Evidence for a Radical-forming Process during the Reaction of Solid NH_4SCN with n-Butyl-lithium and Hexamethylphosphoramide (HMPA) in Toluene:[†] Crystal Structure of the Product, $(LiNCS{\cdot}2HMPA)_2$

Donald Barr, Michael J. Doyle, Simon R. Drake, Paul R. Raithby, Ronald Snaith,* and Dominic S. Wright
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

The complex $(LiSCN{\cdot}2HMPA)_n$, (**1**) [HMPA = $O{:}P(NMe_2)_3$], was synthesised by the reaction of solid NH_4SCN with Bu^nLi and HMPA (1 : 1 : 2 molar ratios) in toluene and shown to have an asymmetrical dimeric structure (n = 2) comprising terminal $(HMPA)_2Li$– and $(SCN)_2Li$– units whose metal centres are then bridged by two μ_2-HMPA ligands; e.s.r. spectroscopic investigations on the reaction system (which proceeds through a series of colours) have detected the intermediacy of thiocyanate-based radical species.

We recently reported a versatile route to anhydrous complexes of type $(LiX{\cdot}xL)_n$, with X = Cl, Br, I, SCN and with L (Lewis bases) = hexamethylphosphoramide (HMPA), tetramethylethylene diamine (TMEDA), pentamethyldiethylene triamine (PMDETA), by reactions of solid ammonium salts, NH_4X, with Bu^nLi solution or with solid LiH in the presence of L.[1] When L = HMPA, unusual (for lithium) colours occur during such reactions: we have now investigated the reasons for these colours in the particular system of $NH_4SCN_{(s)}$ + Bu^nLi + HMPA (2 equiv.) in toluene, and present e.s.r. spectroscopic evidence for the intermediacy of radicals in such a process. The crystal structure of the reaction product, $(LiNCS{\cdot}2HMPA)_2$ (**1**), shows it to be an asymmetric dimer $(HMPA)_2Li{\cdot}(\mu_2\text{-}HMPA)_2{\cdot}Li(NCS)_2$.[‡]

Addition of Bu^nLi solution (10 mmol, in hexane) to a frozen (−196 °C) mixture of solid NH_4SCN (10 mmol), toluene (10 ml), and HMPA (20 mmol) produces a red–orange colour which slowly turns violet (at *ca.* 0 °C), then yellow, then colourless at 25 °C; during these colour changes, vigorous gas evolution occurs. Warming of the final slightly cloudy mixture, with addition of more toluene (10 ml), gives a pale yellow solution, refrigeration of which affords cubic crystals of basic formula $(LiNCS{\cdot}2HMPA)_n$, (**1**).[§][2] Thus, at its simplest, the reaction follows equation (1).

$$Bu^nLi_{(sol)} + NH_4SCN_{(s)} \xrightarrow[\text{toluene}]{\text{2HMPA,}} BuH_{(g)} + NH_{3(g)} + 1/n\,(LiNCS{\cdot}2HMPA)_n \quad (1)$$

However, in fact, the ^1H n.m.r. spectrum of (**1**) displays traces of toluene: the best estimate by signal integration [relative to 36 HMPA protons of (**1**)] is that the true formula of (**1**) is approximately $(LiNCS{\cdot}2HMPA)_n{\cdot}n/2$ toluene.

In the crystal, (**1**) is dimeric (n = 2), and has an unexpected asymmetrical ring structure (Figure 1). Thus the two Li centres present are bridged not by SCN^- *anions* but by formally *neutral* HMPA ligands; furthermore, one Li com-

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[†] The synthetic routes described are the subjects of a preliminary patent (British Patent Application Number 8724662) filed by the Associated Octel Co. Ltd., U.K.

[‡] *Crystal data* for (**1**): $C_{26}H_{72}Li_2N_{14}O_4P_4S_2{\cdot}\frac{1}{2}C_6H_5Me$, M = 892.93, triclinic, space group $P\bar{1}$ (No. 2), a = 11.800(1), b = 12.014(2), c = 20.693(2) Å, α = 92.02(1), β = 94.62(1), γ = 118.35(1)°, U = 2564.2(5) $Å^3$, D_c = 1.156 g cm^{-3}, Z = 2, $F(000)$ = 962, Cu-K_α radiation, λ = 1.5418 Å, μ = 24.57 cm^{-1}. Nicolet R3 mμ diffractometer, 7344 measured reflections, 2θ range 5—116°, 4662 unique with $F > 4\sigma(F)$. Structure solved by direct methods and refined by blocked-cascade least squares to R = 0.078 and R_w = 0.084. 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.

[§] Yield of (**1**), 79—93% depending on precise formulation; m.p. 68—71 °C. Satisfactory analyses (C, H, Li, N, P) were obtained for (**1**).

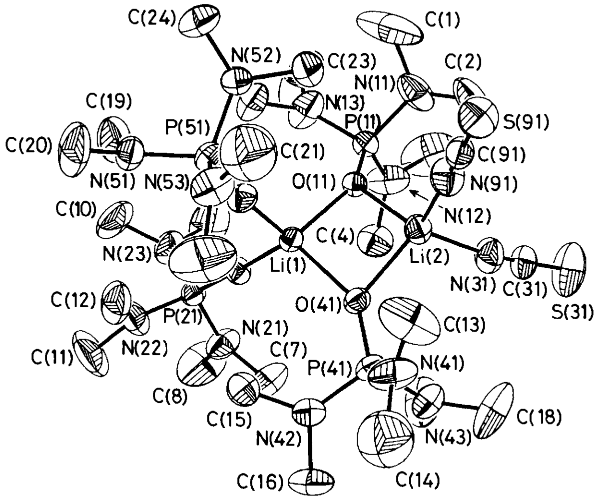

Figure 1. The molecular structure of (**1**) showing the atom numbering scheme. Hydrogens have been omitted for clarity and the thermal ellipsoids represent the 30% probability level.

pletes its four-co-ordination with two terminal HMPA ligands, the other with two N-attached SCN$^-$ ones. A μ_2-mode for HMPA has been observed before, in one isomer of [Ph(2-Pyr)NLi·HMPA]$_2$[3a] and in the cation of [Li(H$_2$O)$_2$HMPA]$_2$$^{2+}$·2Cl$^-$.[3b] The Li–O distances in (**1**) average 1.903 Å for the terminal HMPA ligands and, expectedly longer, 2.015 Å for the bridging ones; these Li–O bridges are asymmetric, ranging 1.984(7)—2.041(11) Å in length.

In the Li(NCS)$_2$ portion of (**1**), Li–N distances average 2.007 Å, and Li–N–C and N–C–S angles 167.5 and 178.7°, respectively. Within the anions, N$\equiv$C distances average 1.156 Å and C$\equiv$S ones 1.629 Å so that, as for the bifunctional thiocynanate ligands in (LiNCS·TMEDA)$_\infty$, (1.144 and 1.643 Å, respectively),[4] N$\equiv$C$\equiv$S$^-$ is an appropriate formulation. This polymeric TMEDA-complex and compound (**1**) are the first structurally characterised examples of LiSCN complexes with other than macrocyclic ligands: crowns, crypts *etc.* give monomers, with or without Li · · · NCS contacts, so that, its unprecedented asymmetrical structure apart, (**1**) is also the first oligomeric LiSCN complex. Toluene solvate molecules are detectable in the crystal structure of (**1**), though they are highly disordered; they appear to hold together, weakly, the dimers of (**1**), imparting an exceptionally low m.p.

Finally, and perhaps most importantly, we have investigated the unusual colours observed during the four-component (NH$_4$SCN, Bu^{n}Li, HMPA, toluene) reaction producing (**1**). In toluene, mixtures of NH$_4$SCN$_{(s)}$ + HMPA and of NH$_4$SCN$_{(s)}$ + Bu^{n}Li are colourless, with no dissolution or reaction apparent. The final binary mix in toluene, Bu^{n}Li + HMPA, produces a deep red colour, attributed to a toluene solvate of a Bu^{n}Li·xHMPA complex and/or to traces of PhCH$_2$Li produced by lithiation of toluene by this complex; however, this colour is stable from −196 to 25 °C. These simple observations imply, then, that the colour changes noted earlier do ensue from the reaction(s) giving (**1**), and that the presence of HMPA is crucial for such reaction(s). Furthermore, the unexpected structure of (**1**) could be viewed as arising from two components, Li(HMPA)$_4$$^+$ and Li(NCS)$_2$$^-$: the former is produced, along with a deep-blue solvated electron, when Li metal itself is dissolved in HMPA.[5] Such thoughts suggest that radicals may be involved in the reaction(s) leading to (**1**); single electron transfer (SET) processes have often been proposed for reactions of organolithiums.[6] To investigate this possibility, all four components were loaded into an e.s.r. tube at −196 °C. A blue colour was observed near the bottom of the tube, just above the NH$_4$SCN solid, and an e.s.r. spectrum could be recorded (Figure 2) on this section of the mixture; the deep red section further up the tube did not afford an e.s.r. spectrum, nor did a red solution of Bu^{n}Li + HMPA, nor a mixture of NH$_4$SCN$_{(s)}$ + Bu^{n}Li, in toluene. In fact e.s.r. spectra recorded on frozen solutions of the reaction mixture were obtainable over the temperature range −269 to −73 °C; they were repeatable and, in each experiment, spectra were totally reproducible after thawing, then re-freezing. The g-value of the frozen solution spectrum is found to be anisotropic, with features present for the three principle values of g. No hyperfine coupling is observed between the unpaired spin and the nuclear spin of any nuclei. At −269 °C, three g tensors are observed: $g_1 = 2.026$, $g_2 = 2.009$, and $g_3 = 1.980$, giving $g_{av} = 2.005$. The line widths and line shapes of all three signals are temperature-dependent over the range −269 to −73 °C and slowly diminish in intensity with progressive warming; above −73 °C, when the solid mixture has melted, no e.s.r. signal is observed. Such results prove that one or more radical species are produced during this unusual reaction; microwave power saturation measure-

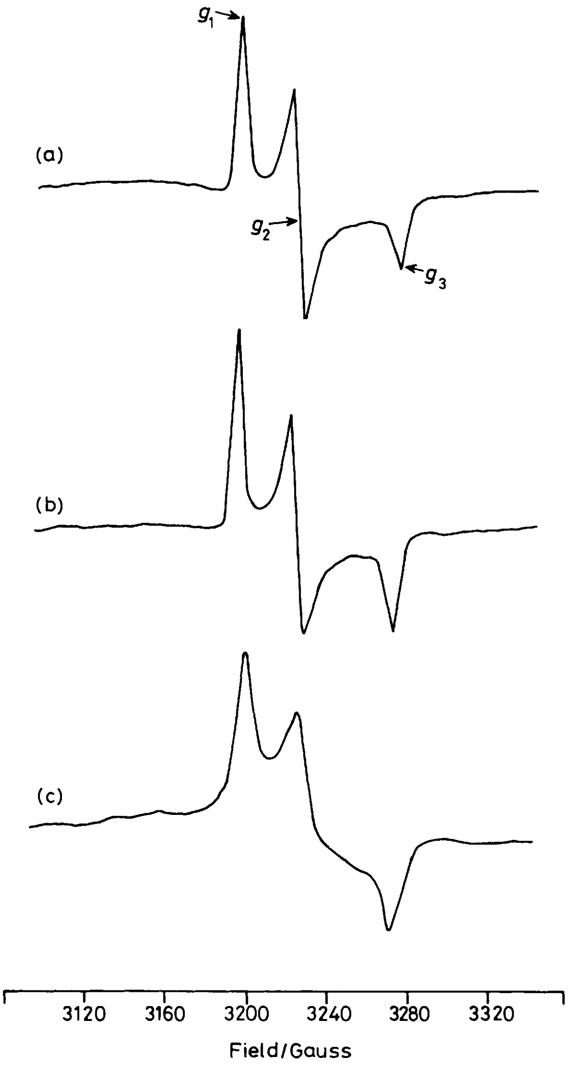

Figure 2. E.s.r. spectra for NH$_4$SCN$_{(s)}$, Bu^{n}Li, 2HMPA mixtures in toluene at (a) −269 °C, (b) −196 °C, and (c) −100 °C.

ments at −269 °C showed that in fact there is only one type of radical present.[7]¶

As to the nature of such a species, oxygen radicals (*e.g.*, O_2^-, O_2^+)[8,9] and solvated electrons[5] can be ruled out since *g* factors do not tally (neither do linewidths, ΔH_{pp}); the same applies for blue S-based radicals such as $S_2^{-\cdot}$ or $S_3^{-\cdot}$,[10] for which, additionally, ^{33}S hyperfine coupling would be expected. One likely possibility is that we are observing thiocyanate-based radical anions such as $(17e^-)SCN^{-\cdot}$ or $(SCN)_2^{-\cdot}$ formed by HMPA-assisted SET from Bu^nLi to SCN^-. Such would explain, firstly, the need for the presence of HMPA to permit reaction between $NH_4SCN_{(s)}$ and Bu^nLi, and, secondly, the appearance of a $Li(HMPA)_4^+$ unit in the final product, (**1**).

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¶ This same radical is also detected when solid NH_4SCN is treated with solid NaH (or solid Na) in toluene/HMPA media; two complexes, $[(NaNCS{\cdot}HMPA)_2]_\infty$ [which has an S · · · Na-linked polymeric structure with a repeat dimer unit of $SCN{\cdot}Na(\mu_2\text{-}HMPA)_2Na{\cdot}NCS$] and $(NaNCS{\cdot}2HMPA)_2$ [which is a symmetrical *trans* dimer $SCN(HMPA)Na{\cdot}(\mu_2\text{-}HMPA)_2{\cdot}Na(HMPA)NCS$] are produced.

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