Synthesis of the Dilithium Salt of Cyanamide in Liquid Lithium; *X*-Ray Crystal Structure of Li_2NCN

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Summary Dilithium acetylide reacts with a solution of lithium nitride in liquid lithium at 530 °C to form the dilithium salt of cyanamide, Li_2NCN; subsequent evaporation of the liquid metal solvent leaves colourless single crystals of the salt which *X*-ray diffraction shows is composed of centrosymmetric NCN^{2-} ions and Li^+ ions surrounded by a distorted tetrahedron of nitrogen atoms.

Previously there have been no reports of the formation of stable, heteroatomic, anionic species in excess of liquid lithium; many simple binary salts of lithium dissolve to a restricted extent in the metal, but no interaction between them has been observed.[1] Those complex salts (*e.g.* Li_2CO_3, $LiNO_3$) which have been added to the liquid metal have invariably decomposed,[2] presumably owing to the high thermodynamic stability of the binary compounds produced.

We now report the synthesis of the crystalline dilithium salt of cyanamide by reaction of lithium nitride with dilithium acetylide in excess of liquid lithium (equation 1). This, therefore, may be the first example of a stable solution

$$4\,Li_3N + Li_2C_2 \xrightarrow[\text{Solvent}]{\text{Li}} 2\,Li_2NCN + 10\,Li \tag{1}$$

of a heteroatomic anion in liquid lithium. Compressed powdered dilithium acetylide was added to liquid lithium under argon in a steel vessel at 530 °C. Nitrogen was then admitted and the formation and solution of lithium nitride was monitored by changes in the electrical resistivity of the metal as it was pumped through a capillary section. The overall C:N ratio was 4:1. After 150 h the excess of lithium was removed by distillation, leaving colourless, single crystals of Li_2NCN adhering to the vessel walls and to undissolved dilithium acetylide. The form and distribution of the cyanamide were consistent with it having been in solution and subsequently crystallising during evaporation of the metal solvent.

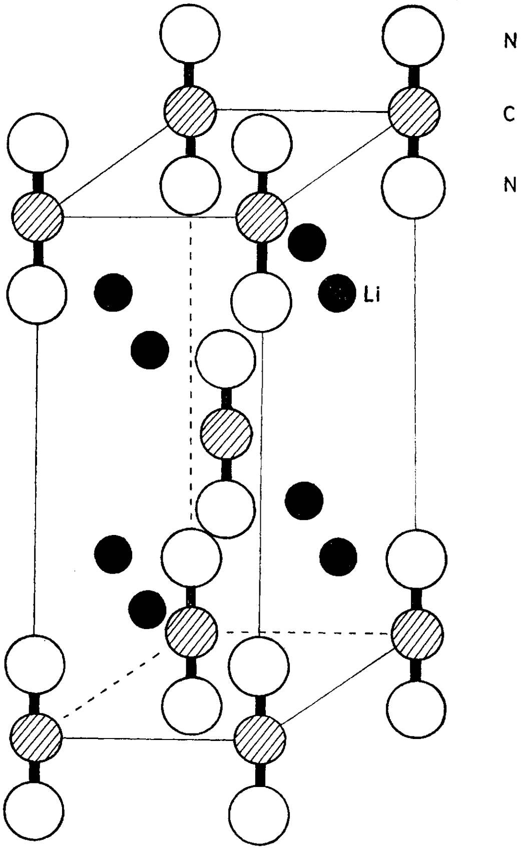

Figure. Crystal structure of Li_2NCN

This is the first time a crystalline sample of Li_2NCN has been prepared. Hitherto the compound was poorly characterised; it was believed to be present as a mixture in conjunction with lithium cyanide, from reactions between carbon and Li_3N,[3] lithium and HCN,[4] and lithium and $(CN)_2$.[4] The present use of a liquid alkali metal as reaction medium thus provides a novel synthetic route to an anhydrous salt, unobtainable by more conventional techniques.

The i.r. spectrum of the extremely hygroscopic salt was determined from 400 to 4000 cm^{-1} in KBr discs and Nujol mulls under a protective atmosphere of pure argon. The material exhibited two characteristic absorptions at 2165 cm^{-1} ($\nu_3\Sigma_u^+$) and 690 cm^{-1} ($\nu_2\pi_u$). The compound is most readily characterised by its *X*-ray powder diffraction pattern. Interplanar spacings with significant intensities are in the Table.

Table

d/Å	4·33	3·39	2·61	2·27	2·23	1·84	1·67	1·62	1·44	1·30	1·27	1·22	1·17
I/I_0	20	90	80	40	40	100	50	50	20	70	27	35	45

Unit cell parameters of a single crystal were determined initially from oscillation and Weissenberg photographs, and subsequently refined using a Hilger and Watts four-circle diffractometer and monochromatic Mo-K_α radiation (λ 0·7107 Å). A set of 119 statistically observed reflections was refined to R 0·036 where $I \geqslant 3\sigma(I)$. *Crystal data:* tetragonal, space group $I4/mmm$ with $a = b = 3{\cdot}687(3)$, $c = 8.668(5)$ Å, $D_m = 1{\cdot}51$ (by flotation), $D_c = 1{\cdot}46$ g cm^{-3} for $Z = 2$. The structure is shown in the Figure and is composed of Li^+ and NCN^{2-} ions. The centrosymmetric NCN^{2-} ions form an elongated body-centered cube with two Li^+ ions $(0,\frac{1}{2},\frac{1}{4})$ in each vertical face. Each NCN^{2-} ion is surrounded by eight Li^+ ions and each Li^+ ion is at the centre of a distorted tetrahedron of nitrogen atoms [r(Li–N) = 2·068(1) Å, ∠NLiN = 101·85(5) and 126·11(13)°]. The centrosymmetric NCN^{2-} ions [r(C–N) = 1·230(3) Å] and the symmetrical co-ordination of the cation are consistent with largely ionic bonding. These features are also found in CaNCN[5] [r(C–N) = 1·224 Å] and SrNCN[6] [r(C–N) = 1·28 Å] whereas asymmetric groups are found in the covalent cyanamides, PbNCN[7] [r(C–N) = 1·17 and 1·25 Å] and H_2NCN[8] [r(C–N) = 1·15 and 1·31 Å.

We thank Professor Trevor J. King for assistance in the structure determination, and the S.R.C. and U.K.A.E.A. (Harwell) for financial support (A.E.T. and M.G.D., respectively).

(*Received, 19th September* 1977; *Com.* 977.)

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