Solutions of Lithium Salts in Liquid Lithium: Preparation and *X*-Ray Crystal Structure of the Dilithium Salt of Carbodi-imide (Cyanamide)

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The salt $Li_2[NCN]$ has been prepared by the solid-state reaction of Li_2C_2 with Li_3N at 600 °C. When the reaction is carried out in molten lithium, colourless single crystals of the salt form on evaporation of the metal. This reaction is pertinent to the purification of liquid lithium for fusion reactors and to corrosion and dissolution of containment metals. An *X*-ray diffraction study has shown that the structure of $Li_2[NCN]$ is tetragonal, space group $I4/mmm$, with unit-cell dimensions $a = b = 3.687(3)$, $c = 8.668(5)$ Å, for $Z = 2$. Full matrix least-squares refinement with anisotropic temperature factors for each atom converged to give an R value of 0.036. The lattice is composed of Li^+ and centrosymmetric $[NCN]^{2-}$ ions [r(C–N) 1.230(3) Å]. Each Li^+ ion is at the centre of a squashed tetrahedron of N atoms [r(Li–N) 2.068(1) Å, N–Li–N 101.85(5) and 126.11(13)°]. The i.r. spectrum of the solid consists of bands at 2 000 ($\nu_3\ \Sigma_u^+$) and 690 cm^{-1} ($\nu_2\ \pi_u$) for the $[NCN]^{2-}$ ion. Comparisons are made with the crystal structures of the analogous compounds MNCN (M = Ca, Sr, or Pb) and H_2NCN. The i.r. spectrum is compared with those of the compounds M_2NCN (M = Na, K, Ag, or Tl) and MNCN (M = Zn or Pb).

In previous work on solubilities [1-4] and reactions [1,5] of salts in liquid alkali metals we noticed that lithium dissolved its own salts to comparatively small extents and that no solubilities had been reported for salts containing heteroatomic anions. Indeed, heteroatomic anions tend to dissociate into simpler anions on contact with the metal. For example, encapsulation of carbonate, cyanide, or nitrate with lithium at 600 °C for up to 65 h followed by hydrolysis results in complete recovery of carbon as acetylene and near complete recovery of nitrogen as ammonia which is consistent with conversion into acetylide and nitride, respectively.[6] Similarly, small amounts of ammonia when admitted to lithium at 400 °C react and dissolve as nitride and hydride, rather than amide.[5] The dissociation can be attributed to the greater cumulative thermodynamic stability of the simpler salts. Enthalpies (in the absence of adequate free energies) of reactions [*e.g.* equation (1)] typifying the action of lithium on ternary compounds are given in Table 1. The reaction enthalpies are negative and the most negative values occur with oxygen-containing salts due to the driving force of the exceptionally large negative enthalpy of formation of Li_2O.

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[5] P. F. Adams, M. G. Down, P. Hubberstey, and R. J. Pulham, *J.C.S. Faraday I*, 1977, 230.

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Recently, however, we reported[7] the dilithium salt of carbodi-imide (cyanamide) and now present details of its preparation both from the solid-state reaction of Li_3N with Li_2C_2 and also as single crystals from liquid lithium solutions. The basic reaction [equation (2)] proceeds whether the salts are solids or are dissolved in liquid metal, and the liberation of lithium and its non-interaction with $Li_2[NCN]$ are contrary to the usual dissociation process and imply considerable stability for $Li_2[NCN]$. Using equation (2) and the values in Table 1,

$$4Li_3N + Li_2C_2 \longrightarrow 2Li_2[NCN] + 10Li \qquad (2)$$

we calculate the enthalpy of formation at 298 K of the cyanamide salt to be at least as negative as —359.5 kJ mol^{-1}. The stability may be partly associated with the strong covalent C–N bonding. Thus Table 1 indicates least instability of ternary compounds towards lithium when carbon and nitrogen are incorporated together as in the $[CN]^-$ anion.

$$Li[NH_2] + 4Li \longrightarrow Li_3N + 2LiH \qquad (1)$$

TABLE 1

Enthalpies (kJ mol^{-1}) of formation (*a*) and of reaction with lithium (*b*) of lithium salts at 298 K

(*a*)				(*b*)	
$Li[CN]$	−126.8	Li_2C_2	−59.4	$Li[CN]$	−67.8
$Li[NH_2]$	−182.0	LiH [a]	−90.4	$Li[NH_2]$	−163.7
$Li[NO_3]$	−482.3	Li_3N [b]	−164.9	$Li[OH]$	−183.1
$Li[OH]$	−487.2	Li_2O [c]	−579.9	$Li_2[CO_3]$	−553.8
$Li_2[CO_3]$	−1 215.6			$Li[NO_3]$	−1 422.3

Data taken from F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, 'Selected Values of Chemical Thermodynamic Properties,' Nat. Bureau Standards Circular 500, 1952, unless otherwise stated.

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Hitherto, $Li_2[NCN]$ was poorly characterised. It was believed to be present in a mixture of products from reactions between Li_2C_2 and nitrogen[8] or NH_3,[9] carbon and Li_3N,[9] and between lithium and $(CN)_2$.[10] In this early work, identification was by precipitation of $Ag_2[NCN]$ from aqueous solution, supported sometimes by Kjeldahl nitrogen analyses. More recently, $Li_2[NCN]$ has been prepared by heating $Li_2[CO_3]$ with $CO(NH_2)_2$ at temperatures up to 800 °C,[11] and a purer form (96—98%) results from the thermal decomposition at 870—900 °C of $Li[HNCN]$.[12]

EXPERIMENTAL AND RESULTS

Preparation.—Solid-state reactions. Pure starting materials for the preparation of $Li_2[NCN]$ according to equation (2) were obtained from the elements. Lithium nitride was made by reaction of nitrogen with a solution of lithium (7 g) in liquid sodium (23 g) at 400 °C in a steel (AISI 321) beaker (diameter 60mm, height 50 mm) contained in a distillation vessel. Sodium[13] and lithium[14] were purified as before and all the operations were performed under argon. The reaction temperature was sufficiently above the consolute temperature (303 °C) of the metal mixture to avoid metallic phase separations.[15] Argon was replaced by nitrogen (Air Products, 99.999%), and the reaction was followed by pressure changes. The gas reacted preferentially with the lithium to form the nitride which initially dissolved. As the concentration of free lithium diminished, crystallisation occurred giving ultimately a suspension of Li_3N in pure sodium. The sodium was distilled off at 300—400 °C under 10^{-5} Torr pressure * leaving ruby-red hexagonal plates of Li_3N in the beaker. The *X*-ray diffraction pattern of the powdered crystals agreed with that of Zintl and Brauer[16] whose proposed structure has recently been confirmed by the single-crystal data of Rabeneau and Schulz.[17]

This method of preparation ensured complete reaction of lithium and avoided the high temperature needed for distillation of any unchanged lithium and the consequent dissociation of Li_3N. The vapour pressure of lithium[18] and the dissociation pressure of nitride[19] at 400 °C are 8.9×10^{-5} and 1.5×10^{-9} Torr (extrapolated from 660 °C) compared with 0.386 Torr for sodium.[20]

Dilithium acetylide was prepared by heating lithium (6 g) with carbon (Johnson, Matthey; Specpure, 6 g) at 650 °C for 100 h under argon. Excess of lithium was distilled off at 600 °C under 10^{-5} Torr pressure leaving a white residue of Li_2C_2 confirmed by its characteristic *X*-ray powder diffraction pattern.[21]

The dilithium salt of cyanamide was prepared by heating Li_3N with Li_2C_2 in 4 : 1 mol ratio at 600 °C for 10 h under argon. The finely ground and intimately mixed reactants were compressed into a block (diameter 5 mm, length 8 mm) and held in a steel thimble within the distillation vessel. Liberated lithium was distilled off as before leaving an off-white block of $Li_2[NCN]$. The reaction temperature was determined in a separate experiment by thermal analysis. A thermocouple was inserted in a similar mixture which was heated *in vacuo* up to 600 °C at 0.2 °C s^{-1} in a steel liner within a silica tube. One thermal change was observed at 310 °C and the liberated lithium [equation (2)] commenced

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* Throughout this paper: 1 Torr = (101 325/760) Pa.

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to distil at 400 °C to form a mirror on cooler parts of the apparatus.

The compound $Li_2[NCN]$ is most readily identified by its *X*-ray powder pattern which was determined by diffraction of Cu-K_{α} radiation by a flat sample (10 × 10 mm) protected by nitrogen. Thirty-two peaks were observed and their relative intensities were measured. No peaks which could be ascribed to Li_3N or Li_2C_2 were observed. Observed spacings and intensities are compared in Table 2 with values calculated from single-crystal data (see later). The calculated intensities were obtained from $I(\text{calc.}) = F^2m/L$ where F is the single-crystal structure factor, m is the multiplicity of crystal planes of a set of *hkl* values, and L is the combined Lorentz and polarisation factor. Values of *hkl* were derived from the tetragonal structure for which $a = b = 3.687$ and $c = 8.668$ Å. There was overall good agreement between d(obs.) and d(calc.) except that the faintest peaks were not observed on the powder pattern. Tentative intensities quoted for powder patterns in our preliminary report [7] are in the correct ratios, except for the strongest line, but are too large due to overexposure of films.

TABLE 2

Observed and calculated interplanar spacings, d/Å, for $Li_2[NCN]$

d		I/I_0		
obs.	calc.	obs.	calc.	*hkl*
4.329	4.334	4	1.9	002
3.392	3.393	100	100.0	011
2.605	2.607	12	20.6	110
2.277	2.274	6	6.1	013
2.234	2.234	6	7.5	112
2.179	2.167	1	0.1	004
1.842	1.844	14	16.0	020
1.697	1.696	1	0.6	022
1.667	1.666	6	6.2	114
1.617	1.620	8	11.5	121
	1.569		0.1	015
	1.447		0.2	006
1.433	1.432	3	1.5	123
1.306	1.304	8	3.9	220
1.265	1.264	6	4.3	116
	1.248		0.2	222
1.219	1.217	3	1.7	031
	1.195		0.1	125
1.176	1.174	5	2.8	017
1.168	1.166	3	1.0	130
1.140	1.137	1	0.3	026
	1.131		0.3	033
1.127	1.126	3	1.4	132
1.086	1.084	2	0.7	008
1.029	1.027	3	1.9	134
1.018	1.016	3	2.1	231
	1.000		0.3	118
0.993	0.990	4	3.6	127
	0.967		0.2	226
	0.964		0.4	233
0.937	0.934	3	2.2	028
	0.932		0.1	019
0.924	0.922	3	1.6	040
0.910	0.907	4	4.2	136
	0.902		0.1	042
0.892	0.889	3	2.1	141
	0.881		0.1	235
0.874	0.872	2	2.0	037
	0.869		0.4	330
	0.867		0.2	0 010
	0.854		0.4	143
0.853	0.852	1	0.6	332
0.836	0.833	3	2.9	228
	0.832		0.2	129
0.826	0.824	4	4.6	240
	0.810		0.1	242
	0.807		1.2	334
	0.795		0.2	145
0.795	0.794	1	1.6	138
0.790	0.789	4	8.8	237

Crystallisation from liquid lithium. The preparation was again based on equation (2) but conditions were arranged to favour solution of reagents in liquid lithium. The apparatus was essentially as described previously [22] and consisted of a cylindrical steel reservoir (length 300 mm, diameter 50 mm) attached through a glass-to-metal seal and tap to a vacuum frame, and equipped below with an electromagnetic pump and a capillary loop (internal diameter 1.5 mm, length 500 mm) on the side to sample liquid from the base of the reservoir and return it as a jet to react with nitrogen in the space above. The pump ensured homogeneity of solution, and the solution and precipitation processes were monitored by changes in the electrical resistivity of the metal passing through the capillary. The reservoir was charged with lithium (30 g) under argon and the entire apparatus heated to 530 °C in an air oven. The molten metal was circulated and small blocks (20 × 0.07 g) of Li_2C_2 were introduced in succession from an inclined side-arm. It was intended to saturate the lithium with acetylide but the resistivity did not increase progressively with successive additions as is usual for salts in metals,[1] due either to slow dissolution, a low solubility of acetylide, and/or small electron scattering by the $[C_2]^{2-}$ ion in liquid lithium. It was not known, therefore, how much of the acetylide dissolved. Nitrogen was then added and the resistivity increased as expected as the gas reacted and nitride dissolved. The overall C : N ratio reached 4 : 1. As conversion of Li_3N into $Li_2[NCN]$ proceeded the resistivity progressively decreased due to loss of dissolved nitride from solution. All the nitride was consumed after 24 h. Excess of lithium was then removed by distillation at 600 °C under 10^{-5} Torr pressure on to the upper cooler walls of the reservoir, which was subsequently opened under argon in a glovebox.

The salt $Li_2[NCN]$ formed as hygroscopic colourless single plates adhering to the base of the reservoir and capillary walls, and to unchanged Li_2C_2. This distribution was consistent with crystallisation from metal solution, either progressively during reaction and/or during concentration of the solution by subsequent lithium evaporation. *X*-Ray diffraction showed the single crystals to be $Li_2[NCN]$. When powdered, the crystals gave an *X*-ray diffraction pattern identical to that shown in Table 2 for the solid-state preparation. We believe this to be the only known example of a salt containing a heteroatomic anion which is stable towards lithium and which dissolves in, and can be crystallised from, the molten metal.

Crystal Structure.—A suitable crystal (0.3 × 0.3 × 0.1 mm) was selected and mounted in a Lindemann tube under argon. Oscillation and Weissenberg photographs revealed cell parameters and systematically absent reflections consistent with an *I*-centred tetragonal cell. The cell parameters were refined by least squares using intense low-

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[22] C. C. Addison, G. K. Creffield, P. Hubberstey, and R. J. Pulham, *J. Chem. Soc.* (*A*), 1971, 1393.

angle reflections measured on a four-circle diffractometer (Hilger and Watts).

Crystal data. CLi_2N_2, $M = 53.9$, Tetragonal, $a = b = 3.687(3)$, $c = 8.668(5)$ Å, $U = 118$ Å^3, $D_m = 1.51$, $Z = 2$, $D_c = 1.52$ g cm^3, $F(000) = 52$, space group $I4/mmm$ from systematically absent reflections hkl for $h + k + l = 2n + 1$, $hk0$ for $h + k = 2n + 1$, $0kl$ for $k + l = 2n + 1$, and hhl for $l = 2n + 1$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,7$ Å, $\mu(\text{Mo-}K_\alpha) = 0.49$ cm^{-1}.

Three sets of data (hkl, $\bar{h}kl$, and $\bar{h}\bar{k}l$) were collected in the range $1 \leqslant \theta \leqslant 40°$ using graphite-monochromated Mo-K_α radiation to provide an averaged intensity for equivalent reflections. Three standard intensities measured every 100 reflections indicated that the crystal was stable throughout the data collection. Of the averaged intensities from the total set of 570 reflection intensities collected, 119 had net counts exceeding $3\sigma_I$ [where $\sigma_I =$ (total background count + integrated count)$^{\frac{1}{2}}$] and were deemed to be observed. Data were corrected for Lorentz and polarisation effects.

From the systematically absent reflections there were five possible space groups ($I422$, $I4mm$, $I\bar{4}m2$, $I\bar{4}2m$, and $I4/mmm$) from which $I422$ was selected in calculating the Patterson map. A strong peak, expected for the N–C vector, was found at 0, 0, 0.140 enabling the C and N atoms to be placed in the special positions 0, 0, 0 and 0, 0, z ($z = 0.140$), respectively. A difference synthesis then revealed a special position for the Li atom at 0, $\frac{1}{2}$, $\frac{1}{4}$, further reducing the choice of space groups to $I422$, $I\bar{4}m2$, or $I4/mmm$. Because of the symmetry of the molecule and its special arrangement in the cell, these three space groups become equivalent. Under these circumstances, it was thought appropriate to refine in the most symmetrical space group $I4/mmm$. Full-matrix least-squares refinement with anisotropic temperature factors for each atom converged to give an R value of 0.036. The final difference Fourier synthesis only contained residual electron density along the C–N bond. Final positional parameters are listed in Table 3. A list of structure factors and thermal parameters is available as Supplementary Publication No. SUP 22321 (6 pp.).* Calculations were performed using the Oxford University CRYSTALS set of programs.

TABLE 3

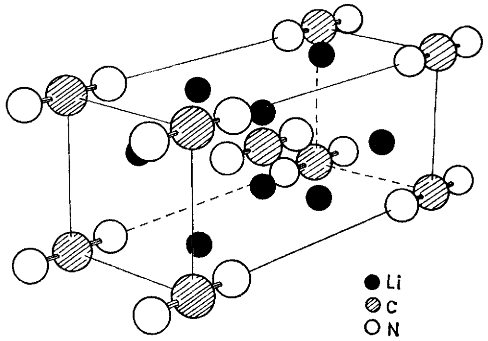
Final positional parameters (× 10^4)

Atom	Site occupancy	x/a	y/b	z/c
C(1)	0.062 5	0	0	0
N(1)	0.125	0	0	1 419 (1)
Li(1)	0.125	0	5 000	2 500

DISCUSSION

The structure is shown in the Figure and is composed of Li^+ and $[NCN]^{2-}$ ions. The anions form an elongated body-centred cube with two Li^+ ions in each long face at 0, $\frac{1}{2}$, $\frac{1}{4}$. Each $[NCN]^{2-}$ ion is surrounded by eight Li^+ ions. The $[NCN]^{2-}$ ion is centrosymmetric [r(C–N) 1.230(3) Å] as is found in the other ionic metal cyanamides, rhombohedral Ca[NCN] [23] and hexagonal Sr[NCN] [24] [r(C–N) 1.224(16) and 1.28(7) Å, respectively]. This contrasts with the covalent compounds, typically PbNCN and H_2NCN, in which the NCN group is asymmetric with one N atom more strongly bonded to Pb and H atoms [r(C–N) 1.25(6) 1.17(8) and 1.31, 1.15 Å for the lead [25] and hydrogen [26] compounds, respectively].

Each Li^+ ion is at the centre of a squashed tetrahedron [N–Li–N 101.85(5) and 126.11(13)°] of N atoms [r(Li–N) 2.068(1) Å] and differs from the regular octahedral environment found [23] for the larger Ca^{2+} ion in Ca[NCN] [r(Ca–N) 2.461(16) Å]. In the related compound Li[CN] the tetrahedral co-ordination at lithium is maintained by including carbon in the co-ordination sphere whose boundaries are set by the Li–C (2.11) and Li–N distances (2.06 and 2.19 Å).[27] The latter dimensions are not dissimilar from the metal–nitrogen separation in $Li_2[NCN]$.



Crystal structure of $Li_2[NCN]$

Infrared Spectroscopy.—The centrosymmetrical $[NCN]^{2-}$ ion should give rise to the fundamental i.r.-active mode ν_2 (NCN) (bend) and ν_3(NCN) (asym stretch). We have determined the i.r. spectrum of $Li_2[NCN]$ in KBr discs and hydrocarbon mulls over the range 400—4 000 cm^{-1} and find the two absorptions at 2 000 (ν_3 Σ_u^+) and 690 cm^{-1} (ν_2 π_u). Bands in these regions, consistent with symmetrical anions, have also been observed for the sodium and potassium salts and ν_3

TABLE 4

Infrared absorption spectra (cm^{-1}) of metal compounds of cyanamide

Compound	ν_3	ν_2	ν_1	ν_4
$Li_2[NCN]$	2 000s	690m		
$Na_2[NCN]$ [a]	2 120s	660s		
		620w		
$K_2[NCN]$ [a]	2 110s	660vw		
ZnNCN [b]	2 080vs	697m	1 175vw	408w
	2 047vs	676m	1 150vw	
Ag_2NCN [a]	1 995s	632s	1 275m	425s
PbNCN [a]	1 995vs	641s	1 306m	397s
	1 950vs	628s		
Tl_2NCN [a]	1 855vs	632m	1 300vw	

[a] Ref. 28. [b] G. M. Galochkina, N. A. Goryunova, G. B. Seifer, A. A. Vaipolin, and Yu. Ya. Kharitonov, *Izvest. Akad. Nauk S.S.S.R., Neorg. Materialy*, 1970, **6**, 486.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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occurs at higher wavenumber for the alkali-metal salts than for the covalent analogues (Table 4).

Definitive evidence for an asymmetrical NCN group is provided by the *X*-ray crystal structure of PbNCN. The Pb–N covalent bond introduces the additional ν_1(NCN) (sym stretch) and ν_4(Pb–N) (stretch) modes observed at 1 306 and 397 cm^{-1}, respectively. This structural feature appears common to Ag_2NCN which also has prominent bands in these regions (Table 4). In ZnNCN the weaker ν_1 and ν_4 may reflect the weaker metal–nitrogen interaction giving a bonding intermediate between that of the alkali-metal and lead or silver compounds. In Tl_2NCN, ν_1 is very weak, inferring that the NCN group is nearly symmetrical. This may be attributable not so much to ionic bonding, however, but rather to a covalent layered structure in which Tl tends to bond equally to both N atoms.[28] Bridging Tl may then reduce ν_4 to below the lower scanned limit of 263 cm^{-1}.

The formation of $Li_2[NCN]$ in liquid lithium from the lithium acetylide and nitride salts is of some importance in the possible use of the metal as a tritium breeder and perhaps as a coolant in controlled thermonuclear reactors. The reactive nature of the metal inevitably means that nitride and acetylide impurities will be difficult to avoid, and these can have a deleterious effect on structural metals. Dissolved nitride, for example, increases the solubility of titanium and nickel at 900 °C by a factor of ten and a hundred, respectively.[29] Although these corrosion and solubility features are recognised, they may be considerably influenced, however, should conditions arise which allow conversion of nitride into $Li_2[NCN]$, the corrosive effect of which on these and other metals is as yet unknown. Some of our preliminary experiments in this area indicate that under conditions of low C : N ratios the apparent solubility of both acetylide and nitride is increased due presumably to formation of even more complex anionic species than $[NCN]^{2-}$ in the liquid lithium. Conversely, an excess of acetylide can trap out dissolved nitride as the sparingly soluble $Li_2[NCN]$ whose properties may also influence the filtration, distillation, and gettering methods of purifying liquid lithium.

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