# The First Lithiated Organic Compound containing Water as a Ligand: Synthesis and Crystal Structure of 2-Mercaptobenzoxazolyl(tetramethylethylenediamine)lithium Monohydrate, $\overline{\mathrm{C_6H_4OC(\cdots S)\cdots N}}\mathrm{Li(tmeda)H_2O}$, a Model Acid–Base Intermediate

**Donald Barr,[a] Paul R. Raithby,[a] Paul von Ragué Schleyer,[b] Ronald Snaith,[a] and Dominic S. Wright*[a]**

[a] *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK*

[b] *Institut für Organische Chemie der Universität Erlangen-Nürnberg, Henkestrasse 42, D-8520 Erlangen, FRG*

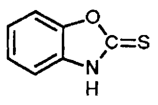
Lithiation of 2-mercaptobenzoxazole, $\overline{\mathrm{C_6H_4OC(SH)=N}}$, in the presence of tmeda $[\mathrm{Me_2N(CH_2)_2NMe_2}]$ and $H_2O$ produces the monomeric title complex, $\overline{\mathrm{C_6H_4OC(\cdots S)\cdots N}}\mathrm{Li(tmeda)H_2O}$ (**1**), the first lithiated organic compound containing water as a ligand; this complex exhibits strong hydrogen bonding between one proton of the co-ordinated $H_2O$ and the $S^{\delta-}$ centre of the organic anion, and so provides the first structural model for the well known hydrolytic sensitivity of organolithium compounds in general.

Organolithium species are well known to be moisture-sensitive, hydrolysis yielding the non-metallated organic species and LiOH.[1] Hence, the present observation of a solid-state structure in which water acts as a polar ligand is startling. Both *X*-ray diffraction and spectroscopic studies show that the water ligand in 2-mercaptobenzoxazolyl(tetramethylethylenediamine)lithium monohydrate (**1**) is attached to Li. At the same time, the $H_2O$ is linked to the anion by intramolecular OH⋯S bonding. As MNDO calculations indicate that the non-lithiated organic acid, 2-mercaptobenzoxazole (**2**), prefers the *thiol* [$\overline{C_6H_4OC(SH)=N}$] rather than the *amine* [$\overline{C_6H_4OC=S(NH)}$] form,† the structure of (**1**) can serve as a model for the proton transfer intermediate during hydrolysis reactions.

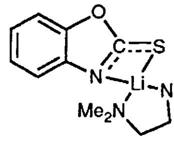
The first preparation of (**1**) was fortuitous. When Bu$^n$Li (5 mmol, in hexane) was added to a solution of 2-mercaptobenzoxazole (5 mmol) in toluene (25 ml) and tmeda [$Me_2N(CH_2)_2NMe_2$] (5 mmol) at 20 °C, a vigorous exothermic reaction occurred and the colour changed from orange–yellow to yellow. The lithiation product isolated from this yellow solution is a [$\overline{C_6H_4OC(\cdots S)\cdots N}Li(tmeda)]_n$ complex (**3**), which probably, if monomeric ($n$ = 1), has a structure involving N and S (rather than O and S) chelation to Li.† However, in one attempt to grow *X*-ray-quality crystals of (**3**), benzene (10 ml) was added to the initial yellow solution and the solution stored at 20 °C for 2 weeks. During this time water was absorbed (from air or solvent) and a crop of faceted rods of (**1**) resulted. A deliberate synthesis was later carried out in which distilled water (5 mmol) was introduced to a freshly prepared solution of (**3**). Storage at 5 °C for 24 h also produced crystals of (**1**).‡

*X*-Ray structure analysis shows (**1**) (Figure 1)§ to be a monomeric amido-lithium complex with a water ligand attached to lithium. Both hydrogen atoms of the $H_2O$ molecule were located in the difference Fourier map and no residual electron density was found about the anion. The co-ordinated water ligand is bound to lithium at a Li–O distance of 1.950(7) Å, which is slightly longer than the Li–O($H_2$) distances in inorganic Li complexes, *e.g.*, 1.936(4) and 1.940(4) Å in the dimeric cationic[2] $[Li(H_2O)_2\{O=P(NMe_2)_3\}]_2{}^{2+}2Cl^-$ and *ca.* 1.94 Å in $LiCl(C_5H_5N)_2(H_2O)_2$.[3] The Li⋯S distance [3.370(5) Å] is clearly too long to be considered as either a direct S–Li bond [*e.g.*, 2.412(6) Å in *o*-$MeC_6H_4SLi\cdot3pyridine$[4]], or as a co-ordinative S → Li bond [*e.g.*, 2.712(5) Å in $(Bu^tSC_6H_4Li)_2(tmeda)$[5]]. However, one water proton is involved in an intramolecular $O–H^{\delta+}\cdots S^{\delta-}$ bond [H(1)⋯S 2.467(80) Å; O(2)⋯S 3.304(4) Å].[6]

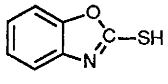
Such bonding also occurs in the solid-state structures of ion-separated dialkylthiocarbamate hydrates, $Li(H_2O)_x{}^+\cdots R_2NCS_2{}^-$ ($x$ = 3 or 4, R = Me, Et, or Pr$^i$; or $R_2N$ = tetrahydropyridyl) [H⋯S 2.16(4)—2.91(12) Å; O⋯S 3.203(7)—3.382(2) Å],[7] and in Schlippe's salt, $Na_3SbS_4\cdot9H_2O$ [H⋯S 2.364(11)—2.411(6) Å; O⋯S 3.305(4)—3.369(4) Å].[8] However, in these examples such interactions occur between complexed aquo-cations and the anions, rather than within the co-ordination sphere of the $Li^+$ cation [as in (**1**)]. The closest example to (**1**) is that of $[PhCH(NO_2)Li\cdot EtOH]_\infty$,[9] where intramolecular $O–H^{\delta+}\cdots O^{\delta-}$ bonds link Li-bound EtOH ligands to the organic anion. The (amido)-N atom of the 2-mercaptobenzoxazolyl group is bound trigonally to the Li [sum of angles about N(1), 359.5(9)°; Li–N(1), 2.051(7) Å]. However, the angle between Li and the $C_6H_4$ ring is widened [LiN(1)C(2), 137.7(3)°]. The organic group is pivoted, about N(1), towards the $H_2O$ ligand. This aligns the S atom for S⋯H bonding. In this way, the structure of (**1**) can be viewed as a model for how hydrolysis of organolithium compounds might occur: initial co-ordination of $H_2O$ to the $Li^+$ centre followed by proton transfer to the carbanion (to give LiOH and the organic acid), this last step being facilitated by $H^{\delta+}$ (of $H_2O$)⋯organic anion hydrogen bonding. The only significant structural changes within the anion, as compared to the



(**2**) amine



(**3**)



(**2**) thiol

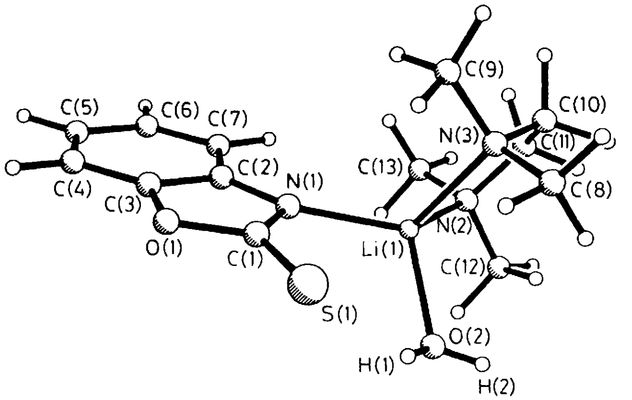


**Figure 1.** Molecular structure of $\overline{C_6H_4OC(\cdots S)\cdots N}Li(tmeda)H_2O$, (**1**).

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† MNDO calculations on $\overline{HC=CHNHC(=S)O}$ and $\overline{HC=CHN=C(-SH)O}$ as models for (**2**) show that the latter is 9.2 kcal mol$^{-1}$ (1 cal = 4.184 J) more stable. Calculations on the lithium derivatives of these models show the (N,S)-chelated Li species to be preferred by 14.0 kcal mol$^{-1}$ over the (O,S)-chelated isomer. Solvation of Li by two $H_2O$ ligands (to mimic one tmeda ligand) leads to the same preference for (N,S)-rather than (O,S)-bridging, the energy difference then being 11.4 kcal mol$^{-1}$.

MNDO programs: M. S. J. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899; W. Thiel, QCPE No. 438, vol. 2, 1982, 63; M. S. J. Dewar and C. H. Reynolds, *J. Comput. Chem.*, 1985, **2**, 140.

Data for (**2**): $^1H$ NMR (250 MHz; $C_6D_6$; 25 °C) δ 6.30 (m, 1H), 6.35 (1H, br s, S-H) and 6.62 (3H, m); $^{13}C$ NMR (100.6 MHz; $C_6D_6$; 25 °C) δ 109.6, 110.0, 123.6, and 124.4 [C(4), C(5), C(6), and C(7)]; C(1)—C(3) signals could not be detected owing to the poor solubility of (**2**) in $C_6D_6$.

Data for (**3**): m.p. 158—161 °C, yield 63%; IR (Nujol) shows no O–H stretching bands, but air-exposure gives a spectrum identical to that of (**1**); $^1H$ NMR (250 MHz; $C_6D_6$; 25 °C) δ 1.87 (4H, s, tmeda), 2.03 (12H, s, tmeda), 6.83 (1H, m), 7.00 (1H, m), 7.15 (1H, m), and 7.31 (1H, m); $^{13}C$ NMR (100.6 MHz; $C_6D_6$; 25 °C) δ 46.0 (Me of tmeda), 56.9 ($CH_2$ of tmeda), 108.7, 114.8, 121.6, 123.2 [C(4), C(5), C(6), and C(7)], 143.9, 152.5 [C(2), C(3)], and 183.6 [C(1)].

‡ Yield 64% by slow unintentional $H_2O$ admission, 69% by deliberate $H_2O$ addition; m.p. 119—121 °C. Satisfactory analyses (C, H, N, Li) were obtained for all samples of (**1**).

§ *Crystal data*: $C_{13}H_{22}LiN_3O_2S$, $M$ = 291.34, monoclinic, $a$ = 7.981(1), $b$ = 12.052(2), $c$ = 17.109(3) Å, β = 100.30(1)°, $U$ = 1619.1 Å$^3$, $Z$ = 4, $D_c$ = 1.195 g cm$^{-3}$, $F(000)$ = 624, λ(Cu-$K_\alpha$) = 1.54178 Å, μ(Cu-$K_\alpha$) = 16.30 cm$^{-1}$, space group $P2_1/c$ (No. 14). 2952 Reflections collected on a Nicolet *R3m*μ four-circle diffractometer in the range $5 \leq 2\theta \leq 120°$ and corrected for absorption. Structure solved by a combination of direct methods and Fourier difference techniques, and refined by full-matrix least-squares (all non-hydrogen atoms anisotropic, aquo H located and refined freely) to $R$ = 0.080, $R_w$ = 0.087 [$w^{-1} = \sigma^2(F) + 0.0013F^2$], for 1887 unique reflections [$F > 5\sigma(F)$]. 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.

neutral organic (**2**),[10] occur within the N$\overset{-}{\cdots}$C($\overset{-}{\cdots}$S)$\overset{-}{\cdots}$O group of the 5-membered ring. The C$\overset{-}{\cdots}$N bond [C(1)–N(1) 1.314(5) Å] is shortened and both the C$\overset{-}{\cdots}$S [C(1)–S(1) 1.692(4) Å] and the C$\overset{-}{\cdots}$O bonds [C(1)–O(1) 1.391(5) Å] are lengthened compared to those in 2-mercaptobenzoxazole [C$\overset{-}{\cdots}$N 1.347(8); C$\overset{-}{\cdots}$S 1.643(3); C$\overset{-}{\cdots}$O 1.369(8) Å]. These variations in C$\overset{-}{\cdots}$N, C$\overset{-}{\cdots}$S, and C$\overset{-}{\cdots}$O distances are consistent with a high degree of negative charge on sulphur, which reinforces the S$\cdots$H bonding.

Spectroscopic techniques (IR, $^1$H, $^{13}$C NMR) confirm the presence of $H_2O$ as a ligand in (**1**) and rule out the alternative Li–OH$\cdots$SH structure.¶ IR spectra of (**1**) in the solid state show no characteristically sharp Li–OH stretching bands (expected at *ca.* 3680 cm$^{-1}$). All O–H stretching vibrations are broad and occur below 3550 cm$^{-1}$. Only a small reduction in hydroxide O–H stretching frequency would be caused by Li–OH$\cdots$SH bonding; compare KOH, where $OH^-$ ions are linked by OH$\cdots$OH bonds (3600 cm$^{-1}$),[11] with $Ca(OH)_2$, where 'free' $OH^-$ ions are found in the solid state (3650 cm$^{-1}$).[12] $^1$H and $^{13}$C NMR spectra (both in benzene) of (**1**) in the aromatic region are identical with those of the non-hydrated complex (**3**)† but differ markedly from those of 2-mercaptobenzoxazole (**2**). These data confirm that (**1**) retains the organic anion ($Li^+$–$OH_2\cdots{}^-S$) rather than containing a protonated one ($Li^+OH^-\cdots SH$). $^1$H NMR spectra of concentrated solutions of (**1**) (40 mg/0.5 ml) in $Me_2SO$ (which displaces the $H_2O$ and tmeda ligands) verify the stoicheiometry of the water present.¶ Finally, a suspension of 2-mercaptobenzoxazole (**2**) in water dissolves on addition of solid KOH. This provides a more qualitative indication that the p$K_a$ of (**2**) is less than the p$K_a$ of water (<14).

These results imply that $H_2O$ and other protic donors *can* be used in organolithium chemistry providing that the p$K_a$ of the organic conjugate base is below that of the protic donor. The isolation of such acid-donor complexes and their subsequent investigation by spectroscopic means, *e.g.*, by variable-temperature $^1$H NMR spectroscopy, may provide a method by which the dynamics of proton transfer and, in particular, cation-dependent effects can be examined. Synthetically, the acidic protons in (**1**) are reactive towards further metallation, by *e.g.*, Bu$^n$Li or other metals, so producing 'mixed' organometallic-hydroxide or -oxide complexes.

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¶ Data for (**1**): IR (Nujol) includes four O–H bands at 3525, 3410, 3340, and 3180 cm$^{-1}$; $^1$H NMR (250 MHz; $C_6D_6$; 25 °C) $\delta$ 1.89 (4H, s, tmeda), 1.95 (12H, s, tmeda), 6.17 (2H, br s, $H_2O$), 6.82 (1H, m), 6.96 (1H, m), 7.12 (1H, m), and 7.25 (1H, m); $^1$H NMR (80 MHz; $CD_3SOCD_3$; 25 °C) $\delta$ 1.96 (12H, s, tmeda), 2.27 (4H, s, tmeda), 2.50 (0.5H, m, $CD_3SOCD_2H$), 3.44 (2H, s, free $H_2O$), and 6.80—7.80 (4H, m) [a $CD_3SOCD_3$ 'blank' using the same batch of this solvent contained a negligible amount of $H_2O$: ratio of $H_2O$ to $CD_3SOCD_2H$ ~1 : 30]; $^{13}$C NMR (100.6 MHz; $C_6D_6$; 25 °C) $\delta$ 45.6 (Me of tmeda), 56.9 ($CH_2$ of tmeda), 108.9, 114.8, 121.7, 123.2 [C(4), C(5), C(6), C(7)], 143.7, 152.3 [C(2), C(3)], and 183.6 [C(1)].