Synthesis and Structure of the One-Dimensional Polymer Li($NHCH_2CH_2NH_2$)

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Introduction

Organolithium compounds are of great importance in synthetic organic chemistry, especially recently in asymmetric syntheses due to their anionic character.[1] Specifically, aggregation of amidolithium complexes is an area of recent extensive research.[2] Difficulties in understanding the association of such species are due to the limited crystallographic information concerning polymeric amides; most lithiated amines form oligomers. The structures of lithiated oligomeric and polymeric ethylenediamine were recently determined to favor laddered structures over stacked dimers on the basis of extensive *ab initio* molecular orbital calculations.[3] Experimental procedures have isolated several oligomeric compounds having laddered (two to four Li−N rungs) structures.[4] However, there are no examples of polymeric lithium-containing amides with laddered structures. The only structurally characterized polymeric lithiated amine, Li(μ-N-*i*-Pr_2), is composed of infinite helical linear Li−N chains.[5] However, an extended ladder structure exists in a Na complex, 2,3,4,5-tetramethyl-1-sodiopyrrole, in which there is significant bonding with the π-system of the pyrrole to the Na atom.[6]

The title compound, Li($NHCH_2CH_2NH_2$), is the first example of an infinite ladder structure containing lithium and protic amide moieties.

Experimental Section

Single crystals of the new one-dimensional polymeric lithiated ethylenediamine compound Li($NHCH_2CH_2NH_2$) have been synthesized by the reaction of Li_3N, $LiNH_2$, or *n*-BuLi with ethylenediamine. Lithium nitride as a starting material provides a kinetically slow and thus favorable pathway leading toward the formation of large well-formed crystals.

Lithium nitride, Li_3N, was prepared by the reaction of nitrogen over lithium metal (Aldrich, ingot, 99.9%) in a molybdenum boat by slowly heating the reactants to 750 °C over 20 h followed by soaking at that temperature for an additional 20 h. In order to reduce a potential oxygen contamination, the N_2 was purified by passing the gas over heated titanium windings. The lithium was continuously exposed to a N_2 overpressure of approximately 1.1 atm. The elimination of gas flow minimizes the potential contamination of the Li_3N from trace impurities in the purified N_2. The Li_3N obtained has a black color with a metallic luster and retains the shape of the lithium metal pieces. However, after grinding, the Li_3N powder exhibits a deep maroon color. An orange phase forms on the molybdenum boat during the synthesis; however, the Li_3N is easily separated from the mixture. The ethylenediamine (Aldrich 99+%) was purified before use first by subsequent distillations from CaH_2 and a dark red solution of K_4Sn_9.[7] The following reagents were used as received: $LiNH_2$ (Aldrich 99%) and *n*-BuLi (Aldrich 2.0 M solution in cyclohexane).

The synthesis of single crystals of Li($NHCH_2CH_2NH_2$) was accomplished by the addition of 0.25 g of a coarse powder of Li_3N to approximately 15 mL of ethylenediamine in a 20 mL glass vial in a helium-filled Vacuum Atmospheres glovebox (<1 ppm of O_2 and <0.01 ppm of H_2O). The Li_3N was not soluble at room temperature. After standing for 3 d, all of the Li_3N solid was consumed, and the solution remained colorless along with clusters of colorless, transparent single crystals of Li($NHCH_2CH_2NH_2$). Crystal growth continued for longer than a month to produce crystals longer than 1 cm on the bottom and sides of the vial. The yield is essentially quantitative (98%), and the product is single phase as observed by powder X-ray diffraction (Scintag XDS2000, Cu Kα radiation) (Figure 1). Elemental analysis was performed by Galbraith Laboratories. Anal. Calcd for $C_2H_7LiN_2$: C, 36.379; H, 10.686; Li, 10.511; N, 42.424. Found: C, 34.90; H, 10.52; Li, 10.80; N, 40.61.

Crystallography

A colorless needle-like crystal of Li($NHCH_2CH_2NH_2$) having the approximate dimensions of 0.40 × 0.25 × 0.15 mm was sealed in a glass capillary. X-ray diffraction data were collected on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation generated from a rotating anode at 50 kV and 250 mA. Crystallographic data are summarized in Tables 1 and 2.

Cell constants that were obtained from 20 centered reflections in the range $14 < 2\theta < 22°$ indicate a monoclinic unit cell.

The Laue check for monoclinic symmetry ($hkl \rightarrow -h,+k,-l$; 2-fold axis parallel to *b*) was passed by comparing the symmetry-equivalent reflections of 17 general reflections of the 20 centered reflections. The R_{merge} after absorption correction (ψ scan) was 2.0%.

The systematic absences ($h0l$, $h + l \neq 2n$; $0k0$, $k \neq 2n$) correspond to a 2_1 screw axis parallel to the *b* axis and an *n*-glide perpendicular to the *b* axis. The centrosymmetric space group was uniquely determined by these conditions to be $P2_1/n$ (No. 14).

The data were collected at room temperature (291(3) K) using the $\omega-2\theta$ scan technique in the 2θ range 5.3−60.1°. Of the 5230 reflections collected, 5033 were unique with $R_{\text{int}} = 5.6\%$. The intensities of the standard reflections were collected every 150 reflections, and there was no observable decay. The linear absorption coefficient, μ, for Mo Kα radiation is 0.7 cm^{-1}. No absorption correction was applied. However, if the empirical absorption correction, DIFABS, was applied, then an unreasonable transmission curve (0.665−1.000 transmission factors) would be applied to the data, resulting in artificially low residual *R* factors ($R = 4.87\%$, $R_w = 3.94\%$ after five least-squares cycles). The data were corrected for Lorentz−polarization effects.

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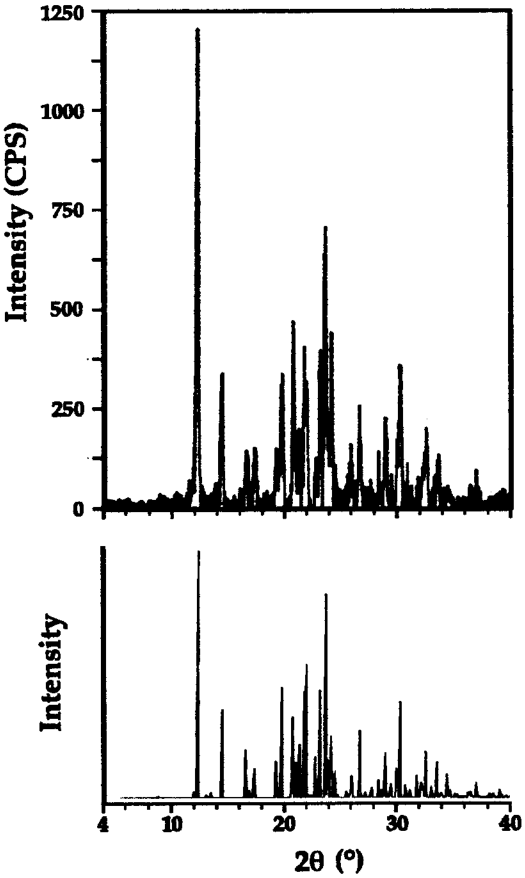

Figure 1. Observed (top and calculated bottom) powder X-ray diffraction patterns of Li($NHCH_2CH_2NH_2$). The observed pattern is in excellent agreement with the calculated pattern based on single-crystal data and indicates single-phase product.

Table 1. Crystallographic Information for Li($NHCH_2CH_2NH_2$)

empirical formula	$C_2H_7LiN_2$
fw	66.03
temperature	18(3) °C
wavelength	Mo Kα (0.71069 Å)
space group	$P2_1/n$ (No. 14)
unit cell parameters	$a = 12.942(3)$ Å, $b = 9.2637(9)$ Å, $c = 13.877(3)$ Å $\beta = 103.25°$
volume	1619.3(4) Å^3
Z	16
density (calcd)	1.08 g/cm^3
abs coeff (μ)	0.7 cm^{-1}
transm coeffs	0.990−0.966
final R indices^a [$I > 3\sigma(I)$]	$R(F) = 5.6\%$, $R_w(F) = 4.7\%$

^{a} $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w(F) = \Sigma[w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2}$ where $w = 1/\sigma^2$.

The structure was solved by direct methods (SAPI90)[8] followed by least-squares refinement in the teXsan software package.[9] All non-hydrogen atoms were refined anisotropically except those which were split due to disorder. All hydrogen atoms were located in Fourier difference maps; however, due to the disorder of the one ethylenediamine, only the hydrogen positions for the C(1) and N(1) with 0.75 occupancy were located. The hydrogen atom positions and isotropic thermal parameters were refined. The final cycle of the full-matrix least-squares refinement was based on 1370 observed reflections ($I > 3\sigma(I)$) and 289 variables leading to a data to parameter ratio of 4.74:1.

Table 2. Fractional Atomic Coordinates for Li($NHCH_2CH_2NH_2$)

	x	y	z	$B_{eq}{}^a$
Li(1)	0.5813(3)	0.0244(5)	0.0673(3)	2.97(8)
Li(2)	0.4870(3)	0.1047(5)	0.1865(3)	3.53(8)
Li(3)	0.5257(3)	−0.1028(5)	0.3069(3)	3.46(7)
Li(4)	0.4273(3)	−0.0207(5)	0.4266(3)	3.56(8)
N(1a)	0.6301(10)	0.185(1)	−0.0295(10)	4.3(3)
N(1)	0.6471(4)	0.2103(5)	0.0132(4)	4.24(9)
N(2)	0.4403(2)	0.1406(3)	0.0373(2)	3.20(5)
N(3)	0.5774(2)	0.2698(3)	0.2732(2)	5.87(8)
N(4)	0.6241(2)	−0.0159(2)	0.2196(2)	3.16(5)
N(5)	0.3902(2)	0.0243(3)	0.2733(2)	3.55(6)
N(6)	0.2798(2)	−0.1384(4)	0.3976(2)	4.93(8)
N(7)	0.5684(2)	−0.1251(3)	0.4616(2)	3.34(5)
N(8)	0.5086(2)	−0.3333(3)	0.3035(2)	4.86(7)
C(1)	0.5512(3)	0.2815(5)	−0.0467(3)	4.27(8)
C(1a)	0.580(1)	0.317(1)	0.0058(10)	4.27(8)
C(2)	0.4607(2)	0.2839(3)	0.0015(3)	4.51(8)
C(3)	0.6640(3)	0.1897(4)	0.3350(3)	5.57(9)
C(4)	0.7077(2)	0.0709(4)	0.2809(2)	4.64(8)
C(5)	0.2877(2)	−0.0439(4)	0.2358(2)	4.52(8)
C(6)	0.2208(3)	−0.0603(4)	0.3116(3)	4.93(8)
C(7)	0.5574(3)	−0.2782(3)	0.4801(2)	4.05(7)
C(8)	0.5751(3)	−0.3785(3)	0.3981(2)	4.60(8)

^{a} $B_{eq} = {}^8/_3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha)$.

The maximum shift/error was 0.10 with a goodness-of-fit of 2.88. The residuals after the final cycle were $R(F) = 5.6\%$ and $R_w(F) = 4.7\%$ with maximum and minimum peaks in the difference Fourier map of 0.23 and −0.18 e/Å^3, respectively.

The disordered carbon atom, C(1), was split by 0.81(2) Å with 0.75 and 0.25 occupancies. The disordered nitrogen atom, N(1), was split by 0.63(2) Å with 0.75 and 0.25 occupancies. Although two $NHCH_2CH_2NH_2$ groups are related by an inversion center, the cell does not appear to be doubled or tripled along the c axis.[10]

Structure Description

The structure of Li($NHCH_2CH_2NH_2$) consists of infinite one-dimensional ladders of double edge-sharing LiN_4 tetrahedra (such that a common vertex is shared) formed from μ_1-NH_2 and μ_3-NH bonding interactions (Figure 2). The ladders run parallel to the crystallographic c axis and are effectively isolated from one another, since the ethylenediamide molecules in a given chain are bent into the chain. No hydrogen-bonding interactions are present between adjacent ladders.

The bonding between the Li and the monoprotonated amide (μ_3-NH) of the ethylenediamine forms the frame of a ladder with a sinusoidal ribbon-like pattern as viewed from the side of the ladder. Repeated long−short bond distances along the ladder frame have been observed for oligomeric species;[2] however, the frame bond distances for Li($NHCH_2CH_2NH_2$) are in the range 2.047(8)−2.113(8) Å without any observed long−short order.

As seen in Figure 3, two bonding environments of the ligand are apparent. The Li_2N_2 rings are rotated such that the NH and NH_2 groups of the same ethylenediamide ligand are bonded to the Li atoms in the form of either the rungs or the frame of the ladder in an alternating fashion.

As an example of the bonding, the Li(2) atom is coordinated to a single ethylenediamine molecule [N(3)−C(3)−C(4)−N(4)] in which the μ_1-N(3)H_2 end is bonded directly to Li(2) at a distance of 2.123(9)Å. The μ_3-N(4)H atom of this ethylenediamine molecule is bonded to Li(2) at a distance of 2.058(8) Å and, in addition, is shared by lithium atoms Li(1) and Li(3)

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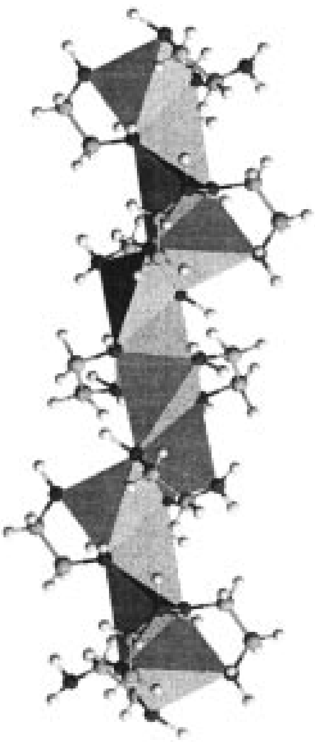

Figure 2. Distorted edge-sharing Li tetrahedra of a single chain of Li($NHCH_2CH_2NH_2$). Each tetrahedron is formed with N atoms on the vertices: one μ_1-NH_2 and three μ_3-NH groups. Disorder of C1 and N1 is omitted for clarity.

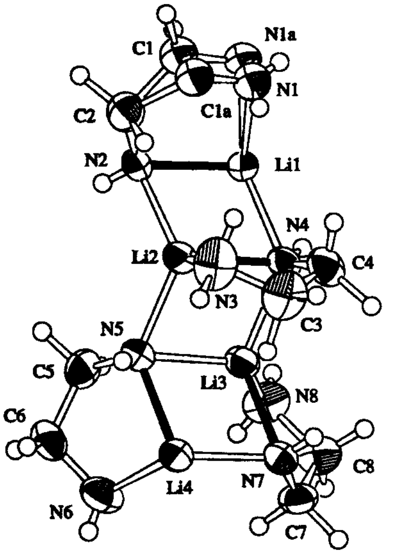

Figure 3. ORTEP plot of the asymmetric unit depicting the disorder of C1 and N1. Thermal ellipsoids are drawn at the 50% probability level. The Li_2N_2 rings are rotated such that the NH and NH_2 groups of the same ethylenediamide ligand are bonded to the Li atoms in the form of either the rungs or the frame of the ladder in an alternating fashion (highlighted with filled bonds). Selected bond distances in ladder to μ_3-NH groups (Å): Li1−N4 2.091(8), Li1−N2 2.076(8), Li2−N2 2.047(8), Li2−N4 2.058(8), Li2−N5 2.065(8), Li3−N4 2.108(8), Li3−N5 2.075(8), Li3−N7 2.099(8), Li4−N5 2.113(8), Li4−N7 2.025(8). Selected bond distances in ladder to μ_1-NH_2 groups (Å): Li1−N1 2.13(1), Li1−N1a 2.19(2), Li2−N3 2.123(9), Li3−N8 2.146(9), Li4−N6 2.156(9). Selected bond angles (deg): N1−Li1−N2 85.1(4), N3−Li2−N4 86.0(3), N5−Li4−N6 85.7(3), N7−Li3−N8 85.8(4).

at distances of 2.091(8) and 2.108(8) Å, respectively. The Li(2) atom sits in a very distorted tetrahedral environment since the ethylenediamine cannot accommodate a 109.5° bond angle. Observed bond angles are within the range 105.0(3)−124.8(4)° with the exception of the ethylenediamine bridge, N(3)−Li(2)−N(4), which has a strained bond angle of 86.0(3)°.

The bonding in Li($NHCH_2CH_2NH_2$) is primarily ionic in character with Li−N bonds being formed through interaction with the monoprotonated NH group and covalent bonds through adduct formation with the lone pair of electrons on the NH_2 group. This is unlike the network structures of (fluorenyl•Li)-2en[11] and lithium halide/ethylenediamine compounds[12] that display adduct formation throughout their structures.

Upon inspection, the monoprotonated N atom in Li($NHCH_2CH_2NH_2$) is in 5-coordination (3 Li, 1 H, 1 C). This hypercoordination, although unusual, is observed in several amides. As in $LiNH_2$, which has a 3-D network structure formed by sharing all edges of the LiN_4 tetrahedra,[13] a Li−N four-rung ladder with 5-coordination (3 Li, 2 H) can be observed which is similar to the fundamental building blocks in Li($NHCH_2CH_2NH_2$). In contrast, the diprotonated N atom of the ethylenediamine ligand that forms the adduct with the Li lies in tetrahedral 4-coordination.

Results and Discussion

As described in the experimental procedure, Li_3N is converted to Li($NHCH_2CH_2NH_2$) by a simple acid−base, proton-transfer reaction according to the following chemical equation:

$$Li_3N + 3NH_2CH_2CH_2NH_2 \rightarrow 3Li(NHCH_2CH_2NH_2) + NH_3$$

Although Li($NHCH_2CH_2NH_2$) can also be made from $LiNH_2$ or *n*-BuLi in excess ethylenediamine, only powders and small crystals in low yield are formed from $LiNH_2$ and *n*-BuLi, respectively. Since the lithium reagents are limiting (i.e., ethylenediamine is in excess), it is not unexpected that only one proton per ethylenediamine is transferred. Experiments at room temperature with ethylenediamine and an excess of Li_3N in tetramethylethylenediamine (TMEDA) or carbon tetrachloride, acting as an inert solvent, produced small single crystals of Li($NHCH_2CH_2NH_2$) and unreacted Li_3N, not a polylithiated ethylenediamine. Solvothermal reactions at 200 °C were attempted in order to drive the kinetics to further lithiation; however, this did not yield a polylithiated product. Due to the high basicity of Li_3N, it may lithiate species that would otherwise be unreactive toward conventional lithiating reagents. Our studies have indicated that Li_3N is the only binary alkali-metal or alkaline-earth-metal nitride that reacts with ethylenediamine to produce single crystals. Although a number of lithium compounds coordinated with TMEDA have been prepared, Li_3N is not soluble nor does it react with TMEDA even up to temperatures of 180 °C. This is not surprising, however, considering the fact that the TMEDA does not have acidic protons.

Work is underway to synthesize polylithiated ethylenediamine compounds and to determine the generality of Li_3N as a lithiating reagent. We expect that many protic lithium alkylamides can be formed from substituted ethylenediamines.

In conclusion, the novel one-dimensional organolithium polymer Li($NHCH_2CH_2NH_2$) has been synthesized stoichiometrically by an acid−base reaction of Li_3N, $LiNH_2$, or *n*-BuLi with ethylenediamine at room temperature. The laddering

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principle, as observed in many oligomeric lithium alkylamides, is demonstrated for the infinite polymer Li($NHCH_2CH_2NH_2$).

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, anisotropic thermal parameters, and bond lengths and angles and additional structural diagrams (22 pages). Ordering information is given on any current masthead page.

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