

# The First Crystal Structure Characterization of an Alkali Metal Monothiocarboxylate, (PhCOSLi-TMEDA)<sub>2</sub> (TMEDA = tetramethylethylenediamine): a Chair-shaped Eight-membered (COSLi)<sub>2</sub> Ring System

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An X-ray diffraction study of the title compound, a TMEDA complexed lithium monothiobenzoate, has shown that it is a centrosymmetric dimer with an eight membered ring composed of coplanar C, O, and S atoms and tetrahedrally co-ordinated Li atoms above and below this plane; *ab initio* optimisation calculations on (HCOSLi)<sub>2</sub>, which is *all-planar*, imply that displacement of the Li atoms in the complex occurs in order to reduce excessively large ring angles at O and, most crucially, at Li, in order to accommodate the TMEDA donor.

Lithium compounds are widely used as intermediates in organic synthesis. Consequently there is considerable current interest in the structure and bonding of these compounds, both in the solid state and in solution. Hitherto, most X-ray structural studies have been carried out on compounds with Li-O, Li-C, or Li-N bonds.<sup>1</sup> However, few structures are known for Li-S species;<sup>2-5</sup> the first X-ray crystal structure determination of a lithium alkyl thiolate was described only recently.<sup>5</sup>

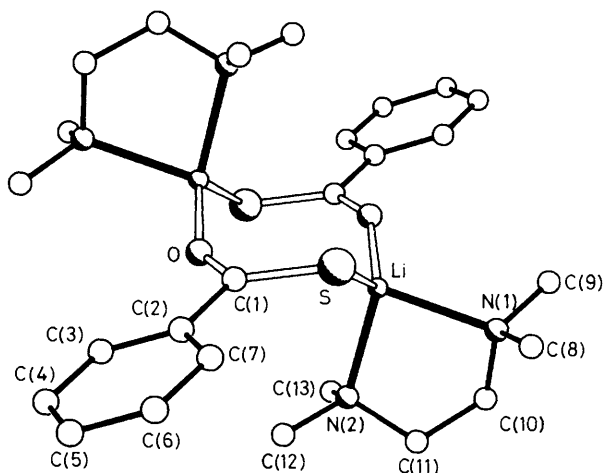
Furthermore, lithiated carboxylic acids have been predicted by M.O. calculations to adopt highly ionic structures in which Li bridges the O atoms of a (O=C=O)<sup>-</sup> unit.<sup>6</sup> Given such background it is especially interesting to examine the nature of a lithium salt where the anion contains one oxygen atom and a similarly placed but more polarisable atom such as sulphur.

We now report the first structure determination of a lithium monothiocarboxylate (PhCOSLi-TMEDA)<sub>2</sub>, (1), (TMEDA = tetramethylethylenediamine). The complex was synthesised by addition of thiobenzoic acid to a chilled solution of *n*-butyl-lithium and TMEDA in toluene. This produced a yellow solution and a pale yellow solid which redissolved on warming (*ca.* 60°C). Filtration and cooling gave transparent pale yellow crystals *m.p.* 122°C.†

As illustrated in Figure 1, the complex, (1), crystallises as a centrosymmetric dimer with coplanar thiobenzoate anions.‡ Each lithium completes its approximately tetrahedral environment by bonding to the N atoms of a TMEDA molecule; the Li-N distances, N-Li-N angles, and C-N-Li angles are typical of other TMEDA-lithium complexes.<sup>4</sup> *Ab initio* M.O. calculations (6-31G level) were carried out for uncomplexed HCOSLi and (HCOSLi)<sub>2</sub> (in the monomer with Li bridging O and S atoms and in the dimer with all atoms optimising planar, see below) and show that there is an appreciable exothermic dimerisation energy of 52.4 kcal mol<sup>-1</sup> (1 kcal = 4.18 kJ).

In the anion of (1) both the C-O and C-S distances, 1.246(2) and 1.704(2) Å respectively, point to considerable multiple bond character (*cf.* 1.233 ± 0.001 Å for the shorter C-O bond in carboxylic acids and esters, 1.160 ± 0.001 Å for the C-O bond in CO<sub>2</sub>, 1.71 ± 0.01 Å for the C-S bond in thioureas, 1.555 ± 0.001 Å for the C-S bond in CS<sub>2</sub>, COS, and CSe<sup>7</sup>), implying that the PhCOS units are predominantly ionic, and held together by (TMEDA)Li cations. In the *ab initio* structure of (HCOSLi)<sub>2</sub>, the C-O and C-S distances are in close agreement with the above, being 1.270 and 1.725 Å respectively and the bond indices for these bonds are 1.559 and 1.572 respectively. The charges on O (-0.780 e), S (-0.166 e), and Li (+0.697 e) also support a largely ionic formulation.

However, in the crystal structure of (1), the remarkable difference (almost 50°) between C-S-Li [98.1(1)°] and C-O-Li [147.1(2)°] suggests that there is significantly more covalent character in the Li-S bond compared with Li-O. Again, this is



**Figure 1.** Molecular structure of (PhCOSLi-TMEDA)<sub>2</sub>. Key dimensions: Li-S 2.478(4), Li-O 1.881(4), S-C(1) 1.704(2), O-C(1) 1.246(2), C(1)-C(2) 1.501(3) Å, S-Li-O 124.2(2), Li-S-C(1) 98.4(1), C(1)-O-Li 147.1(2), S-C(1)-O 124.5(2)°.

† Satisfactory C,H,N,S,Li elemental analysis has been obtained.

‡ Crystal Data: (PhCOSLi-TMEDA)<sub>2</sub>, C<sub>26</sub>H<sub>42</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>Li<sub>2</sub>, M<sub>r</sub> = 520.64, triclinic, P $\bar{1}$ , a = 8.876(2), b = 9.411(2), c = 10.438(2) Å,  $\alpha$  = 106.34(1),  $\beta$  = 94.10(1),  $\gamma$  = 110.83(1)°, U = 767.57 Å<sup>3</sup>, Z = 1 dimer, D<sub>c</sub> = 1.126 g cm<sup>-3</sup>, F(000) = 280,  $\lambda$ (Mo-K $\alpha$ ) = 0.71073 Å,  $\mu$  = 0.191 mm<sup>-1</sup>.

Data collection and processing: Crystal 0.38 × 0.69 × 0.73 mm, Siemens AED diffractometer, T = 293 K, cell parameters from 2 $\theta$  values of 32 reflections (20 < 2 $\theta$  < 23°),  $\omega/\theta$  scan, scan width 1.19° +  $\alpha$ -doublet splitting, scan time 14-56 s, h -10 → 2, k -11 → 11, l -12 → 12, 2 $\theta_{max}$  50°. 3 Standard reflections, no significant changes. No absorption or extinction corrections. 3597 reflections, 2693 unique (R<sub>int</sub> = 0.016), 2226 with F > 4 $\sigma$ (F).

Structure determination: Direct methods, blocked-cascade refinement on F, w<sup>-1</sup> =  $\sigma^2(F) + 0.00019F^2$ . Anisotropic thermal parameters for non-H atoms, aromatic H on external bisectors of ring angles, aliphatic H-C-H 109.5°, C-H 0.96 Å, U(H) = 1.2U<sub>eq</sub>(C). 175 parameters, R = 0.043, R<sub>w</sub> = 0.061, max. (shift/e.s.d.) = 0.002, mean = 0.001, slope of normal probability plot = 2.11, max. peak in difference synthesis 0.20 eÅ<sup>-3</sup>, largest hole -0.17 eÅ<sup>-3</sup>. Scattering factors from 'International Tables for X-ray Crystallography,' Vol. IV, pp. 99, 149. Programs: SHELXTL (G. M. Sheldrick, Göttingen, 1985, Revision 5).

supported by the *ab initio* calculations on  $(\text{HCOSLi})_2$  which gives Li-S and Li-O bond indices of 0.487 and 0.360 respectively.

The particularly interesting structural feature found for complex (1) is the placement of the Li atoms above and below the  $(\text{COS})_2$  ring plane. Unfortunately there are no directly comparable  $(\text{RCOOLi}\cdot\text{D})_n$  (D = ligand) structures available. However, lithium amides  $(\text{R}_2\text{NLi})_n$  also often adopt an  $(\text{NLi})_n$  ring structure (*cf.* organolithiums and alkoxylithiums which commonly prefer clustered arrangements),<sup>1,8</sup> but these are perfectly planar, *e.g.*, when  $n = 4$ , by calculation with  $\text{R} = \text{H}$ ,<sup>9</sup> and by X-ray diffraction with  $\text{R} = \text{Me}_2\text{C}(\text{CH}_2)_3\text{CMe}_2\text{N}$ .<sup>10</sup> Furthermore, our calculations on  $(\text{HCOSLi})_2$  show that this also is completely planar; indeed a starting model based on the chair-shaped structure of (1) becomes planar during optimisation. However, in this optimised structure, although the preferred angle at S ( $70.2^\circ$ ) is already low (with S well away from the TMEDA) the angles at O ( $185^\circ$  *i.e.* re-entrant O) and at Li ( $162.7^\circ$ ) are very much larger [*cf.*  $147.1^\circ$  and  $124.2^\circ$  respectively in (1)]. Clearly the Li atoms of  $(\text{HCOSLi})_2$  could not possibly accommodate a bidentate donor each, and hence approximately tetrahedral environments, whilst retaining coplanarity with the  $(\text{COS})_2$  unit; the angles at O and Li need to be considerably reduced, and this is accomplished in (1) by the Li atoms displacing themselves out of the ring plane.

$^7\text{Li}$  high field n.m.r. spectra at 20 and  $-95^\circ\text{C}$  in  $[\text{}^2\text{H}_8]\text{toluene}$  solutions show only a sharp singlet, indicating the presence of only one lithium species in solution. In view of the structure in the solid, it seems likely that the dimer only is present in solution and that there is no detectable equilibrium

between chair and boat conformations of the dimeric ring at the lowest temperature used.

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