

## Synthesis, and Crystal and Solution Structures of the 1 : 1 TMEDA Complex of Lithium Thiocyanate, $(\text{LiSCN}\cdot\text{TMEDA})_n$ [TMEDA = $\text{Me}_2\text{N}(\text{CH}_2)_2\text{NMe}_2$ ]: a Polymeric Solid with $\text{Li}^+$ Ions linked by Bifunctional Linear $\text{SCN}^-$ Ligands

Donald Barr,<sup>a</sup> Michael J. Doyle,<sup>a</sup> Robert E. Mulvey,<sup>b</sup> Paul R. Raithby,<sup>a</sup> Ronald Snaith,<sup>a\*</sup> and Dominic S. Wright<sup>a</sup>

<sup>a</sup> University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

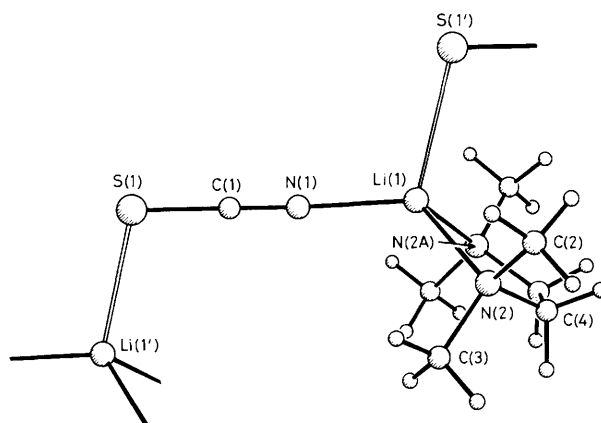
<sup>b</sup> Department of Pure & Applied Chemistry, Strathclyde University, Glasgow G1 1XL, U.K.

The anhydrous complex  $(\text{LiSCN}\cdot\text{TMEDA})_n$  (**1**) [TMEDA =  $\text{Me}_2\text{N}(\text{CH}_2)_2\text{NMe}_2$ ] has been synthesised by a novel *in situ* route from solid  $\text{NH}_4\text{SCN}$  and  $\text{Bu}^n\text{Li}$  in TMEDA/hexane, and shown to have a polymeric chain crystal structure with  $\text{Li}-\text{N}\equiv\text{C}-\text{S}\cdots\text{Li}$  repeat units; in hydrocarbon solvents, however, (**1**) adopts a dimeric, purely N-Li bridged structure.

Rather few structures of lithium halide or pseudohalide complexes are known.<sup>1</sup> Those that are can be broadly sub-divided into contact-ion species such as  $(\text{LiCl}\cdot\text{HMPA})_4$ ,<sup>2</sup> [HMPA =  $\text{O}\cdot\text{P}(\text{NMe}_2)_3$ ],  $(\text{LiBr}\cdot\text{PMDETA})_2$ ,<sup>3</sup> [PMDETA =  $\text{MeN}(\text{CH}_2\text{CH}_2\text{NMe}_2)_2$ ], and  $\text{LiSCN}\cdot(\text{dibenzo-14-crown-4})$ ,<sup>4</sup> and into ion-separated ones, like  $\text{Li}(\text{Ph}_3\text{P}=\text{O})_4^+\cdot(\text{Ph}_3\text{P}=\text{O})\cdot\text{I}^-$ <sup>5</sup> and  $\text{Li} [10,10'\text{-ethylene-bis}(1,4,7\text{-trioxo-10-azacyclododecane})]^+\cdot\text{SCN}^-$ .<sup>6</sup> Specifically for lithium thiocyanate complexes, the seven so far structurally characterised<sup>1</sup> all employ crown or crypt ligands, with metal-anion involvement (if any) restricted to terminal Li-NCS bonding. Direct syntheses of all such complexes by dissolution of the salt in donor or in donor/organic solvent media can suffer from dual problems: firstly, difficult, often incomplete, dissolution reflecting lattice energy barriers, and secondly, the often unavoidable prior hydration of such salts. Here we report an *in situ* route to thiocyanate complexes (which route can be modified to give halide complexes<sup>7</sup>) from reaction of ammonium thiocyanate with  $\text{Bu}^n\text{Li}$  in various donors: such a procedure circumvents both the above-mentioned difficulties. In addition, one so-synthesised complex,  $(\text{LiSCN}\cdot\text{TMEDA})_n$  (**1**) [TMEDA =  $\text{Me}_2\text{N}(\text{CH}_2)_2\text{NMe}_2$ ], has been shown by X-ray diffraction to be polymeric in the crystal, with Li centres linked by bifunctional linear  $\text{N}\equiv\text{C}-\text{S}$  ligands which provide, for the first time, both Li-N and Li-S bonds within the one structure; in solution, spectroscopic evidence shows that a dimeric, purely N-Li bridged structure is adopted.

A suspension of  $\text{NH}_4\text{SCN}$  (5 mmol) in toluene (8 ml) and TMEDA (5 mmol) was treated at  $-40^\circ\text{C}$  with  $\text{Bu}^n\text{Li}$  (5 mmol, in hexane). Warming to room temperature caused a solution colour change from colourless to bright yellow as the

ammonium salt reacted. Concurrently,  $\text{NH}_3$  and butane were evolved and a white solid was deposited. This dissolved on warming to  $70^\circ\text{C}$ , subsequent chilling of the solution affording colourless needles of  $(\text{LiSCN}\cdot\text{TMEDA})_n$  (**1**).<sup>†</sup> Key synthetic points are, firstly, that the crystals show no evidence of



**Figure 1.** The structure of  $(\text{LiSCN}\cdot\text{TMEDA})_n$  showing the unique fragment of the polymeric chains (the primed atoms denote symmetry related atoms). Selected bond angles:  $\text{N}(1)-\text{Li}(1)-\text{N}(2)$ ,  $119.4(3)^\circ$ ;  $\text{N}(1)-\text{Li}(1)-\text{S}(1')$ ,  $106.2(4)^\circ$ ;  $\text{N}(2)-\text{Li}(1)-\text{S}(1')$ ,  $112.3(3)^\circ$ ;  $\text{N}(2)-\text{Li}(1)-\text{N}(2\text{A})$ ,  $86.5(4)^\circ$ ;  $\text{C}(1)-\text{N}(1)-\text{Li}(1)$ ,  $177.4(5)^\circ$ ;  $\text{S}(1)-\text{C}(1)-\text{N}(1)$ ,  $179.6(6)^\circ$ ;  $\text{C}(1)-\text{S}(1)-\text{Li}(1')$ ,  $104.0(3)^\circ$ .

<sup>†</sup> Yield of first batch, 87%; m.p.  $168-171^\circ\text{C}$ . Satisfactory analyses (C,H,Li,N) were obtained for (**1**).

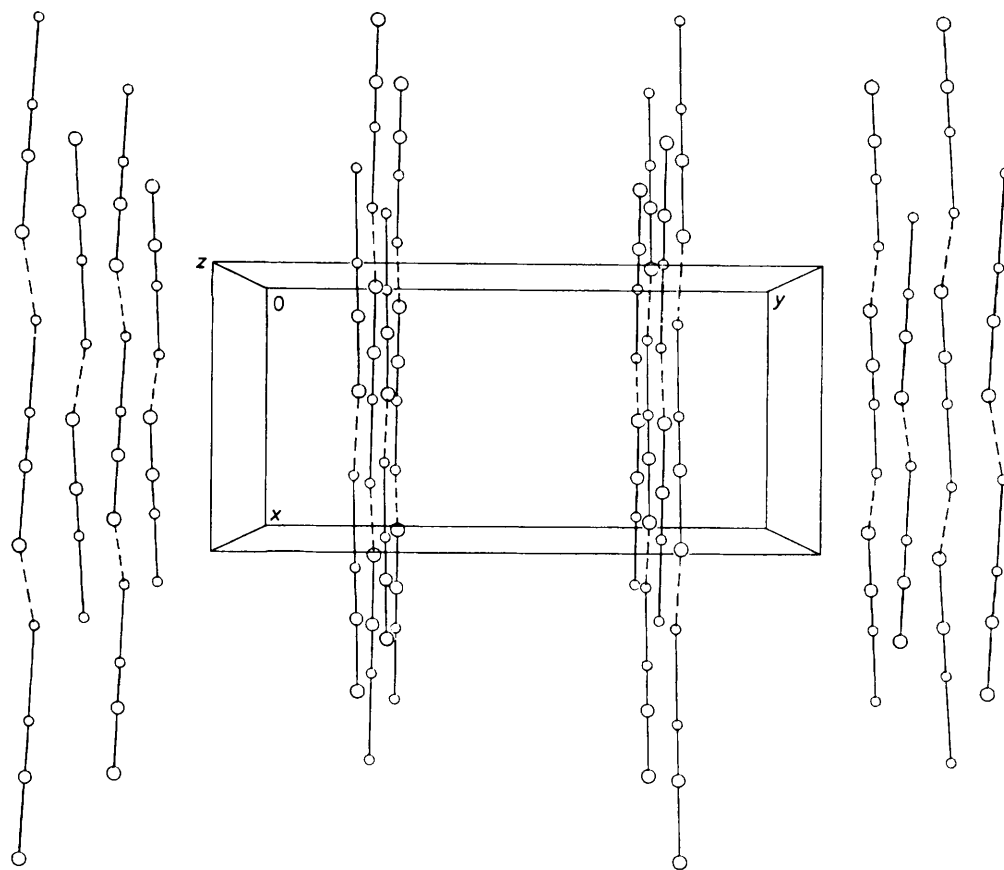


Figure 2. Representative crystal packing of  $(\text{LiSCN})_{\infty}$  units of (1).

hydration even though 'shelf'  $\text{NH}_4\text{SCN}$  was used without drying or other purification, and secondly, that the procedure is rapid and seemingly quantitative; after isolation of the crystals, an i.r. spectrum of the filtrate did not reveal  $\nu(\text{NH})$  absorptions. Furthermore, the route works for related complexes, so far  $\text{LiSCN}\cdot\text{PMDETA}$  and  $\text{LiSCN}\cdot 2\text{HMPA}$ .

Structural studies of  $\text{LiSCN}$  complexes with non-macrocyclic ligands have hitherto been restricted largely to solution i.r. spectroscopic ones. For example,  $\text{LiSCN}$  in certain ethers appears to form  $(\text{LiN})_2$  ring dimers [ $\nu(\text{CN}) \sim 2030 \text{ cm}^{-1}$ ],<sup>8</sup> while in other ethers and in amines  $\mu_3\text{-N-Li}$  bridging is implicated within tetrameric pseudocubanes [ $\nu(\text{CN}) \sim 1990 \text{ cm}^{-1}$ ].<sup>9</sup> However, the Nujol mull i.r. spectrum of (1) showed a strong absorption at  $2074 \text{ cm}^{-1}$ , so hinting at a rather different bonding mode for its  $\text{SCN}^-$  anion in the solid. This prospect has now been confirmed by an X-ray diffraction study<sup>‡</sup> which shows that (1) has a zig-zag polymeric structure with both

$\text{Li-N}$  and  $\text{Li-S}$  interactions; the main structural features are shown in Figure 1 which includes selected bond angles. The basic unit, which lies on a crystallographic mirror plane, contains a lithium centre [ $\text{Li}(1)$ ] joined to a bidentate TMEDA molecule with quite typical  $\text{N} \rightarrow \text{Li}$  bond lengths [ $2.121(7) \text{ \AA}$ ] and, more closely [ $1.956(10) \text{ \AA}$ ], to the N end of a thiocyanate ligand whose NCS backbone is essentially linear [ $179.6(6)^\circ$ ]. Each such Li is also co-ordinated to the S end [ $\text{S}(1')$ ] of a neighbouring unit [ $2.566(9) \text{ \AA}$ ], so giving the metal a distorted tetrahedral four-co-ordination. Such a bifunctional mode for  $\text{SCN}^-$  is very uncommon for a Main Group metal species; it does occur in  $\text{K}[\text{Me}_3\text{Al-SCN-AlMe}_3]$ ,<sup>10</sup> but has not been observed before for an alkali metal compound. It is found, but also only rarely, in transition metal compounds, e.g., in  $\alpha\text{-}[\text{Pt}_2(\text{SCN})_2\text{Cl}_2(\text{PPR}_3)_2]$  which contains a  $\text{PtSCNPtSCN}$  ring,<sup>11</sup> and in  $\text{AgSCN}$ , which has a covalently-bonded chain structure.<sup>12</sup> In (1), the  $\text{Li-N}(\text{CS})$  distances are unremarkable [cf.  $\text{Li-terminal N}(\text{CS})$  distances of  $1.96\text{--}2.04 \text{ \AA}$  in  $\text{LiSCN}$  complexes with macrocycles<sup>1</sup>], though the  $\text{Li-S}$  ones are noticeably longer than those in the few reported organosulphur-lithium structures, e.g., most recently, ca.  $2.48 \text{ \AA}$  in  $(\text{PhCH}_2\text{SLi}\cdot\text{NC}_5\text{H}_5)_{\infty}$ .<sup>13</sup> Within the  $\text{SCN}^-$  ligand, the distances involved prompt a formulation as  $[\text{S}^-\text{C}\equiv\text{N}]^-$  since the C-N distance [ $1.144(7) \text{ \AA}$ ] is very much shorter than that expected for a double bond (ca.  $1.26 \text{ \AA}$ ), while the C-S link [ $1.643(6) \text{ \AA}$ ] is rather longer than that expected for a double bond (ca.  $1.57 \text{ \AA}$ ).<sup>13,14</sup> Figure 2 illustrates a segment of the crystal packing in (1). The  $\cdots\text{Li}\cdots\text{N}\equiv\text{C}\cdots\text{S}\cdots\text{Li}$  strands run alternately in opposite directions forming, pictorially, layers; however, there are no significant bonding contacts

<sup>‡</sup> Crystal data for (1):  $\text{C}_7\text{H}_{16}\text{LiN}_5\text{S}$ ,  $M = 181.23$ , orthorhombic, space group  $Pcma$  (alt.  $Pnma$ , No 62),  $a = 5.944(1)$ ,  $b = 12.580(2)$ ,  $c = 14.793(3) \text{ \AA}$ ,  $U = 1106.2(3) \text{ \AA}^3$ ,  $D_c = 1.087 \text{ g cm}^{-3}$ ,  $Z = 4$ ,  $F(000) = 392$ ,  $\text{Cu-K}\alpha$  radiation,  $\lambda = 1.5418 \text{ \AA}$ ,  $\mu = 21.81 \text{ cm}^{-1}$ . Nicolet R3m diffractometer, 1837 measured reflections,  $2\theta$  range  $5\text{--}120^\circ$ , 798 unique (merging  $R = 0.020$ ), 648 observed,  $F > 4\sigma(F)$ . Structure solved by centrosymmetric direct methods. Refined by blocked-cascade least squares with all non-hydrogen atoms anisotropic; methyl- and methylene-H placed in idealised positions and allowed to ride on the relevant carbon atom; converged  $R = 0.065$ ,  $R_w = 0.074$ . 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.

between the individual strands (all contacts  $>3 \text{ \AA}$ ). The distances between these 'layers' exceed  $3.32 \text{ \AA}$ . These features, along with the conjugation apparent within the linear anions which continuously join metal cations, promise unusual pseudo-one-dimensional conduction properties for (1).

Complex (1) dissolves, albeit slowly, in hydrocarbon solvents, e.g. ca.  $0.2 \text{ g cm}^{-3}$  in aromatic solvents at  $18^\circ\text{C}$ , so heralding a change from the polymeric solid-state structure. I.r. spectra of toluene solutions ( $100\text{--}40 \text{ mmol dm}^{-3}$ ) show a dominant absorption now at  $2032 \text{ cm}^{-1}$ , assignable to  $\mu_2$ -NCS modes in  $(\text{LiNCS}\cdot\text{TMEDA})_2$ . Confirming this, cryoscopic measurements in benzene solutions ( $45\text{--}15 \text{ mmol dm}^{-3}$ ) give association values of 2.2—2.1, and  $^7\text{Li}$  n.m.r. spectra ( $77\text{--}35 \text{ mmol dm}^{-3}$ , at  $25$  to  $-90^\circ\text{C}$ ) exhibit just one very sharp singlet ( $\delta -2.02$  to  $-2.11$  p.p.m. relative to PhLi in toluene). The conclusion must be that the relatively weak  $\text{Li}\cdots\text{S}$  contacts of solid (1) cleave on dissolution, so allowing formation of a purely  $\mu_2$ -N-Li bridged dimer.

We thank the S.E.R.C. (D.B., P.R.R., R.S.), I.C.I. (M.J.D.), the Royal Society (R.E.M.), and the Associated Octel Co. Ltd. (R.S., D.S.W.) for financial support, and Dr. D. Reed (S.E.R.C., Edinburgh University) for n.m.r. results.

Received, 13th October 1987; Com. 1495

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