Synthesis and Crystal Structure of Bis(12-crown-4)lithium Bis[*N,N'*-bis(trimethylsilyl)benzenesulphinamidino]lithiate(1−); the First Observation of Three Different Lithium-7 Environments in High-resolution Solid-state NMR Spectroscopy

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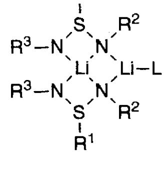
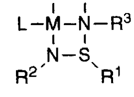
$[Li(12\text{-crown-}4)_2]^+[Li(\{N(SiMe_3)\}_2SPh)_2]^-$ **1** is the product of the reaction of $Me_3SiN{=}S{=}NSiMe_3$ with phenyllithium using 12-crown-4 as a donor and has an ion-separated structure which is unique for alkali metal sulphinamidino derivatives; at room temperature **1** undergoes a phase transformation, and a preliminary examination of this process by high-resolution solid-state ^7Li NMR spectroscopy shows, for the first time, the presence of three resolvable resonances.

Sulphinamidino alkali metal compounds are widely used in main group and transition metal chemistry.[1–5] The reason for using the sulphinamidino ligand is the good solubility of the products in hydrocarbons and its similar steric demand as those of the cyclopentadienyl ligand. Their structures and chemistry have been probed by us recently and these studies have revealed three classes of structures **a**–**c**.[6,7] In **a**, two SN_2Li four-membered rings are placed on adjacent sides of the central Li_2N_2 four-membered ring which results in a twisted

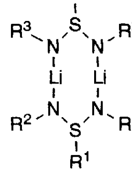


a



M = Li, Na, K, Rb, Cs

b



c

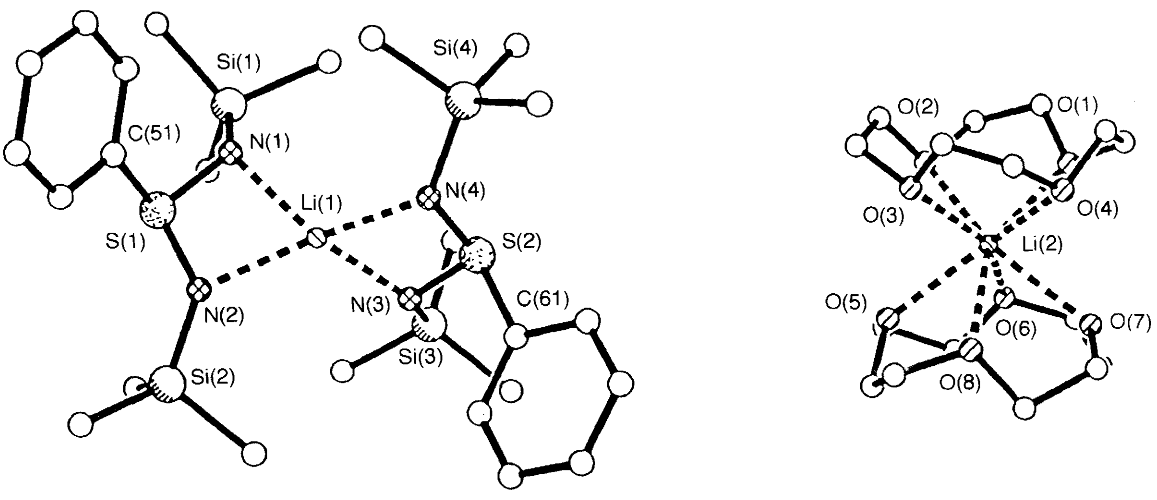


Fig. 1 The X-ray structure of **1**. For clarity, the uncomplexed crown ether molecule is not shown. Selected distances (pm) and angles (°): Li(1)–N(1) 208.8(8); Li(1)–N(2) 216.9(8); Li(1)–N(3) 214.0(8); Li(1)–N(4) 210.4(8); S(1)–N(1) 159.9(4); S(1)–N(2) 160.4(4); S(1)–C(51) 182.1(5); S(2)–N(3) 160.3(4); S(2)–N(4) 159.8(4); S(2)–C(61) 181.8(5); N(1)–S(1)–N(2) 105.2(2); N(3)–S(2)–N(4) 103.5(2); N(1)–Li(1)–N(2) 73.4(3); N(3)–Li(1)–N(4) 72.7(3); Li–O in the range 225.7(9)–263.5(9), av. 235.9(9).

tricyclic structure with C_2 symmetry. In **b**, the two SN_2Li four-membered rings are on opposite sides of the central M_2N_2 four-membered ring. Both this stair shaped tricycle in **b** (otherwise termed a ladder)[8] and the eight-membered ring in **c** have C_i symmetry. In this communication we report a further, new and distinct structural type obtained by the reaction of bistrimethylsilyl sulphur diimide with phenyllithium, using the cyclic ether 12-crown-4 as a donor for the lithium atom.†

$[Li(12\text{-crown-}4)_2][Li(\{N(SiMe_3)\}_2SPh)_2]$ **1** has been shown by X-ray crystallography‡ to form a solvent-separated ion-pair structure with one lithium atom in the anion (Fig. 1); only one other related $[RLiR]^-$ structure is known.[9] Li(1) is coordinated to two $\{N(SiMe_3)\}_2SPh$ ligands giving overall a singly charged anion. Li(2) is complexed by two crown ether molecules giving a singly charged cation. The Li–N bond lengths in the anion are in the range 208.8–216.9 pm, longer than those found in the related **a–c** system.[7] Owing to electrostatic repulsion, the two sulphinamidino anions maximise their separation; the angle of 174.2(3)° between the S(1) · · · Li(1) and S(2) · · · Li(1) vectors deviates by only 5.8° from the optimum value of 180°. This indicates a negative charge on $\{N(SiMe_3)\}_2SPh$ and a positive, rather than a negative, charge on Li(1). The Li–O distances in the cation are typical of crown ether-coordinated lithium structures.[10] The $\{N(SiMe_3)\}_2SPh^-$ ion appears to be a better donor than the 12-crown-4 molecule in the solid state and this is supported by the fact that the lattice contains an uncomplexed 12-crown-4 molecule. In addition, crystal packing forces lead to the formation of **1** rather than the expected free $\{N(SiMe_3)\}_2SPh^-$ ion and the lithium crown ether, $[Li(12\text{-crown-}4)_2]^+$, ion because of the cation–anion size mismatch in the latter case.

The solution ^7Li NMR spectrum of **1** in toluene displays a single resonance, even on cooling the solution to −90 °C, instead of the two signals one might expect to be given (were the solid-state structure retained) by two lithium atoms in very different environments.[6,11] These results, however, do indicate that only one species is present in solution. Despite its ionic 'ate' nature in the solid state, **1** is very soluble in hydrocarbons. We suggest that **1** rearranges to form $[PhS\{(Me_3Si)N\}_2Li(12\text{-crown-}4)]$ **2**, which may also be the product of a solid-state phase transition; at room temperature under dry argon the colourless crystals of **1** slowly transform (*ca.* 50% in four days) into a dark-brown oil.

To study this transformation in more detail, solid-state magic-angle spinning (MAS) ^7Li NMR spectra of **1** have been recorded at room temperature. Preliminary results show the presence of two groups of signals at δ −0.5 to 1 and at δ *ca.* −2.7. The line at high frequency exhibits two maxima, at δ 0.8 and −0.2, which may be due to the partial overlap of (at least) two ^7Li resonances. ^7Li quadrupole nutation MAS NMR spectroscopy[12] supports the former case, *i.e.* the overlap of two resonances (Fig. 2). The F_2 axis of the two-dimensional NMR spectrum (in the magnitude mode) contains a combination of the chemical shift and the second-order quadrupole shift and the F_1 axis contains only quadrupolar information. This technique permits ^7Li environments with different quadrupole coupling constants, C_Q, to be resolved along F_1. Fig. 2 clearly shows that the maxima at δ 0.8 and −0.2 are,

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† *Synthesis*: To a mixture of $Me_3SiN{=}S{=}NSiMe_3$ (10 mmol) and 12-crown-4 (40 mmol) in hexane (20 ml), phenyllithium (10 mmol; 2 mol dm^{-3} solution in Et_2O–cyclohexane) was added at 0 °C. The mixture was allowed to warm to room temperature and refluxed for 1 h. After cooling to room temperature, crystals began to grow in the crown ether phase. These were recrystallised from hexane to give suitable single crystals for X-ray study. Yield of **1**: 4.8 g, 94%; ^1H NMR (C_6D_6, room temp.) δ 0.41 (s, $SiMe_3$) 3.28 (s, $[O(CH_2)_2]_4$) and 7.1–8.0 (m, Ph); ^7Li NMR (C_6D_6, room temp.) δ 0.2; (C_7D_8, room temp.) δ 1.2; ^{13}C NMR (C_7D_8, room temp.) δ, 2.76, 3.19 ($SiMe_3$), 70.38 ($[O(CH_2)_2]_4$), 126.52, 128.57, 129.39 (C_6H_5); ^{29}Si NMR (C_7D_8, room temp.) δ −4.8 (br.s).

‡ *Crystal data* for **1** (−120 °C): $C_{44}H_{86}Li_2N_4O_{10}S_2Si_4$, monoclinic, space group $C2/c$, $a = 1795.4(2)$, $b = 1561.1(2)$, $c = 4083.3(6)$ pm, $\beta = 93.97(2)°$, $U = 11.417$ nm^3, $Z = 8$, $D_c = 1.189$ Mg m^{-3}, $\mu = 0.23$ mm^{-1}, 10001 measured reflections, 7396 unique, 5319 observed reflections ($F_o > 3\sigma F_o$), $2\theta_{max} = 45°$, $R = 0.063$, $R_w = 0.064$ [$w^{-1} = \sigma^2(F) + 0.0006\,F^2$], 618 refined parameters, data to parameter ration = 1:8.6, max. residual electron density: 5.5 × 10^2 e nm^{-3}. Data were collected on a Stoe-Siemens diffractometer using graphite-monochromated Mo-Kα radiation (λ = 71.073 pm). The structure was solved by direct methods and refined by full-matrix least-squares techniques.[13] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions. The residual electron density indicates disordering in one of the lithium-coordinated and lattice crown ether molecules. This disorder could not be modelled. Atomic coordinates, bond lengths and angles, and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

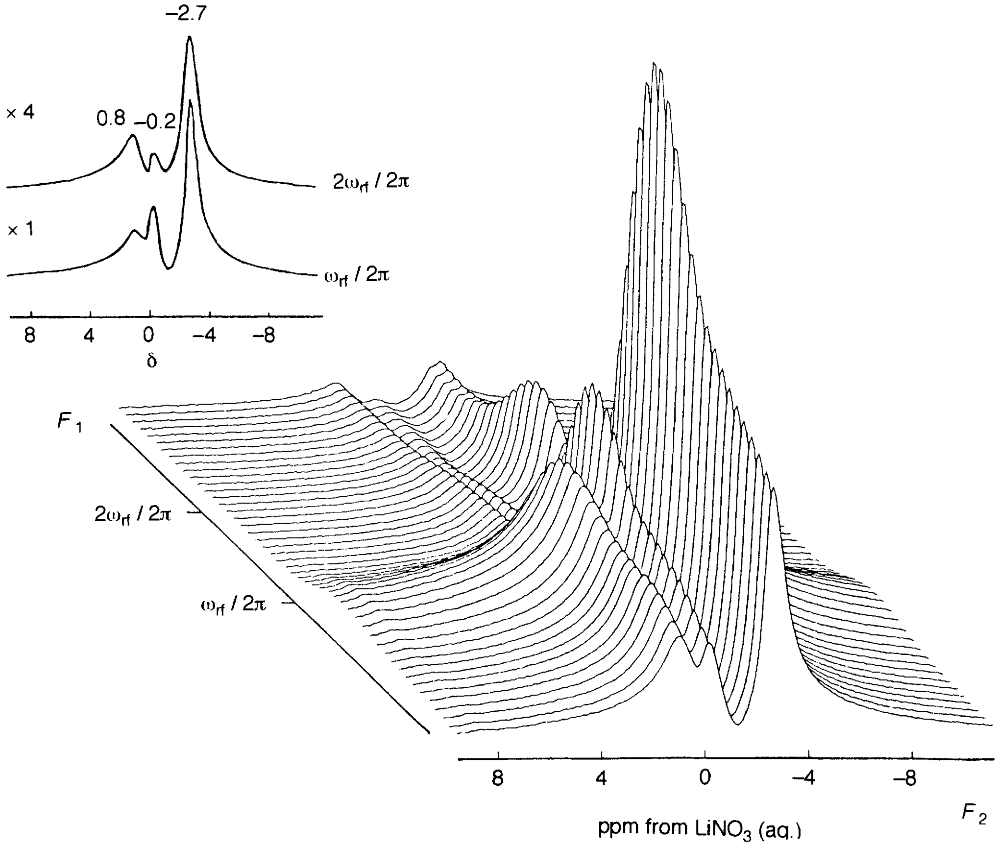

Fig. 2 ^{7}Li quadrupole nutation MAS NMR spectrum of partially transformed **1**, recorded with a 35 ± 5 kHz radio-frequency excitation field, $\omega_{rf}/2\pi$, 5 s recycle delay and *ca.* 3.5 kHz spinning rate. The F_2 axis contains combined chemical shift and the second-order quadrupole shift while the F_1 axis contains only quadrupolar information. The technique permits ^{7}Li environments with different quadrupole coupling constants to be resolved along F_1. A relatively strong quadrupole interaction corresponds to a crowding of the signal to the $2\omega_{rf}/2\pi$ side of the F_1 axis. The inset depicts F_2 cross-sections taken at the coordinates given.

indeed, due to two different resonances and not to second-order quadrupole effects. Therefore we tentatively assign them to the distinct Li(1) and Li(2) environments in the structure of **1**. Since the resonance at δ 0.8 arises from the ^{7}Li environment with a larger quadrupole coupling constant (larger degree of local distortion and higher nutation frequency), it is probably due to Li(2). The resonance at δ − 2.7 may be assigned **2**, the product of the transformation of **1**. Further solid-state NMR studies (in particular *in situ* variable-temperature studies) are clearly needed to clarify the tentative spectral assignments given here and to elucidate the nature of the transformation. Such studies are now in progress. Meanwhile, we point out that this is, to our knowledge, the first time three resonances have been resolved in solid-state ^{7}Li NMR spectroscopy.

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