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The stabilisation of water as a ligand in lithiated organic compounds: intra- and inter-molecular hydrogen bonding in the structures of the aquo complexes $[\overline{C_6H_4OC(=S)=N}Li\cdot HMPA\cdot H_2O]_2$ and $[\overline{C_6H_4OC(=S)=N}Li\cdot HMPA]_2\cdot H_2O$

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Abstract

The feasibility of using water as a ligand within lithiated organics has been confirmed through the syntheses and crystal structures of the dimeric 2-mercaptobenzoxazoyllithium complexes $[\overline{C_6H_4O(C=S)=N}Li\cdot HMPA\cdot H_2O]_2$ (**1**) and $[\overline{C_6H_4O(C=S)=N}Li\cdot HMPA]_2\cdot H_2O$ (**2**) which exhibit intramolecular hydrogen bonding between H_2O and the $S^{\delta-}$ centre of the organic anion and also intermolecular hydrogen bonding, which serves to sew these dimers into extended arrays: *ab initio* MO calculations on model aquo species have clarified the effects of H_2O complexation and hydrogen bonding, in particular, by demonstrating that incorporated H_2O molecules are activated, e.g. towards further metallation.

We recently reported the synthesis and solid-state structure of the first lithiated organic compound containing water as a ligand, 2-mercaptobenzoxazoyllithium tetramethylethylenediamine monohydrate, $\{\overline{C_6H_4OC(=S)=N}Li\cdot TMEDA\cdot H_2O\}$ [1]. This is a discrete monomer, with short *intramolecular* hydrogen bonds between one proton of the complexed H_2O ligand and the uncoordinated $S^{\delta-}$ centre of the organic anion. As such, the structure is a model for the first stage of the well-known deprotonation of H_2O by lithiated organics, i.e. their moisture sensitivity. To investigate further the coordinative role of H_2O in such species, and the nature of its stabilisation by hydrogen bonding, two new aquo complexes of 2-mercaptobenzoxazoyllithium were prepared with monodentate hexamethylphosphoramide (HMPA, $O=P(NMe_2)_3$) as the co-complexant, viz. the monohydrate, $[\overline{C_6H_4OC(=S)=N}Li\cdot HMPA\cdot H_2O]_2$, (**1**) and the hemihydrate, $[\overline{C_6H_4OC(=S)=N}Li\cdot HMPA]_2\cdot H_2O$ (**2**). In the solid state, both new complexes exhibit intramolecular hydrogen bonding within their dimeric molecular units, but also intermolecular hydrogen bonding, so leading to extended arrays. *Ab initio* MO calculations have been successfully employed to probe the cause and effect of hydrogen bonding in such aquo complexes.

Both aquo complexes were prepared via the intermediacy of the anhydrous complex, $[\overline{C_6H_4OC(=S)=N}Li\cdot HMPA]_n$ (**3**), itself prepared by lithiation, using n-butyl lithium, of 2-mercaptobenzoxazole, $\overline{C_6H_4OC(=S)N}H$ or $\overline{C_6H_4OC(-SH)=N}$, in toluene containing one equivalent of HMPA. Complex **1** was obtained by treatment of a freshly prepared solution of **3** with one equivalent of H_2O; after brief sonication and heating (to effect miscibility), cooling of the resulting solution produced crystals of **1**. Complex **2** was prepared by dissolving equimolar amounts of crystals of **1** and **3** in toluene, then recrystallising. The identities of both aquo products were confirmed by elemental analyses, IR spectroscopy (ν(N–H), (S–H) bands absent, ν(O–H) of H_2O present), and ^1H NMR spectroscopy (in d_6-benzene and, to prove the stoichiometric amounts

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of H_2O present, in d_6-DMSO (which displaces the H_2O)).

1, **2** and **3** are colourless crystalline materials: first batch yields, 68%, 73% and 72%, respectively; m.p. 99–103, 105–108 and 143–145 °C, respectively. Satisfactory analyses (C,H,Li,N,P) were obtained for all samples.

IR (Nujol mull) spectra include O–H stretching bands centred at 3538, 3358, 3170 cm^{-1} for **1** and at 3397, 3351, 3174 cm^{-1} for **2**; such bands are not found in the spectrum of **3**.

^{1}H NMR (250 MHz, 25 °C): **1** (C_6D_6) δ 7.96 (1H, m), 7.19 (4H, including H_2O, m), 6.19 (1H, m), 2.23 (18H of HMPA, d, J 9.5 Hz); **1** (C_2D_6SO) δ centred 6.9 (4H, C_6H_4, broad m), 3.58 (2H, H_2O, s), 2.51 (18H of HMPA, d, J 9.4 Hz). **2** (C_6D_6) δ 7.67 (2H, m), 7.20 (6H, including H_2O, m), 6.87 (2H, m), 2.25 (36H of HMPA, d, J 9.5Hz); **2** (C_2D_6SO) δ 7.05 (4H, m), 6.91 (2H, m), 6.82 (2H, m), 3.46 (2H, H_2O, s), 2.50 (36H of HMPA, d, J 9.5 Hz). **3** (C_6D_6) δ 7.84 (1H, m), 7.17 (1H, m), 7.07 (1H, m), 6.87 (1H, m), 2.26 (18H of HMPA, d, J 9.5 Hz).

The syntheses of the title compounds stress further the feasibility of using water as a ligand in the chemistry of selected lithiated organic compounds and demonstrate the complexities which may be expected. They also illustrate the effects of successive hydration within a particular system. Thus, an X-ray crystallographic study of **1*** has shown it to be a symmetric *trans*-aquated dimer in the solid state (Fig. 1(a)). Two HMPA ligands bridge the two Li^+ cations, so giving a central Li_2O_2 ring (Li–O distances, 1.946(7) and 1.978(8) Å); such a μ_2-O mode is quite common for dimeric lithium complexes, both organic and inorganic [2]. Each Li^+ centre is rendered pseudo-tetrahedral by the amido-N atom of an oxazoyl anion (Li–N, 2.067(8) Å) and by a bonded H_2O ligand (Li–O, 1.913(8) Å). As in the previous monomeric aquo complex, $\{\overline{\text{C}_6\text{H}_4\text{OC}(\text{=S})\text{=N}}\text{Li}\cdot\text{TMEDA}\cdot\text{H}_2\text{O}\}$ [1], the $S^{\delta-}$ of the anion is not bonded to the metal. However, these S atoms are involved in both intramolecular (S...O, 3.235(6) Å) and intermolecular (3.330(6) Å) hydrogen bonds [3]. The latter sew the dimers together in a pseudo-2D polymeric array (Fig. 1(b)).

The crystal structure of **2** reveals an asymmetric mono-aquated dimer (Fig. 2(a)). As in **1**, μ_2-HMPA ligands help form a central Li_2O_2 ring (av. Li–O, 1.942(12) Å). One Li^+ ion (Li(2)) is chelated by the oxazoyl anion, through the N (Li–N, 2.056(13) Å) and the S centres (Li–S, 2.757(12) Å, cf. the coordinative interaction in $(\text{Bu}^t\text{SC}_6\text{H}_4\text{Li})_2\cdot\text{TMEDA}$ [4], Li–S, 2.712(15) Å). The other Li^+ is complexed in a manner identical to **1**, by the N atom only of the anion (Li–N, 2.019(12) Å) and by an H_2O ligand (Li–O, 1.930(10) Å). Also as in **1**, there is intramolecular hydrogen bonding between this H_2O ligand and the uncoordinated $S^{\delta-}$ centre (S...O, 3.246(8) Å). The dimeric units of **2** are then linked together into polymeric chains by intermolecular hydrogen bonds (Fig. 2(b)). However, unlike in **1**, these form between the H_2O ligand in one dimer and the Li-attached (i.e. chelating) S centre in an adjacent dimer (O...S, 3.325(7) Å).

Intermolecular $O-H^{\delta+}...S^{\delta-}$ hydrogen bonding has been observed in the solid-state structures of ion-separated dialkylthiocarbamate hydrates $Li(H_2O)_x{}^+...R_2NCS_2{}^-$ ($x = 3$ or 4, R = Me, Et, Pr^i; $R_2 = C_5H_8$) [5]. However, in these examples such interactions occur between complexed aquo-cations and the anions (i.e. solvent-separated ion pairs) rather than, as in **1** and **2**, between ion-paired molecular complexes (contact ion pairs). $(\alpha\text{-C}_6\text{H}_5\text{CHNO}_2\text{Li}\cdot\text{EtOH})_\infty$ provides a closer analogy to **1** and **2**; intra- and intermolecular $O-H^{\delta+}...O^{\delta-}$ bonds link Li-bonded EtOH ligands to the organic anion moieties both within and between monomeric units [6]. However, **1** and **2** are the first examples of oligomeric Li complexes (and, uniquely, aquo ones) which are associated further by intermolecular hydrogen bonding interactions.

Insights into the nature of the intramolecular hydrogen bonding and its effect on the remainder of the molecule have come from *ab initio* MO calculations (6-31G(dS) basis set level, i.e. d orbitals included on S only) on a number of model species involving the key N=C=S unit common to **1** and **2**. The findings are illustrated by the simplest systems, $(HN{=}CH{=}S)^-Li^+$ and $(HN{=}CH{=}S)^-Li^+\cdot nH_2O$,

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*Crystal data: **1**, $C_{26}H_{48}N_8O_6P_2S_2Li_2$, $M = 708.7$, monoclinic, space group $P2_1/c$, $a = 11.888(3)$, $b = 10.680(2)$, $c = 15.724(3)$ Å, $\beta = 108.58(2)°$, $U = 1892.3(7)$ Å^3, $Z = 2$, $D_c = 1.244$ g cm^{-3}, $F(000) = 752$, Cu Kα radiation, $\lambda = 1.54178$ Å, $\mu = 24.44$ cm^{-1}; **2**, $C_{26}H_{46}N_8O_5P_2S_2Li_2$, $M = 690.95$, monoclinic, space group $P2_1/a$, $a = 15.985(2)$, $b = 15.008(2)$, $c = 16.004(2)$ Å, $\beta = 104.36(1)°$, $U = 3719.3(8)$ Å^3, $Z = 4$, $D_c = 1.233$ g cm^{-3}, $F(000) = 1464$, Cu Kα radiation, $\lambda = 1.54178$ Å, $\mu = 23.53$ cm^{-1}.

Both structures were determined by direct methods and Fourier difference techniques. **1** was refined from 2044 unique observed reflections ($F > 4\sigma(F)$) measured at room temperature with a Nicolet R3mμ diffractometer ($2\theta_{max} = 120°$), with anisotropic thermal parameters, and with H atoms in fixed positions after location in the difference map; $R = 0.061$, $R_w = 0.075$ for 210 parameters. **2** was refined from 3578 unique observed reflections ($F > 5\sigma(F)$) measured at room temperature with a Nicolet R3mμ diffractometer ($2\theta_{max} = 120°$), with anisotropic thermal parameters, and with isotropic H atoms in calculated positions; $R = 0.089$, $R_w = 0.099$ for 430 parameters. See also 'Supplementary material'.

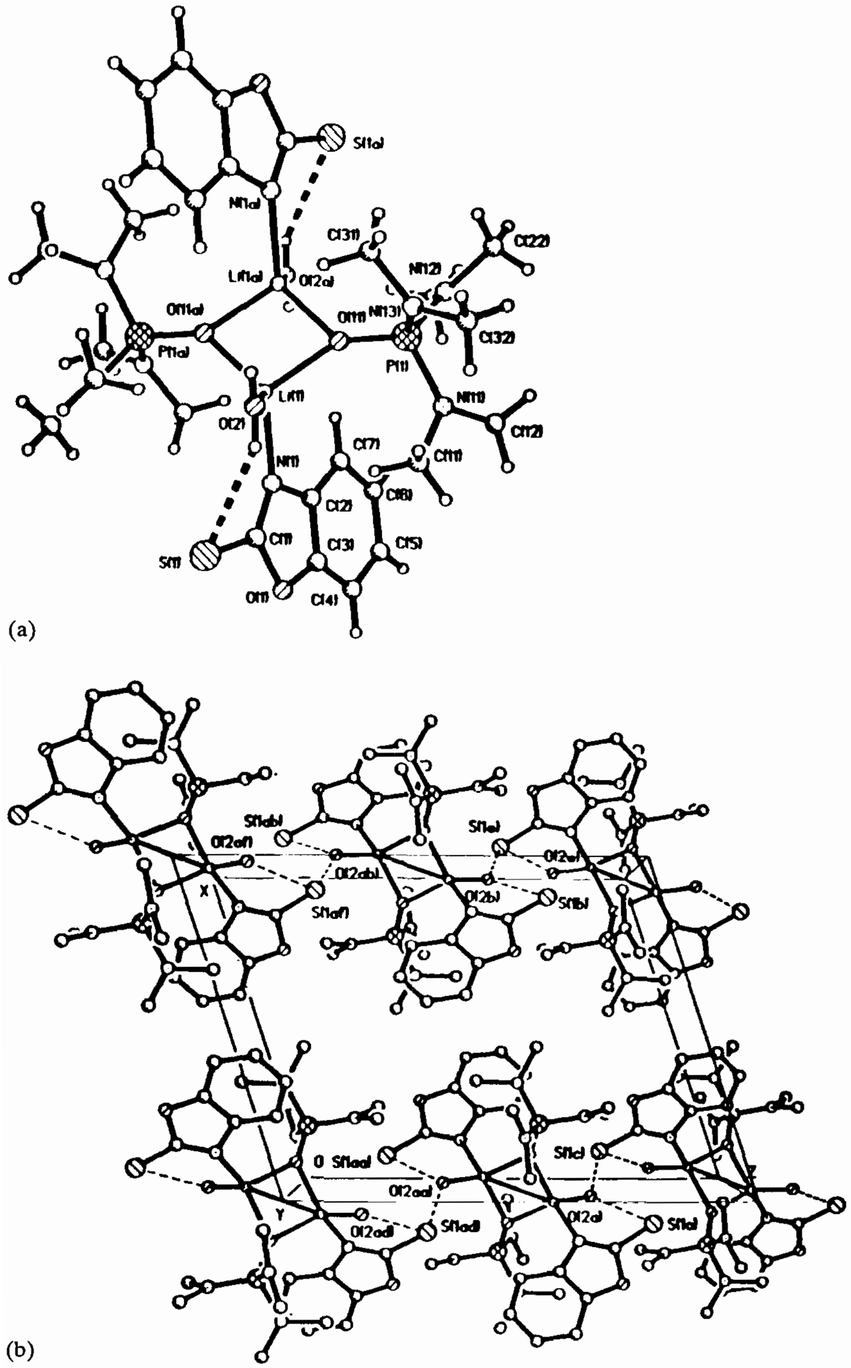

Fig. 1. (a) Molecular (dimeric) structure of **1**. (b) Hydrogen bonding interactions in a cross section of the crystal lattice of **1**.

$n = 1$, 2 and 3*. Their minimum energy optimised structures (confirmed by frequency analysis) are shown in Fig. 3. The water-free compound (Fig. 3(a)) prefers the NS-chelate mode; alternative structures with an Li—N bond *trans* to the C═S bond, with a purely Li-S bond pointing away from N, and with a Li—S bond *cis* to the NH bond are less stable by 19.8, 29.4 and 30.1 kcal mol^{-1}, respectively. Addition of H_2O molecules stabilises the

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*The *ab initio* optimised geometries described were obtained using the programs given in ref. 7. For details of the 6-31G (ds) basis set used, see ref. 8. The total energies (in a.u.) calculated for the optimised structures of $(HN{=}CH{=}S)^{-}Li^{+}$ and $(HN{=}C{=}S)^{-}Li^{+} \cdot nH_2O$, $n = 1$, 2 and 3, are -498.45044, -574.47691, -650.49574 and -726.50160, respectively.

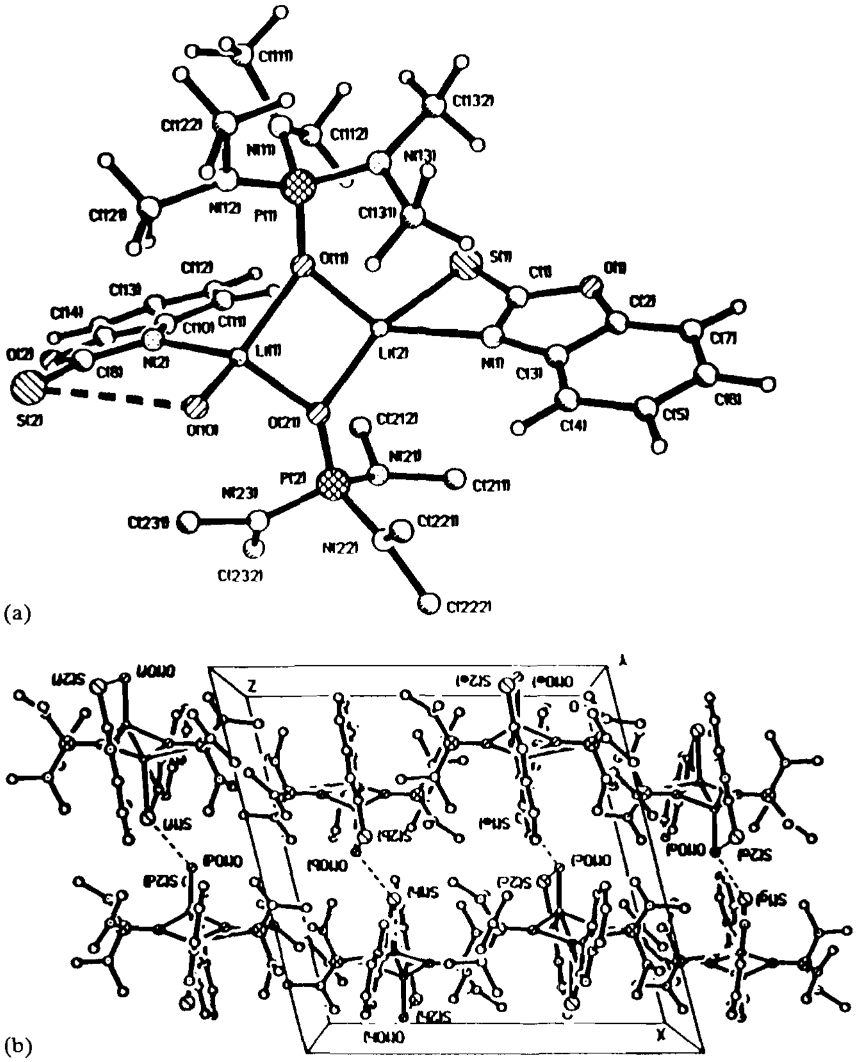

Fig. 2. (a) Molecular (dimeric) structure of 2. (b) Hydrogen bonding interactions in a cross section of the crystal lattice of 2.

$(HN{=}CH{=}S)^{-}Li^{+}\cdot nH_2O$ structure, total solvation energies for $n = 1$, 2 and 3 being 25.8, 46.8 and 59.7 kcal mol^{-1}, respectively (i.e. 25.8, 23.4 and 19.9 kcal mol^{-1} per mol of H_2O). If only one H_2O molecule is added (Fig. 3(b)) the $\overline{NSLi}$ chelate structure is maintained and there is little or no OH...S hydrogen bonding: the $S\hat{Li}O$ angle is 121.9° and both the S...O and S...H distances are long (>3.7 Å). Rotation around the Li−O bond is nearly free. This implies that intramolecular hydrogen bonding will only come into play if Li is at least bis-complexed, i.e. by H_2O and at least one other ligand. This of course is the case in **1**, in one half of **2**, and in the TMEDA·H_2O complex noted above. The implication is confirmed in the optimised structure of the bis(aquo) complex (Fig. 3(c)). The H_2O molecules bend over ($S\hat{Li}O$ angles decrease to 80.5°) and hydrogen bond to the S (S...H 2.520, S...O 3.276 Å; cf. values in **1** and **2**); concomitantly the Li−S link is weakened, and the chelate feature essentially lost. These trends continue in the tris(aquo) species (Fig. 3(d)) which, in fact, is an excellent model for **1** and for the H_2O-complexed half of **2**. Two of the H_2O ligands mimic the bridging HMPA ligands of **1** and **2**. The third H_2O is then free to engage in strong hydrogen bonding to S (S...H 2.212, S...O 3.150 Å) since the $S\hat{Li}O$ angle is now only 60.5°; S−Li bonding has been lost entirely. The calculations point to an additional feature: the H_2O is activated both by complexation and by hydrogen bonding. For example, in the tris(aquo) complex the H−O bond involved with S has a length of 0.975 Å and the charge on H is

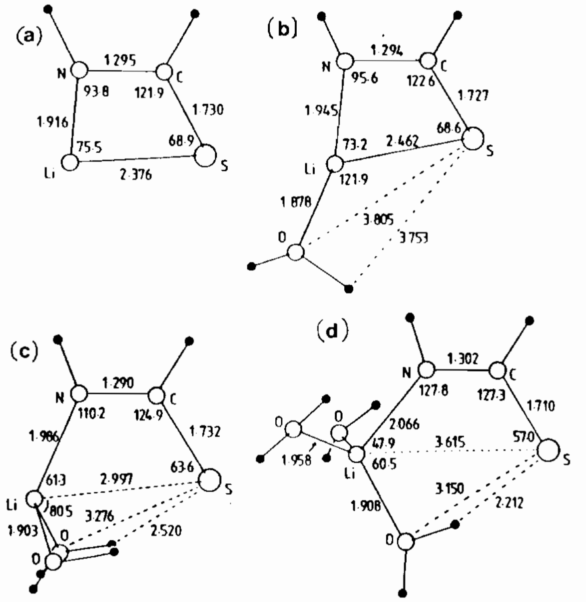

Fig. 3. Key bond distances (Å) and angles (°) in the *ab initio* (6-31G+) optimised structures of (a) $(HN{=}CH{=}S)^{-}Li^{+}$, (b) $(HN{=}CH{=}S)^{-}Li^{+}\cdot H_2O$, (c) $(HN{=}CH{=}S)^{-}Li^{+}\cdot 2H_2O$, (d) $(HN{=}CH{=}S)^{-}Li^{+}\cdot 3H_2O$.

+0.48, while the other H−O bond (of the same H_2O) is of length 0.946 Å and the charge on H is +0.43; both sets of values can be compared with those in the optimised structure of isolated H_2O (0.950 Å, +0.41). Such results are highly relevant to our preliminary observations that the H_2O molecules in the experimentally observed aquo complexes can be metallated, so producing 'mixed' organometallic-metal hydroxide complexes.

Supplementary material

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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