Structure of the Lithium Thiocyanate–Tetramethylpropylenediamine Complex Dimer, $[LiNCS{\cdot}Me_2N(CH_2)_3NMe_2]_2$, with Asymmetric NCS-Bridge Bonding: A New Bonding Mode for the Thiocyanate Ligand

David R. Armstrong,[1a] **Amit H. Khandelwal,**[1b] **Paul R. Raithby,**[1b] **Ronald Snaith,***[,1b] **Dietmar Stalke,**[1b] **and Dominic S. Wright**[1b]

University Chemical Laboratory, Cambridge CB2 1EW, U.K., and Department of Pure & Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, U.K.

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The new complex $[LiNCS{\cdot}Me_2N(CH_2)_3NMe_2]_2$ has been prepared in high yield by reacting Bu^nLi with a suspension of solid NH_4NCS in toluene containing the ligand $Me_2N(CH_2)_3NMe_2$[TMPDA]. Its crystal structure has been determined by X-ray crystallography at 153 K. Crystal data: monoclinic, space group $P2_1/c$, $a = 10.616(2)$ Å, $b = 13.309(3)$ Å, $c = 16.694(3)$ Å, $\beta = 101.09(3)°$, $Z = 4$. In the structure, two complexed (TMPDA)Li^+ units are bridged through N-bonded NCS^- anions. However, an unprecedented feature is that these μ_2-NCS^- bridges are asymmetric; each leans over toward one Li^+ and away from the other, but each does so to different extents, so leading to four distinct $Li\hat{N}C$ angles [range 108.8(1)–167.0(2)°] and to four distinct Li–N ring distances [range 1.978(3)–2.095(3) Å]. These structural features are interpreted in terms of the supposed dimer being actually two loosely-associated monomers, each slightly distorted from the ideal linearity of a complexed LiNCS monomer. Such an interpretation is supported by the results of 6-31G basis set ab initio MO calculations on LiNCS and $(LiNCS)_2$ and on their complexes with NH_3; in particular, the lowest energy optimized structure of $(LiNCS)_2{\cdot}4NH_3$, a model for the title complex, has also an asymmetric μ_2-NCS bonding mode. Solution studies (IR spectroscopic and cryoscopic) on the complex indicate extensive dissociation of the solid-state structure into separate monomers but cast doubts on the proposed correlation between ν(NCS) stretching frequencies and NCS^- bonding modes.

Introduction

We have reported recently the structures of a series of alkali metal thiocyanate (MNCS) complexes with acyclic mono- and bidentate ligands (L).[2] Prior to this work, all complexed MNCS structures had contained macrocyclic (crown, cryptand) ligands, and were usually $M^+{\cdots}NCS^-$ ion-separated species or monomers with M–NCS terminal bonds.[3] In contrast, the new complexes displayed varied aggregation states and NCS-bonding modes: viz. the dimers $(HMPA)_2Li{\cdot}2(\mu_2\text{-}HMPA){\cdot}Li(NCS)_2$[2a] and $(HMPA)SCN{\cdot}Na(\mu_2\text{-}HMPA)_2Na{\cdot}NCS(HMPA)$,[2b] and the trimer $(KNCS)_3{\cdot}5HMPA$,[2c] all with terminal M–NCS units, and the polymers $(LiNCS{\cdot}TMEDA)_\infty$[2d] and $(NaNCS{\cdot}HMPA)_\infty$[2b] with bifunctional $M\text{–}NCS{\cdots}M'$ bonding [HMPA, $O{=}P(NMe_2)_3$; TMEDA, $Me_2N(CH_2)_2NMe_2$]. However, a further feasible bonding mode for the NCS^- ligand, that of two such ligands bridging two metal centers (μ_2), has not hitherto been found for alkali metal thiocyanates in the solid state [although complexed $(LiNCS)_2$ dimers, presumably having μ_2-NCS^- ligands, have been detected spectroscopically in solution[4]]. Here we report the synthesis and structure of $(LiNCS{\cdot}TMPDA)_n$ (**1**) [TMPDA = tetramethylpropylenediamine, $Me_2N(CH_2)_3NMe_2$] which contains such μ_2-NCS^- anions within a solid-state dimeric ($n = 2$) structure. Surprisingly, though, these NCS^- bridges are asymmetric, each NCS^- anion leaning over toward one Li^+ ion but each doing so to different degrees and thus causing all four Li–N bonds around the central Li_2N_2 ring to be of different lengths. These features, not seen before for *any* metal thiocyanate complex, suggest that the dimer **1** is better regarded as consisting of two loosely-associated monomers, a supposition supported by the results of ab initio MO calculations.

Results and Discussion

Synthesis of 1. Complex **1** was prepared by the "ammonium salt route"[5] which has afforded numerous salt complexes of type $MX_n{\cdot}xL$, with X = NCS^-, halide, BF_4^-, PF_6^-, or NO_3^- and with M = an alkali metal,[2] an alkaline earth,[6a] a transition metal, or a lanthanide.[6b] In this route, an ammonium salt NH_4X, suspended in toluene containing stoichiometric quantities of a Lewis base L, is reacted with the solid metal or metal hydride or with a solution of an organometallic. Such reaction affords presumably monomeric MX_n units in the first instance, and these (or small oligomers formed from their limited aggregation) are "captured" by the ligands L under the conditions of the reaction, rather than associating extensively to $(MX_n)_\infty$ lattices. An in situ strategy of assembling MX_n units has several noted[2,5,7] advantages over the obvious alternative one,[7] dissolution and thereby breakdown of an already formed $(MX_n)_\infty$ lattice. First, numerous such salts fail to dissolve, or dissolve incompletely, even in neat liquid ligands L; their lattice energies are presumably much greater than most complexation energies. Second, it is often extremely difficult to obtain fully anhydrous salts, particularly halide salts; any water present may turn up in the resulting complex and in variable,

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(1) (a) University of Strathclyde. (b) University of Cambridge.

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Table I. Crystallographic Data for [$LiNCS{\cdot}Me_2N(CH_2)_3NMe_2]_2$ (**1**)

formula	$C_{16}H_{36}Li_2N_6S_2$	λ(Mo Kα), Å	0.710 73
fw	390.5	ρ_{calcd}, Mg m^{-3}	1.121
space group	$P2_1/c$ (No. 14)	μ, mm^{-1}	0.241
a, Å	10.616(2)	*F*(000)	848
b, Å	13.309(3)	2θ range, deg	5–45
c, Å	16.694(3)	no. of measd reflcns	7992
β, deg	101.09(3)	no. of unique reflcns with $F > 4\sigma(F)$	4517
V, Å^3	2314.6(8)		
Z	4	R^a	0.055
T, K	153	$R_w{}^b$	0.071

[a] $R = \sum(F_o - F_c)/\sum(F_o)$. [b] $R_w = \sum w^{1/2}(F_o - F_c)/\sum w^{1/2}(F_o)$.

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$)^a for **1**

	x	*y*	*z*	*U*(eq)^a
Li(1)	7488(3)	8052(2)	1665(2)	34(1)
Li(2)	5209(3)	7304(2)	842(2)	31(1)
N(1)	7006(1)	6830(1)	909(1)	36(1)
C(1)	7852(2)	6319(1)	832(1)	32(1)
S(1)	9042(1)	5627(1)	725(1)	51(1)
N(2)	5717(2)	8552(1)	1601(1)	38(1)
C(2)	4800(2)	8968(1)	1675(1)	32(1)
S(2)	3499(1)	9531(1)	1768(1)	61(1)
C(3)	8479(3)	8966(2)	383(2)	68(1)
C(4)	8813(3)	9921(2)	1579(2)	73(1)
N(3)	8821(1)	8926(1)	1262(1)	38(1)
C(5)	10102(2)	8493(2)	1514(1)	45(1)
C(6)	10534(2)	8304(2)	2417(1)	48(1)
C(7)	9848(2)	7466(2)	2758(1)	43(1)
N(4)	8501(1)	7659(1)	2797(1)	34(1)
C(8)	7928(2)	6742(2)	3007(1)	52(1)
C(9)	8405(3)	8372(2)	3429(2)	61(1)
C(10)	4469(3)	6947(2)	−896(2)	71(1)
C(11)	4767(2)	8615(2)	−529(1)	54(1)
N(5)	4254(2)	7685(1)	−311(1)	36(1)
C(12)	2871(2)	7803(2)	−332(1)	44(1)
C(13)	2202(2)	6951(2)	−11(1)	55(1)
C(14)	2546(2)	6784(2)	894(1)	45(1)
N(6)	3860(1)	6428(1)	1210(1)	31(1)
C(15)	4027(3)	5426(1)	955(2)	54(1)
C(16)	4058(2)	6458(2)	2107(1)	49(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

nonstoichiometric amounts over several preparations. In contrast, ammonium salts have rather low lattice energies and most of them are anhydrous and nonhygroscopic.

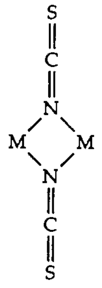
In the case of **1**, ambient temperature reaction of Bu^{n}Li solution with solid NH_4NCS (1:1 molar equiv) suspended in toluene containing TMPDA (also 1 equiv) gave rapidly, after gas evolution, a clear solution. Refrigeration gave crystals of **1** in high yield, identification being achieved initially by elemental analyses and IR and ^{1}H NMR spectroscopies (see Experimental Section).

Crystal Structure of 1. The crystal structure of **1** was determined by low-temperature single-crystal X-ray diffraction analysis. Selected crystallographic data are given in Table I, atomic coordinates (non-H atoms) and isotropic displacement parameters in Table II, and selected bond parameters in Table III.

Table III. Selected Bond Parameters for **1**

Bond Distances (Å)			
Li(1)–N(1)	2.061(3)	Li(1)–N(2)	1.978(3)
Li(2)–N(1)	1.992(3)	Li(2)–N(2)	2.095(3)
Li(1)–N(3)	2.045(4)	Li(1)–N(4)	2.053(3)
Li(2)–N(5)	2.060(3)	Li(2)–N(6)	2.031(3)
Li(1)···C(1)	2.759(4)	Li(2)···C(2)	2.693(4)
N(1)–C(1)	1.153(2)	C(1)–S(1)	1.601(2)
N(2)–C(2)	1.146(2)	C(2)–S(2)	1.606(2)
Bond Angles (deg)			
N(1)–Li(1)–N(2)	96.4(1)	N(1)–Li(2)–N(2)	94.9(1)
Li(1)–N(1)–Li(2)	84.6(1)	Li(1)–N(2)–Li(2)	84.1(1)
N(3)–Li(1)–N(4)	100.1(1)	N(5)–Li(2)–N(6)	100.0(1)
Li(1)–N(1)–C(1)	115.3(1)	Li(2)–N(1)–C(1)	159.8(2)
Li(1)–N(2)–C(2)	167.0(2)	Li(2)–N(2)–C(2)	108.8(1)
N(1)–C(1)–S(1)	178.9(2)	N(2)–C(2)–S(2)	178.8(2)

The molecular structure of **1** would normally be described as being that of a dimer, $(LiNCS{\cdot}TMPDA)_2$; a plot is shown in Figure 1. Two Li$^+$ cations, each complexed terminally by a TMPDA ligand, are bridged by the N centers of two NCS$^-$ anions. A μ_2-mode for the NCS$^-$ ligand is rare between any two metals, though it is known in, for example, bis(monoaza-15-crown-5)$\cdot$2KNCS$\cdot$H$_2$O,[8] in which just one NCS$^-$ bridges two K$^+$ ions, and in $Re_2(NCS)_{10}{}^{3-}$, where two NCS$^-$ ligands link two Re atoms.[9] However, in all previously known examples the bridging is symmetric in that near-linear NCS$^-$ ligands project directly outwards from a planar MN_2M ring such that they are essentially perpendicular to and bisect the M···M internuclear axis, as in structure A. The striking feature of the structure of **1** is that the μ_2-NCS$^-$ bridges are decidedly asymmetric. Each NCS$^-$ anion tilts toward one metal cation and away from the other, as in structure B.



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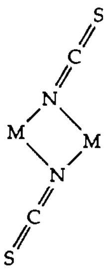

B

Moreover, in **1** the tilts of the NCS$^-$ bridges are not regular but occur to different extents. The four Li$\widehat{N}$C angles external to the ring are all significantly different, being approximately 115(1) and 109(1)° in the case of the more acute angles and 160(1) and 167(1)° in the case of the more open ones (Table III). This leads to all four Li–N distances around the central Li_2N_2 ring being different. Each anion has a short bond to one Li$^+$, 1.978(3) and 1.992(3) Å, these being the bonds along the more open Li$\widehat{N}$C angles (Figure 2, full Li–N bonds). The N of each anion has also a longer bond to a second Li$^+$, 2.061(3) and 2.095(3) Å (Figure 2, broken line Li- - -N bonds). Such Li–N distances can be compared to those typically found for terminal Li–NCS attachments [e.g., average 2.007 Å in $(LiNCS{\cdot}2HMPA)_2$[2a]] and for bifunctional Li–NCS···Li′ arrangements [1.956(10) Å in $(LiNCS{\cdot}TMEDA)_\infty$[2d]]. This observation of four distinct ring bonds within a dimer is certainly unprecedented in lithium structural chemistry. In dimers of the types $L{\cdot}Li(X)_2Li{\cdot}L$ and $2L{\cdot}Li(X)_2{\cdot}LiL_2$, with bridging groups (X) such as amide R_2N^- [10] or halide (Cl$^-$, Br$^-$, I$^-$),[7,10] the norm is to find centrosymmetric

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(7) Lithium halide complexes, prepared by direct or in situ methods, and their ring dimer structures: (a) Hall, S. R.; Raston, C. L.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **1983**, *22*, 4070. (b) Raston, C. L.; Whitaker, C. R.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1988**, 991. (c) Raston, C. L.; Skelton, B. W.; Whitaker, C. R.; White, A. H. *Aust. J. Chem.* **1988**, *41*, 1925. (d) Raston, C. L.; Whitaker, C. R.; White, A. H. *Ibid.* **1989**, *42*, 201. (e) Raston C. L.; Whitaker, C. R.; White, A. H. *Inorg. Chem.* **1989**, *28*, 163. (f) Raston, C. L.; Robinson, W. T.; Skelton, B. W.; Whitaker, C. R.; White, A. H. *Aust. J. Chem.* **1990**, *43*, 1103.

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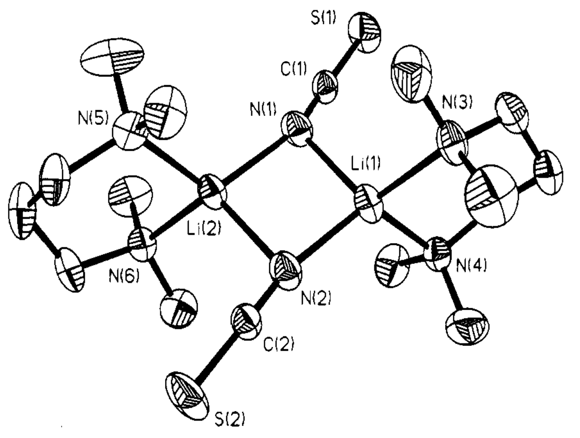

Figure 1. ORTEP plot of the molecular structure of **1**.

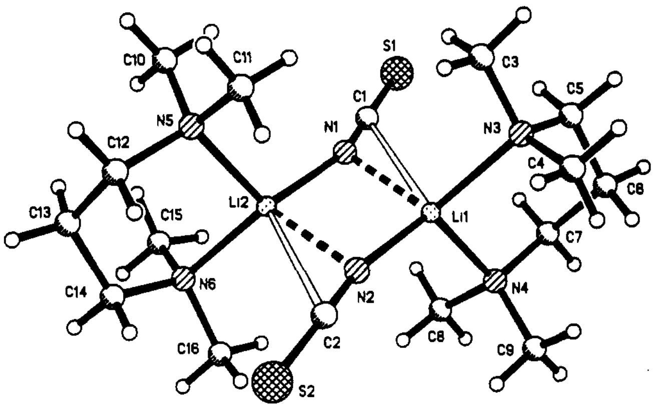

Figure 2. The molecular structure of **1**, viewing it as an asymmetric μ_2-NCS$^-$ dimer with possible Li···C interactions.

dimers with a crystallographic inversion center and two sets of Li–X distances such that shorter and longer bonds alternate around the ring. For example, in (LiBr·2-methylpyridine)$_2$ the Li–Br distances are 2.555(7) and 2.573(8) Å,[7b] while in [LiI·2-(2,6-dimethylpyridine)]$_2$ the Li–I distances are 2.913(7) and 2.932(6) Å.[7e]

Although no alkali metal species of type nL·M(μ_2-NCS)$_2$M·nL have been previously structurally characterized in the solid state, they have been proposed to exist in solution on the basis of ν(NCS) IR stretching frequencies.[4] However it has been implicitly assumed that, as in all known binuclear metal thiocyanate species, the μ_2-NCS$^-$ ligands would be symmetric bridges, as in structure A. The key question therefore is, why do the μ_2-NCS$^-$ ligands in **1** tilt and bond in an asymmetric manner, as in structure B? This tilting cannot be attributed to steric effects within each dimer. As Figure 2 makes clear, the optimum position for the NCS$^-$ ligand would be to project straight out from the ring; in any case, even when tilted, the tetrahedral coordination around Li$^+$ precludes any close contacts between, for example, the S atom of NCS$^-$ and the N–Me units of the terminal TMPDA ligand. Nor is the tilting explicable in terms of intermolecular steric or crystal packing effects. Figure 3 illustrates that the dimers in the lattice are discrete ones, with no significant interdimer contacts.

It seems then that there must be an electronic reason for the adoption of asymmetric NCS-bridge bonding in **1**. One such possible reason is illustrated in Figure 2 in that the tilt of the two NCS$^-$ anions causes two Li····C contacts (open Li···C "bonds"). However, such contacts, being of lengths 2.693(4) and 2.759(4) Å, may or may not reflect bonding.[10,11] Thus, while short Li···CH$_3$ distances of 2.37 Å unquestionably link the (MeLi)$_4$ tetramers in the methyllithium lattice,[11a] much longer Li···C distances also appear to have bonding significance, for example, intermolecularly in the "loose dimer" [Ph(Naphthyl)NLi·TMEDA]$_2$ {Li···C of

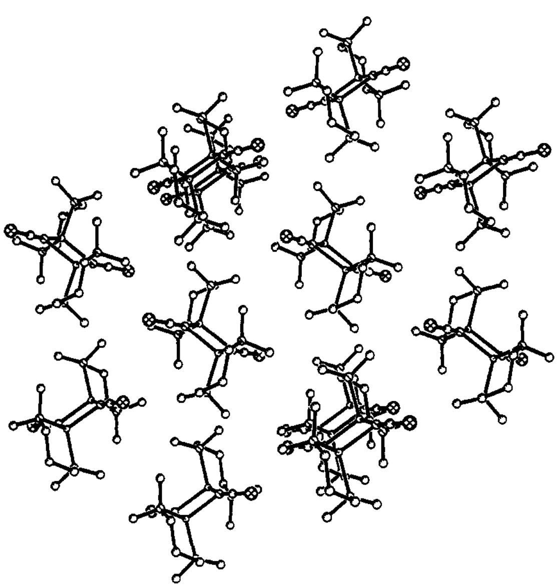

Figure 3. Crystal packing within the structure of **1**.

neighboring Ph, 3.12–3.15 Å}[11b] and intramolecularly in the trimer [(PhCH$_2$)$_2$NLi]$_3$ {Li···C(benzyl), 2.60–2.70 Å}.[11c] If there is indeed Li···C bonding in **1**, then the μ_2-NCS$^-$ bridges here are reminiscent of asymmetric σ/π-alkynyl bridges (usually taken as 3e$^-$ donors, 1σ-2π) in R$_2$Al·2(μ_2-R'C≡C)·AlR$_2$ dimers.[12] For example, in (Ph$_2$AlC≡CPh)$_2$ each alkynyl α-C atom forms a shorter (1.992 Å) and a longer (2.184 Å) C–Al bond, and the Al$\hat{C}$≡C angles are 172° (incorporating the shorter C–Al bond) and 96°.[12a] However, distances within the anions of **1** give little indication of any bonding involvement between the thiocyanate C atoms or the N$\overset{-}{=}$C π-bonds and the Li$^+$ centers. The N$\overset{-}{=}$C and C$\overset{-}{=}$S distances average 1.150 and 1.604 Å respectively, very similar to those found for terminal NCS$^-$ ligands, e.g., 1.156 and 1.629 Å in (LiNCS·2HMPA)$_2$.[2a] These features suggest that **1** cannot be regarded as a dimer with σ/π-NCS$^-$ bridge bonding; such an interpretation would also fail to explain the inequivalence of all four Li–N ring bonds.

A remaining possibility is that **1** is not a dimer at all in the usual sense but rather that it is better considered as two loosely aligned complexed monomers. Figure 4, generated by a rotation of Figure 2, presents a view of **1** looking down on its central Li$_2$N$_2$ ring. Complexed LiNCS monomers might be expected to have all-linear Li–NCS backbones. Thus, while Figure 2, taking **1** as an asymmetrical dimer, gave the impression that, for example, (N(1)C(1)S(1))$^-$ bent *toward* Li(1)$^+$, in Figure 4, which views **1** as two complexed monomers, the opposite is true. Thus (N(1)C(1)S(1))$^-$, as part of the hitherto linear (Li(2)N(1)-C(1)S(1)) monomer, is now seen to bend *away* from Li(1)$^+$; the Li$\hat{N}$C angles internal to the Li(1)N(2)Li(2)N(1) ring are 192.9(2)° at N(2) and 199.9(2)° at N(1). The key structural features of **1**, perplexing if **1** is taken as a dimer, can now be explained quite readily in terms of two independent complexed monomers, Li(1)N(2)C(2)S(2)·TMPDA and Li(2)N(1)C(1)S(1)·TMPDA, coming together. The separate monomers will have linear LiNCS backbones (as confirmed later by MO calculations), and their Li–N bond lengths (Li(1)–N(2), Li(2)–N(1)) will be similar but different. Monomer association requires a slight distortion of each LiNCS unit away from linearity so that electron density at

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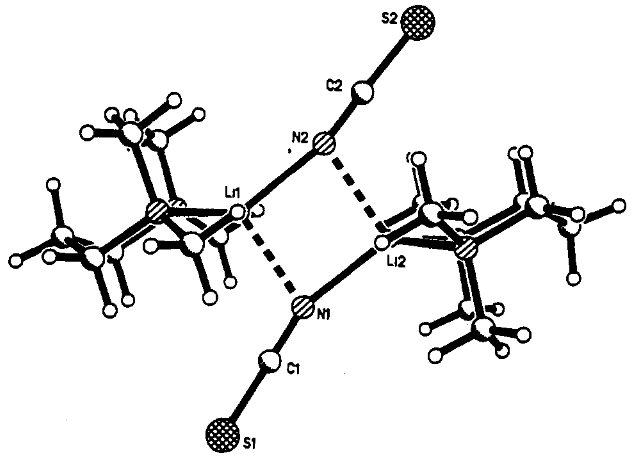

Figure 4. A view of **1** perpendicular to the Li(1)Li(2)N(1)N(2) plane, showing **1** as two loosely-linked monomers.

each N center can be directed toward the Li$^+$ in the neighboring monomer (N(2) to Li(2), N(1) to Li(1)); it will also require repositioning of the TMPDA ligands.

One interesting implication of the above structural analysis is that other ring dimers of general type xL·M(X)$_2$M·xL might be better considered as two loosely-associated monomers MX·xL, particularly where there are two distinct sets of M–X bond lengths.

Ab Initio MO Calculations. Ab initio MO calculations (6-31G basis set plus d orbitals on S) were carried out on LiNCS and (LiNCS)$_2$ and on their complexes with NH$_3$ ligands (see Experimental Section). The purpose was to probe the bonding preferences of the NCS$^-$ anion toward Li$^+$ and in particular to see if the asymmetric NCS$^-$ bridge bonding observed in the solid-state structure of **1** could be reproduced by calculation. A selection of key results is shown in Figure 5.

For an uncomplexed monomer, the most stable optimized structure (relative energy, 0.0 kcal mol^{-1}) has a fully linear Li—N≡C—S arrangement (Figure 5i). A linear Li—S—C≡N structure is 29.9 kcal mol^{-1} less stable and in fact is not a local minimum, while a structure with a Li–S bond and a bent anion [Figure 5ii] is of intermediate stability (+13.6 kcal mol^{-1}). Complexation of these monomers by two NH$_3$ ligands (as a model for a single bidentate donor such as TMPDA or TMEDA) narrows the preference between the two stable forms. Thus, the relative energies for 2H$_3$N·LiNCS (whose LiNCS backbone remains, as anticipated above, linear) and for bent 2H$_3$N·LiSCN are 0.0 and +8.0 kcal mol^{-1}, respectively; this narrowing is the result of a larger total complexation energy for LiSCN (58.2 kcal mol^{-1}) than for LiNCS (52.6 kcal mol^{-1}).

Calculations on uncomplexed (LiNCS)$_2$ dimers, starting with an initial geometry of two aligned LiNCS monomers, pinpoint two viable structures. The most stable is an eight-membered LiNCS·LiNCS ring (Figure 5iii). Less stable (relative energy, +4.4 kcal mol^{-1}) is a four-membered Li$_2$N$_2$ ring structure (Figure 5iv); the dimerization energy from two linear LiNCS molecules is 46.3 kcal mol^{-1}. Its NCS bridges are perfectly symmetrical and its four Li-N bonds are equivalent: the key structural features of **1** are not reproduced. However, and crucially, complexation of these dimers causes startling changes. The most stable optimized structure of 2H$_3$N·2LiNCS is a four-membered N-bridged ring (Figure 5v) and not an eight-membered one (a bis-complexed LiNCS·LiNCS system has a relative energy of +0.23 kcal mol^{-1}). The key finding is that now the NCS bridges are asymmetric and there are alternating shorter and longer Li–N bonds around the N$_2$Li$_2$ ring. Thus the features seen in **1** are beginning to emerge. However, it is clear that the precise disposition of the NH$_3$ ligands is important. In this optimized structure two N-H bonds (one on each NH$_3$) are coplanar with the (LiNCS)$_2$ system. Rotation of one of these NH$_3$ ligands to give C_{2v} symmetry results in adoption of an almost symmetric dimer (Li–N distances, 1.985 and 1.986 Å; all Li$\hat{N}$C angles, 140.5°) of relative energy +0.06 kcal mol^{-1}. Finally, complexation by two NH$_3$ ligands per Li (so providing the closest model to **1**) increases the preference for a four-membered 2NH$_3$·Li(μ_2-NCS)$_2$-Li·2NH$_3$ ring structure; a (LiNCS·LiNCS)·4NH$_3$ system is 2.0 kcal mol^{-1} less stable. Furthermore, the lowest energy freely optimized four-membered ring structure is asymmetric (Figure 5vi): the NCS$^-$ bridges are tilted (Li$\hat{N}$C angles external to the ring, 176.9 and 98.0°; cf., mean values in **1**, 163.4 and 112.1°), and there are short and long Li–N ring bonds (1.962 and 2.397 Å; cf., mean values in **1**, 1.985 and 2.078 Å). A symmetric N-bridged structure (all Li–N distances, 2.060 Å; all Li$\hat{N}$C angles, 139.4°) can only be obtained if symmetry is imposed, i.e., the NH$_3$ ligands have to have a special arrangement (D_{2h}) to maintain a four-membered Li$_2$N$_2$ ring with four equal sides.

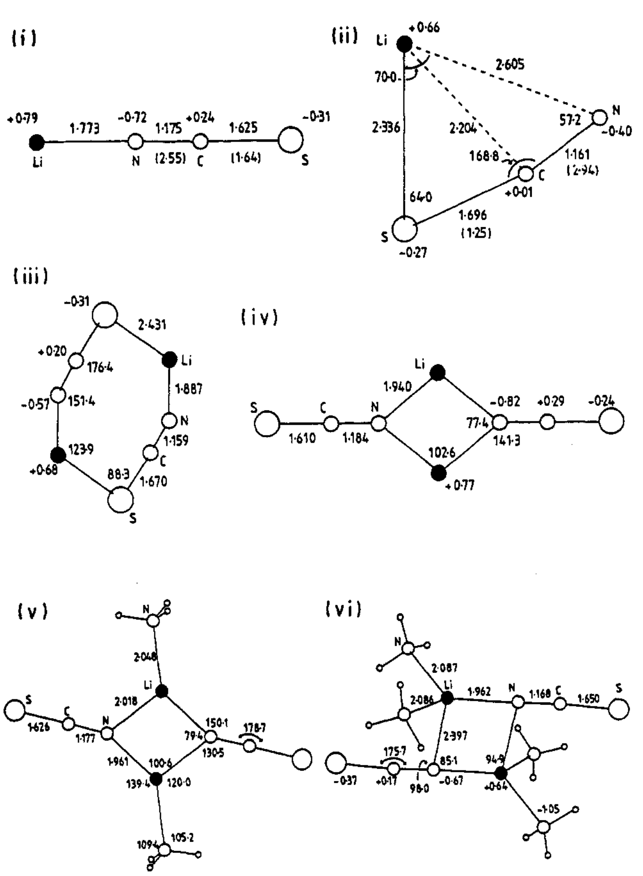

Figure 5. Ab initio optimized geometries showing key bond lengths (Å) and angles (deg) and, in selected cases, bond indices (in parentheses) and atomic charges; (i) linear LiNCS monomer; (ii) bent LiSCN monomer; (iii) LiNCS·LiNCS dimer; (iv) symmetric (μ_2-N)(LiNCS)$_2$ dimer; (v) asymmetric (H$_3$N)$_2$(LiNCS)$_2$ complexed dimer; (vi) asymmetric (H$_3$N)$_4$-(LiNCS)$_2$ complexed dimer.

Overall, these calculational results support the contention made earlier that the "dimer" **1** is better thought of as two loosely-connected monomers. In essence, it seems that the bis-complexation energy of a LiNCS monomer, which is highest when the monomer is linear, slightly outweighs the dimerization energy of two LiNCS monomers, which is highest when a symmetrically-bridged structure forms, i.e., when the Li$\hat{N}$C angles are severely distorted from linear (Figure 5iv; Li$\hat{N}$C 141.3°). Thus, a complexed linear LiNCS monomer distorts such that its N center can bond to a Li in a nearby monomer, but it does so only slightly. This maintains not only a high complexation energy, but also strong π-bonding within the NCS$^-$ anion. However, it is apparent that the energy differences between alternative structures are very small, and that the nature of the complexant L can have profound effects. For example, whereas **1** is a dimer or two loosely-associated monomers, $(\mathrm{LiNCS{\cdot}TMEDA})_\infty$, having merely a slightly smaller ligand (one fewer CH_2 between NMe_2 groups cf. TMPDA), is a polymer with Li–NCS···Li chains.[2d]

Solution Studies. Profound structural changes can also occur on switching from the solid to the solution phase. For metal thiocyanates, the best probe here is the ν(NCS) stretching frequency: solution studies on LiNCS in amine and ether solvents have assigned bands at 2060–2070 cm^{-1} to monomers (terminal NCS$^-$),[4a] those at 2030–2040 cm^{-1} to dimers (μ_2-NCS$^-$, but without specifying whether the bridge is symmetric or not),[4b] and ones at 1990–2000 cm^{-1} to cubane tetramers (μ_3-NCS$^-$).[4c] Earlier studies[2d] on $(\mathrm{LiNCS{\cdot}TMEDA})_\infty$ showed that in the solid the ν(NCS) stretch appeared at 2074 cm^{-1}, indicative of a terminal (though bifunctional) Li–NCS unit. However, in benzene solutions the band shifts to 2032 cm^{-1} and relative molecular mass cryoscopic measurements on such solutions gave association state values of 2.2–2.1 (45–15 mmol dm^{-3} concentrations, expressed relative to a monomer formula mass). Such results implied that dissolution of the polymer afforded a dimer, $(\mathrm{LiNCS{\cdot}TMEDA})_2$. Given the elucidated structure of **1**, it now seems likely that the μ_2-NCS$^-$ bridges in such a dimer are asymmetric ones.

We have now carried out similar IR spectroscopic and cryoscopic studies on **1**. The results do cast doubt on the diagnostic value of ν(NCS) stretching frequencies. For solid **1**, this band appears at 2033 cm^{-1}; the indication of a μ_2-NCS$^-$ mode is broadly correct, although of course the mode is actually asymmetric. Cryoscopic measurements on benzene solutions of **1** (40–10 mmol dm^{-3} concentrations) show extensive dissociation into monomers in that association state values fall from 2.1–1.1 as the concentration is lowered; this could be expected given the interpretation of the solid structure of **1** as two loose monomers. However, the IR spectra of benzene solutions of similar concentrations reveal single and strong ν(NCS) bands at a consistent 2032–2031 cm^{-1}; there are no signs of bands at 2060–2070 cm^{-1}, hitherto expected for complexed LiNCS monomers. The implication is that a straight correlation between ν(NCS) stretching frequencies and NCS$^-$ bonding modes may be too simplistic.

Experimental Section

Synthesis of 1. *n*-Butyllithium (6.2 mL of a 1.6 M solution in hexane, 10 mmol) was added to a chilled and stirred suspension of ammonium thiocyanate (0.76 g, 10 mmol) in toluene (10 mL) containing TMPDA (1.30 g, 10 mmol). After the mixture was allowed to warm slightly, a vigorous exothermic reaction ensued. On cessation of gas evolution (BuH, NH_3), all of the ammonium salt had dissolved, leaving a pale yellow solution. Refrigeration of this solution afforded colorless cubic crystals of **1** (first batch yield 1.49 g, 76%); mp 166–169 °C. Anal. Calcd: C, 49.2; H, 9.2; Li, 3.6; N, 21.5. Found: C, 47.9; H, 9.2; Li, 3.3; N, 21.2. ^{1}H NMR (250 MHz, 25 °C, C_6D_6): δ 2.30 (t, 4 H, $-CH_2CH_2CH_2-$), 2.23 (s, 12H, $-NMe_2 \times 2$), 1.30 (m, 2H, $-CH_2CH_2CH_2-$).

X-ray Structure Determination of 1. Data were collected on a Stoe four-circle diffractometer at 153 K using graphite-monochromated Mo Kα radiation. Crystal parameters and details of the data collection are given in Table I. The structure was solved by a combination of direct methods and difference Fourier techniques and refined by full-matrix least-squares methods with all non-hydrogen atoms anisotropic; hydrogen atoms were placed in idealized positions and allowed to ride on the relevant carbon atom. The function minimized during refinement was $\sum w(F_o - F_c)^2$ where $w^{-1} = \sigma^2(F) + 0.0003F^2$.

Ab Initio MO Calculations. The ab initio geometries described were obtained from the computer program GAMESS[13] using the 6-31G basis set.[14] The total energies (in au) calculated for the optimized structures referred to in the text are as follows: linear LiNCS, –497.289890; bent LiSCN, –497.268222; linear LiSCN, –497.242306; $2H_3N{\cdot}LiNCS$, –609.704659; bent $2H_3N{\cdot}LiSCN$, –609.691949; $(\overline{\mathrm{LiNCS{\cdot}LiNCS}})$, –994.660376; symmetric $(\mu_2\text{-N})(\mathrm{LiNCS})_2$, –994.653435; asymmetric $2H_3N{\cdot}2LiNCS$, –1107.070306; near-symmetric $2H_3N{\cdot}2LiNCS(C_{2v})$, –1107.070264; $2H_3N{\cdot}(\overline{\mathrm{LiNCS{\cdot}LiNCS}})$, –1107.069934; asymmetric $4H_3N{\cdot}2LiNCS$ –1219.455304; $4H_3N{\cdot}(\overline{\mathrm{LiNCS{\cdot}LiNCS}})$, –1219.452151; symmetric $4H_3N{\cdot}2LiNCS$, –1219.450578.

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, bond lengths, bond angles, anisotropic displacement coefficients, and hydrogen atom coordinates and isotropic displacement coefficients (7 pages). Ordering information is given on any current masthead page.

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