

Notes

New Synthesis Routes to Lithium and Cesium Cyanide Salts

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Introduction

In the course of our work on cyanocobaltate metal complex oxygen carriers,¹ we desired convenient synthetic routes to lithium and cesium cyanide that do not require the use of HCN and very reactive materials (organolithium compounds, Li, LiH, or Cs).² Lithium cyanide is available commercially as a tetrahydrofuran adduct but supplies that we received proved to be of insufficient purity for our purposes.³ Metathetical routes to convert NaCN and LiCl to solvated LiCN have been reported, though only a partial reaction to the LiCN product was realized at room temperature. However, when the metathesis of LiCl and NaCN was carried out in the melt at 560 °C, followed by grinding of the solid and extraction, it was possible to isolate LiCN·amide adducts (e.g., dimethylformamide (DMF), dimethylacetamide (DMAc) in up to a 74.5% yield.⁴ We report here significantly more convenient, laboratory-scale syntheses for two alkali-metal cyanide salts, LiCN and CsCN, via metathetical reactions with solutions of NaCN at ambient temperature. Furthermore, we have grown single crystals of a solvated LiCN and determined the structure of LiCN·0.6DMF·0.4DMAc (**1**).

Experimental Section

General Methods. The reagents NaCN, LiCl, and CsF were purchased from commercial sources and used without any purification. Anhydrous DMF, DMAc, methanol, and ethanol were purchased from Aldrich as Sure/Seal reagents and used as received. All chemical syntheses were performed under a nitrogen atmosphere to prevent any water incorporation. Thermogravimetric analysis experiments were carried out by using a Perkin-Elmer TGS2 instrument under a nitrogen atmosphere. Infrared spectra were recorded with a Nicolet 510 FTIR spectrometer, and mass spectroscopy experiments were carried out using a Finnigan 4500 single-quadrupole mass spectrometer. Samples were

Table 1. Comparison of LiCN Syntheses

	method 1	method 2	method 3 ^a	method 4 ^b
reactn time	4 days	1, 2, 3 or 4 days	1 day	1 h
temp, °C	23	23	170	23
amt of LiCl, g (mol)	2.32 (0.055)	2.10 (0.05)	2.10 (0.05)	2.10 (0.05)
amt of NaCN, g (mol)	2.45 (0.05)	2.45 (0.05)	2.45 (0.05)	2.45 (0.05)
amt of DMF, mL	100	100	100	110
amt of methanol, mL				50
[CN ⁻], M	0.483	0.2062–0.4931	0.4589	0.5141
[Na], M	0.0096			0.045
[Li], M	0.503			0.476
[Cl], M				0.018
% conversion (based on [CN ⁻])	94.9	41.2–98.6 ^c	91.8	91.5

^a This gave a clear orange LiCN solution which is seen in commercial LiCN solutions and believed to be due to the formation of a small amount of HCN oligomers. Even very dark reddish brown solutions appear to be quite pure by cyanide analysis. ^b After 1 h, the methanol was removed by vacuum distillation and the NaCl filtered off. ^c See Figure 1.

Table 2. Crystal Data

formula	C _{4.4} H _{7.8} LiN ₂ O	<i>T</i> , K	296
fw	111.65	<i>D</i> _{calc} , g cm ⁻³	1.123
space group	<i>Pnma</i>	data: param ratio	10:1
<i>a</i> , Å	13.807(5)	<i>λ</i> , Å	0.710 73
<i>b</i> , Å	13.262(4)	<i>μ</i> , cm ⁻¹	0.70
<i>c</i> , Å	7.211(2)	<i>R</i> _w ^a , %	9.3
<i>V</i> , Å ³	1320.4(7)	<i>R</i> _w ^b , %	7.4
<i>Z</i>	8		

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

prepared for metals analysis by digestion with nitric and sulfuric acids. The samples were analyzed for sodium and lithium by ICP-AES, or flame atomic absorption spectroscopy (F-AAS), and cesium was analyzed by flame atomic emission spectroscopy (F-AES). Samples were prepared for halogen analysis by fusion with KOH and then analyzed by a specific-ion electrode for each halide chosen. Cyanide in DMF containing LiCN was determined by potentiometric titration with aqueous 0.1 N AgNO₃. Sample aliquots were dissolved in distilled water just prior to titration and stabilized by adjusting the solution to pH > 12.

Synthesis of LiCN solutions. Four variations of the metathesis route were used to synthesize LiCN solutions. The NaCN was ground to a fine powder in all cases except when methanol was used. Table 1 gives the conditions used for these four methods. The synthesis (methods 1 and 2) leading to the highest yield was as follows: NaCN and LiCl was added to an Erlenmeyer flask with a magnetic stir bar along with 100 mL of DMF. The solution was allowed to stir for 4 days at room temperature. The solution was then filtered, separating NaCl from the clear LiCN solution.

Single-Crystal Studies of LiCN·0.6DMF·0.4DMAc (1). A summary of the crystallographic data and structure refinement is given in Table 2. Well-formed, white prisms of **1** were obtained by slow crystallization (3 days) from 30 mL of a 0.48 N LiCN solution in DMF to which 15 mL of DMAc was added at room temperature. These crystals were then filtered off, washed with diethyl ether, and dried. The FTIR spectrum confirmed the expected presence of both solvents by their two carbonyl stretching frequencies: CN⁻ stretch, 2109 cm⁻¹; carbonyl stretches 1650 cm⁻¹ (DMF), 1613 cm⁻¹ (DMAc). Solvent incorporation was also indicated by TGA analysis. A 70.3% weight loss was seen when the sample was heated to 250 °C under nitrogen, corresponding to a DMF:DMAc ratio of ~1.86:1. This proportion of

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- (2) (a) Johns, I. B. U.S. Patent 3,189,410, 1965. (Monsanto Research Corp.). (b) Rossmanith, K. *Monatsh. Chem.* **1965**, *96*, 1690. (c) Grant, L. R.; Taylor, M. D. U.S. Patent 3,049,406, 1962. (Callery Chemical Co.). (d) DeLong, M. C.; Rosenberger, F. *J. Cryst. Growth* **1986**, *75*, 164.
- (3) Solid LiCN·THF from a commercial vendor appeared brown and bubbled rapidly when dissolved in methanol or water due to significant contamination by unreacted LiH or lithium metal.
- (4) Hoffman, D. K.; Bach, R. O. U.S. Patent 3,846,494, 1974. (Gulf Resources & Chemical Corp.).

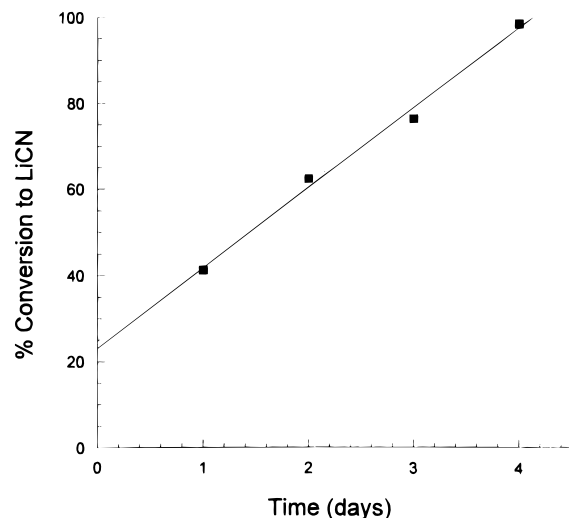


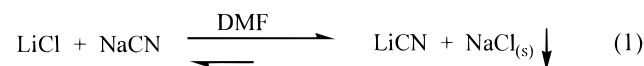
Figure 1. Conversion of NaCN to LiCN in DMF based on cyanide analysis.

solvents was confirmed by mass spectroscopy. Attempts to produce single crystals from either pure DMF or pure DMAc solutions were unsuccessful.

Synthesis of CsCN (2). Sodium cyanide (0.3082 g, 0.00629 mol) was ground to give a fine powder. This was added to 15 mL of ethanolic CsF (0.955 g, 0.00629 mol). This solution was allowed to stir for 3 days at room temperature and then filtered, to separate NaF from the clear CsCN solution. To this was added 25 mL of diethyl ether to precipitate **2**. This sample was then washed with additional ether and dried under vacuum. Sample weight was 0.372 g or 37.2% of the theoretical yield. Anal. Found: Cs, $80.2 \pm 1.6\%$; Na, $< 0.2\%$; F, $< 0.3\%$. Theory: Cs, 83.6%. FTIR spectrum: CN^- stretch at 2065 cm^{-1} .

Results and Discussion

New Synthesis Route to LiCN Solutions. A new simple metathetical route to high-purity LiCN solutions, based on eq 1, has been developed. Prior attempts to effect this synthesis



at room temperature resulted in only a limited conversion to product.⁴ We have shown that eq 1 is not equilibrium limited since the conversion of NaCN to LiCN does not increase upon adding excess LiCl. Finely ground NaCN reacted with LiCl (which is very soluble in DMF), giving LiCN solutions in 95% conversions over 4 days of reaction at room temperature. Surprisingly, the conversion rate appears to remain constant during the course of the reaction (see Figure 1). We ascribe these apparent zero-order kinetics to the dissolution of NaCN as being the rate-limiting step. Consistent with this notion, we observed a substantial increase of reaction rate on heating: at 170°C , a 91.8% conversion was seen in 24 h (method 3). By starting with solutions of NaCN in methanol (a good solvent for NaCN) and LiCl in DMF, respectively, we achieved the same conversion in 1 h at 23°C ; however, this is not a good synthetic route because of substantial Na contamination.

Crystal Structure of $\text{LiCN} \cdot 0.6\text{DMF} \cdot 0.4\text{DMAc}$ (1). Figure 2 shows the Li coordination environment. The structure can be described as infinite sheets of Li pairs, linked end-on by cyanide ligands. The Li pairs are joined above and below each sheet by a DMF or DMAc oxygen atom. The crystal structure was solved by using direct methods (Siemens SHELXTL Plus)

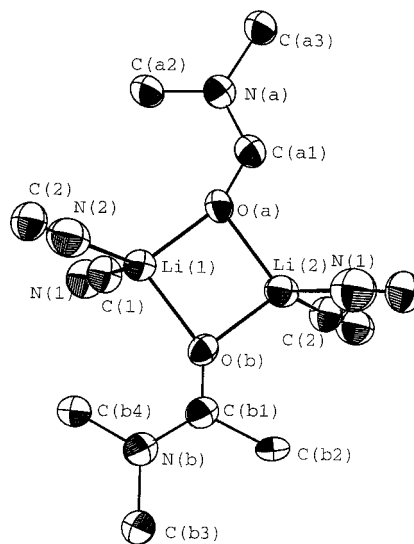


Figure 2. ORTEP drawing of LiCN solvates showing the Li coordination for $\text{LiCN} \cdot 0.6\text{DMF} \cdot 0.4\text{DMAc}$. Thermal ellipsoid boundaries are drawn at the 50% probability level. Of the four superimposed solvent molecules, the highest occupancy DMF and DMAc molecules are shown.

Table 3. Selected Interatomic Distances (Å) and Angles (deg)

Li(1)–Li(2)	2.832(16)	Li(2)–Li(1)–C(1)	114.1(6)
Li(1)–C(1)	2.039(14)	Li(2)–Li(1)–N(2)	128.6(6)
Li(1)–N(2)	2.078(14)	Li(2)–Li(1)–O(a)	46.9(4)
Li(1)–O(a)	1.941(12)	C(1)–Li(1)–N(2)	117.3(6)
Li(2)–N(1)	2.072(13)	C(1)–Li(1)–O(a)	112.2(9)
Li(2)–C(2)	2.018(13)	N(2)–Li(1)–O(a)	110.0(8)
Li(2)–O(a)	2.067(12)		
N(1)–C(1)	1.163(8)		
N(2)–C(2)	1.163(8)		
Li(1)–Li(2)–N(1)	129.9(6)	Li(1)–Li(2)–N(1)	129.9(6)
Li(1)–Li(2)–C(2)	118.4(6)	Li(1)–Li(2)–C(2)	118.4(6)
Li(1)–Li(2)–O(a)	43.27(34)	Li(1)–Li(2)–O(a)	43.27(34)
N(1)–Li(2)–C(2)	111.6(6)	N(1)–Li(2)–C(2)	111.6(6)
N(1)–Li(2)–O(a)	112.9(8)	N(1)–Li(2)–O(a)	112.9(8)
C(2)–Li(2)–O(a)	115.8(8)	C(2)–Li(2)–O(a)	115.8(8)
Li(2)–N(1)–C(1)	170.4(8)	Li(1)–O(a)–C(a1)	156.1(6)
Li(1)–C(1)–N(1)	179.22(1)	Li(2)–O(a)–C(a1)	114.0(5)
Li(1)–N(2)–C(2)	175.6(7)		
Li(2)–C(2)–N(2)	174.2(8)		

and was refined using the GSAS package.⁵ Difference Fourier maps showed the presence of two superimposed solvent molecules sharing approximately the same O and N positions but rotated 180° from each other. The presence of both DMF and DMAc in each orientation was indicated by the presence of a peak corresponding to the acetamide methyl group carbon and was confirmed by subsequent refinement of occupancies. Due to the complexity of the disorder, the internal geometry of the two DMF and two DMAc molecules was constrained to that obtained from force-field minimization of an isolated molecule.⁶ Initially, the total occupancy for the four molecules was constrained to total to 1, but in later refinements these constraints were removed. The total occupancy refined to 0.976 with a DMF:DMAc ratio of 1.5:1, in fair agreement with mass spectrometric measurements. The majority of the solvent molecules (82%) are located in single orientation. A single set of group anisotropic temperature factors (TL matrices) were used for these two majority-orientation solvent molecules, and a single isotropic temperature factor was used for the other two

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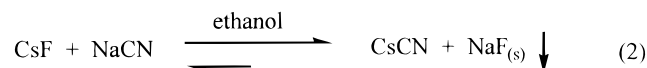
Table 4. Selected Atomic Positions (Fractional Coordinates, $\times 10^4$) and Equivalent Isotropic Temperature Factors (\AA^2 , $\times 10^2$)^a

atom	x	y	z	U_{equiv}
Li(1)	1887(9)	2500	5374(15)	4.29
Li(2)	647(8)	2500	8503(16)	4.40
N(1)	4148(5)	2500	6360(10)	7.24
C(1)	3326(5)	2500	6016(11)	5.07
N(2)	1518(5)	2500	2580(10)	6.59
C(2)	1250(5)	2500	1052(10)	4.72
O(a)	1185(15)	3557(5)	6665(27)	4.35
N(a)	1267(6)	5232(4)	6075(10)	4.41
C(a1)	886(9)	4420(5)	6939(15)	4.06
C(a2)	2075(9)	5106(7)	4738(18)	5.96
C(a3)	863(9)	6239(5)	6488(20)	5.74

^a Note that the occupancy for the DMF atoms [O(a)–C(a3)] is 0.519(9).

solvent molecules. The agreement factors obtained from refinement of this model were $R_w = 7.4\%$ and $R = 9.3\%$ with a data to parameter ratio of 10:1. Disordered structures may be a symptom of an incorrect space-group setting; however, if this were the case, it would be expected that the ratios of the superimposed molecules be near 50% rather than 80%. Selected interatomic distances and angles are given in Table 3; selected atomic positions, in Table 4. Complete atomic positions and temperature factors, anisotropic thermal parameters, rigid-body descriptions, and further X-ray diffraction conditions are given in the Supporting Information.

New Synthesis Route to CsCN (2). A new simple meta-theoretical route to solid CsCN, based on eq 2, was developed.



Here CsF is reacted with NaCN in a solvent in which both reactants have some solubility and the product **2** is also soluble. The driving force is the precipitation of NaF. Since CsF is very soluble in ethanol the product can be precipitated by adding diethyl ether while CsF remains in solution. This method afforded relatively pure samples of **2** in a 37% yield. No attempts were made to increase this yield due to the likelihood of contaminating the product with unreacted CsF or NaCN.

The differences in the cyanide stretching frequencies for **1** and **2** are of interest. One sharp absorption is seen at 2065 cm^{-1} for **2**, which is characteristic of ionic cyanide. In contrast, one sharp cyanide stretch was seen at 2108 cm^{-1} for **1**, which is consistent with a more covalent interaction of the Li^+ with cyanide as compared to interaction of Cs^+ .⁷

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Supporting Information Available: Tables S1–S3, giving atomic positions and temperature factors, rigid-body descriptions, and a summary of the data collection and structure solution and refinement procedures (6 pages). Ordering information is given on any current masthead page.

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