. Barr, M. J. Doyle, S. R. Drake, P. R. Raithby, R. Snaith, and D. S. Wright, *Inorg. Chem.*, 1989, **28**, 1767.

2 'Lithium: Current Applications in Science, Medicine, and Technology,' ed. R. O. Bach, Wiley-Interscience, New York, 1985; see especially ch. 9—11.

3 D. R. Armstrong, A. J. Banister, W. Clegg, and W. R. Gill, *J. Chem. Soc., Chem. Commun.*, 1986, 1672.

4 A. J. Banister, W. Clegg, and W. R. Gill, *J. Chem. Soc., Chem. Commun.*, 1987, 850.

5 A. J. Banister, W. Clegg, and W. R. Gill, *J. Chem. Soc., Chem. Commun.*, 1988, 131.

6 D. R. Armstrong, W. Clegg, H. M. Colquhoun, J. A. Daniels, R. E. Mulvey, I. R. Stephenson, and K. Wade, *J. Chem. Soc., Chem. Commun.*, 1987, 630.

7 J. M. Lalancette, A. Frêche, and R. Monteux, *Can. J. Chem.*, 1968, **46**, 2754.

8 J. M. Lalancette, A. Frêche, J. R. Brindle, and M. Laliberte, *Synthesis*, 1972, 526, and references cited therein.

9 (a) F. Fehér and H. J. Berthold, *Z. Anorg. Allg. Chem.*, 1953, **273**, 144; **274**, 223; (b) R. P. Martin, W. H. Doub, J. L. Roberts, and D. T. Sawyer, *Inorg. Chem.*, 1973, **12**, 1921; (c) G. J. Janz, J. W. Coutts, J. R. Downey, and E. Roduner, *ibid.*, 1975, **15**, 1755; (d) B. Kelly and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1976, 1314; (e) P. Dubois, J. P. Lelieur, and G. Lepoutre, *Inorg. Chem.*, 1988, **27**, 73.

10 G. M. Sheldrick, SHELXTL: an integrated system for solving, refining, and displaying crystal structures from diffraction data. Revision 5. Univ. of Göttingen, 1985.

11 H. Wang and B. E. Robertson, 'Structure and Statistics in Crystallography,' ed. A. J. Wilson, Adenine Press, New York, 1985, 125.

12 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.

13 S. C. Abrahams and E. Grison, *Acta Crystallogr.*, 1953, **6**, 206.

14 T. Chivers and I. Drummond, *Inorg. Chem.*, 1972, **11**, 2525.

15 R. D. Rauh, F. S. Shuker, J. M. Marston, and S. B. Brummer, *J. Inorg. Nucl. Chem.*, 1977, **39**, 1761, and references cited therein.

16 J.-M. Letoffe, J.-M. Blanchard, and J. Bousquet, *Bull. Soc. Chim. Fr.*, 1976, 395.

17 T. Chivers, in 'Homoatomic Rings, Chains and Macromolecules of Main Group Elements,' ed. A. L. Rheingold, Elsevier, Amsterdam, 1979, ch. 22, pp. 499—537.

18 R. J. H. Clark and D. G. Cobbold, *Inorg. Chem.*, 1987, **17**, 3169.

19 T. Chivers and C. Lau, *Inorg. Chem.*, 1982, **21**, 453.

20 F. A. Cotton, J. B. Harmon, and R. M. Hedges, *J. Am. Chem. Soc.*, 1976, **98**, 1417.

¶ Received in amalgamated form, 26th October 1989.