Lithiation and Dethiacarbonylation of a Heterocyclic Thioamide $\overline{C_6H_4O\cdot C(=S)N}H$ by Reaction with Solid Li_2S in the Presence of Hexamethylphosphoramide: Synthesis and Crystal Structure of $[\overline{C_6H_4O\cdot C(=S)N}Li\cdot HMPA]_2\cdot C_6H_4(OH)NH_2$

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Solid Li_2S reacts with a solution of $\overline{C_6H_4O\cdot C(=S)N}H$ and hexamethylphosphoramide (HMPA) in toluene to give $[\overline{C_6H_4O\cdot C(=S)N}Li\cdot\mu_2\text{-}HMPA]_2\cdot C_6H_4(OH)NH_2$, **1**, in which two equivalents of the organic acid have been lithiated while a third equivalent has been stripped of its C=S group and di-protonated; structurally, complex **1**, which can also be prepared directly by reacting Bu^nLi, $\overline{C_6H_4O\cdot C(=S)N}H$, HMPA and $NH_2C_6H_4OH$ in 2 : 2 : 2 : 1 amounts, is unique in having a heterobifunctional ligand ($NH_2C_6H_4OH$) bridging two Li^+ centres in the same molecule.

We described recently, several early main group metal complexes of types $(\overline{Y\text{–}R\text{–}X)_nM}\cdot xL$ and $(Y\text{–}R\text{–}X)_nM\cdot xL\cdot yH_2O$.[1] In these, the organic anion $(Y\text{–}R\text{–}X)^-$ has two electronegative centres (X, Y; combinations of N, O, S) as in 2-mercaptobenzoxazolyl $[\overline{C_6H_4O\cdot C(\cdots S)\cdots N}]^-$ (OxS^-; X=N, Y=S), M is drawn from Li, Na,[1a,b] Ca, Sr, Ba,[1c] and L is a Lewis base, *e.g.* TMDA $[Me_2N(CH_2)_2NMe_2]$ (TMDA = tetramethylethylenediamine),[1a] or HMPA $[O{=}P(NMe_2)_3]$.[1b,c] Key structural features are that, whilst in the anhydrous complexes X and Y chelate the M^{n+} ion, in the aqua species one centre (Y; S in OxS^-) is displaced from the cation by H_2O insertion and then stabilises this H_2O by hydrogen bonding to it. Direct syntheses of the aqua complexes assemble the H_2O by reacting Y–R–XH and L in solution with solid metal hydroxides, *e.g.* solid LiOH reacts with OxSH and HMPA in toluene to give the dimer $[(OxS)Li\cdot(\mu_2\text{-}HMPA)_2\cdot Li\text{-}(SOx)]\cdot 2H_2O$,[1b] [eqn. (1)] in which each $Li(H_2O)^+$ unit is bonded to the N of OxS^-, with S being displaced. Here, we describe the results of a seemingly similar system expected to assemble H_2S, *viz*. reacting solid Li_2S with OxSH and HMPA [eqn. (2)]. The anticipated product, $(OxSLi\cdot HMPA)_2\cdot H_2S$, is not in fact obtained. Instead, although every two OxSH molecules are indeed lithiated, a third is dethiacarbonylated to give 2-aminophenol, which then bridges the two lithium centres in the overall product $(OxSLi\cdot HMPA)_2\cdot(NH_2\text{-}C_6H_4OH)$, **1**.

$$2LiOH + 2OxSH + 2HMPA \rightarrow (OxSLi\cdot\mu_2\text{-}HMPA)_2\cdot 2H_2O \quad (1)$$

$$Li_2S + 2OxSH + 2HMPA \not\rightarrow (OxSLi\cdot\mu_2\text{-}HMPA)_2\cdot H_2S \quad (2)$$

Initially, solid Li_2S (1 equiv.) was added to a solution of OxSH and HMPA (2 equiv. of each) in toluene. After identification of the product as **1** rather than as $(OxSLi\cdot HMPA)_2\cdot H_2S$, the reaction was repeated using the correct 1 : 3 : 2 (Li_2S : OxSH : HMPA) stoichiometry.†

The solid-state structure of **1** (Fig. 1) was determined by X-ray diffraction.‡ Much of the molecular core resembles that of $(OxSLi\cdot HMPA\cdot H_2O)_2$.[1b] Thus, two Li^+ cations are bridged

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† **1**: Solid Li_2S (2.5 mmol) was added under nitrogen to a solution of $\overline{C_6H_4O\cdot C(=S)N}H$ (OxSH) (7.5 mmol) and HMPA (5.0 mmol) in toluene (10 cm^3). At this stage the mixture was brown and had a strong smell of H_2S. Heating of the mixture at 80 °C for 12 h caused gradual dissolution of the solid, giving a brown solution. Refrigeration resulted in a crop of pale golden-brown cubic crystals of **1**; first batch yield 0.92 g, 47%; m.p. 119–120 °C; ^1H NMR $[(CD_3)_2SO$, 250 MHz, 20 °C] δ 9.10 (s, 1H, OH), 7.08–6.35 (m, 12H, C_6H_4 of $2OxS^-$ + $NH_2C_6H_4OH$), 4.47 (s, 2H, NH_2), 2.25 (d, 36H, 2HMPA).

‡ *Crystal data* for **1**: $C_{39}H_{59}Li_2N_9O_5P_2S_2$, M = 873.89, monoclinic, space group $P2_1/c$, a = 11.256(2), b = 29.247(6), c = 15.041(3) Å, β = 111.04(3)°, U = 4621.4(16) $Å^3$, Z = 4, D_c = 1.256 Mg m^{-3}, $F(000)$ = 1856, λ = 0.71073 Å, T = 153 K, μ(Mo-Kα) = 0.235 mm^{-1}. Data were collected on a Siemens-Stoe AED using an oil-coated rapidly cooled crystal of dimensions 0.4 × 0.5 × 0.6 mm by the $2\theta\text{–}\omega$ method ($8° \leqslant 2\theta \leqslant 45°$). Of a total of 6872 collected reflections, 6082 were unique. The structure was solved by direct methods (SHELXS 92) and refined by full matrix least-squares analysis on F^2 to R^1 and $wR2$ values of 0.049 and 0.125, respectively (SHELXL 92); largest difference peak and hole 0.39 and −0.33 $eÅ^{-3}$. All hydrogen atoms were located in a difference Fourier map and their positions were refined freely with common refined U values for chemically equivalent atoms.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

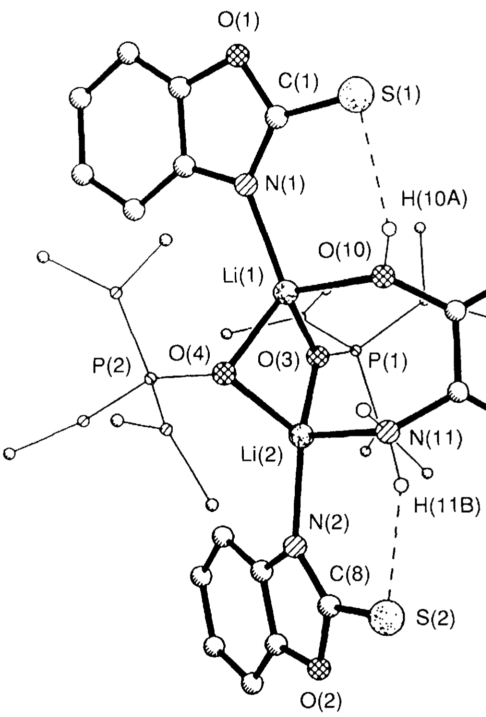
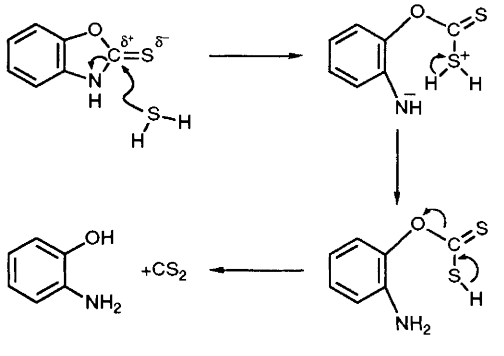


Fig. 1 The molecular structure of $[\overline{C_6H_4O{\cdot}C({=}S)N}Li{\cdot}HMPA]_2{\cdot}NH_2C_6H_4OH$. Except for those of the NH_2 and OH groups, hydrogen atoms have been omitted for the sake of clarity.



Scheme 1

by two HMPA ligands [Li(1)–O(3), 1.953(6); Li(1)–O(4), 1.957(6); Li(2)–O(3), 1.967(6); Li(2)–O(4), 1.968(6)Å *cf.* 1.946(7) and 1.978(8) Å in the aqua complex]; such a μ_2-mode is quite common for dimeric lithium-HMPA complexes.[2] Each Li^+ is bonded terminally to an N atom of an OxS^- anion [Li(1)–N(1), 2.062(6); Li(2)–N(2), 2.058(6)Å *cf.* 2.067(8) Å in the aqua complex]. In both structures, the S centres of OxS^- anions are not bonded to the Li centres. However, whilst in $(OxSLi{\cdot}HMPA{\cdot}H_2O)_2$ such displacement is symmetrical, owing to each Li^+ being complexed by an H_2O molecule [Li–O, 1.913(8) Å], in **1** it is asymmetrical, being caused by the coordination of a bridging bifunctional $NH_2C_6H_4OH$ molecule [Li(1)–O(10), 2.036(6); Li(2)–N(11), 2.054(7)Å]. In effect, O(10) and N(11) of this molecule each direct a lone pair downwards, to Li(1) and Li(2), respectively. The H [H(10A)] of the OH group points upwards from the NC_6H_4O plane whereas one H [H(11B)] of the NH_2 group points downwards, towards the $(OxSLi{\cdot}HMPA)_2$ core. Thus, in order to engage the displaced S atoms of the OxS^- anions in hydrogen bonding [S(1) to H(10A) 2.359, S(2) to H(11B) 2.291 Å] the OxS(1) and OxS(2) ligands are twisted markedly with respect to each other (angle between planes 23.4°).

These results are significant on several fronts. First, **1** is unique in containing a heterobifunctional ligand ($NH_2C_6H_4OH$), which bridges two Li^+ centres intramolecularly; the ligand itself is also unusual in being one susceptible to lithiation. Usually, bifunctional donors (notably TMDA) are deliberately chosen to lack acidic protons, and moreover normally they chelate just one Li^+ centre, *e.g.* as in the dimer $(PhLi.TMDA)_2$,[3a,4] or they bridge two such centres intermolecularly, *e.g.* as in the linked tetramer $(MeLi)_4{\cdot}(TMDA)_2$.[3b,4] Further, alkali metal complexes containing organic ligands which might themselves be metallated are rare, though known in, for example, the amine complex $[(PhCH_2)_2NLi{\cdot}HN(CH_2Ph)_2]_2$[5] and the imine complex $(Bu^t_2C{=}NNa)_4{\cdot}(HN{=}CBu^t_2)_2$.[6] However, these are made by adding a metallating agent to an excess of the organic compound, leaving unaffected amine *etc.* to act as neutral monofunctional ligands, which are terminal on the metal. Once more the case of **1** is very different, since the $NH_2C_6H_4OH$ ligand is made during the reaction, it is bifunctional, and it bridges. Interestingly, it is easy to prepare **1** (in 70% yield) by adding Bu^nLi solution (2 equiv.) to a solution of OxSH (2 equiv.) *and* $NH_2C_6H_4OH$ (just 1 equiv.) in toluene containing HMPA (2 equiv.). The synthesis relies presumably on OxSH having a lower pK_a than $NH_2C_6H_4OH$. By implication it should be possible to take a judiciously chosen mixture of different organic acids, metallate one such, but leave the other(s) to act as a neutral ligand (which might, however, be metallated subsequently).

A second point of interest concerns the actual mechanics of the synthesis of **1**. We have established that OxSH heated in toluene, with or without HMPA, does not rearrange to give $NH_2C_6H_4OH$. Neither does bubbling H_2S gas through a solution of OxSH and HMPA afford this ligand. Thus, it seems that the reaction giving **1** is concerned intimately with the presence of lithium. A tempting scenario has Li_2S reacting with OxSH/HMPA to give the core of **1**, $(OxSLi{\cdot}HMPA)_2$, and H_2S. However, instead of then acting as a ligand (as envisaged originally), the *in situ* generated H_2S (or SH^-) reacts instead with a third equivalent of OxSH, as outlined in Scheme 1. The energetics of such a process are at least feasible. Our *ab initio* MO calculations§ show that the summed absolute energies of the 'products' ($NH_2C_6H_4OH$ + CS_2) amount to 14.4 kcal mol^{-1} (1 cal = 4.184 J) less than those of the 'reactants' (OxSH + H_2S). Entropy changes are presumably minimal. Experimentally, it is noticeable that solid Li_2S in air smells strongly of H_2S (presumably owing to reaction with atmospheric moisture) and addition of Li_2S under dry nitrogen to a toluene solution of the acid OxSH and of HMPA generates this gas also (along with gaseous CS_2 on heating the mixture).

The results described promise several synthetic extensions. On the organic front, we are investigating the potential of solids Li_2S and Li_2O to remove, under the mild conditions described, various $>C{=}X$ units from various heterocyclics, *e.g.* $>C{=}S$ with Li_2S to eliminate CS_2 (as for **1**), $>C{=}O$ with Li_2O to eliminate CO_2, and $>C{=}NR$ with either to eliminate R–N=C=S or R–N=C=O. Coordination studies are concentrating on syntheses, by the routes described, of dimeric alkali metal complexes containing bridging ligands with –XC=CY– groupings, *e.g.* substituted arenes and alkenes with X, Y being –OH, –OR, $-NH_2$, $-NR_2$ *etc.*, or combinations thereof. The reactivities of such ligands 'on site' (including metallation) are also being explored.

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§ The *ab initio* calculations were performed at the MP2 level[7] by means of the computer program GAUSSIAN 90[8] using the 6-31G (ds) basis set.[9] The absolute energies (in a.u.) calculated for the optimised structures were: $NH_2C_6H_4OH$ −361.1935380 and CS_2 −833.2078060 (sum, −1194.4013440), and $\overline{C_6H_4O.C({=}S)N}H$(OxSH) −795.5903676 and H_2S −398.7880757 (sum, −1194.3784433).

We thank the SERC (PhD quota award to F.A.B.), the SERC and the Associated Octel Co. Ltd. (CASE award to M.G.D.), and the DAAD, NATO Scholarship (D. S.) for financial support. Thanks are also due to Dr I. Fleming (Cambridge) for useful discussions.

Received, 23rd June 1992; Com. 2/03280E

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