Nonsolvated Li–Amide Clusters. Preparation and Crystal Structure of the Adduct {(*meso*-octaethylcalix-[4]-pyrrole)$\mathrm{Li_4}$}(*t*-BuLi)$_2$ and of the Tetrameric [(cyclohexyl)$_2$NLi]$_4$

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Introduction

There is a continuous growth of interest in the preparation and characterization of lithium complexes,[1] mainly because of their fundamental importance as synthetic reagents.[2] Therefore, the elucidation of the molecular structures of these species both in the solid state and in solution is of paramount importance, since they have come to play a pivotal role in chemical syntheses and transformations.[3] Remarkable and unpredictable molecular complexity is the distinctive feature of lithium chemistry.[4] The lithium compounds reported so far exist as both *solvated complexes*[5] and *nonsolvated complexes*. In this latter class of compounds, the lithium cation has no coordinated solvent and may have σ- or even π-interactions with either the donor atom or the π-system of the organic moiety.[1c,d,6] The common thread between all of these complexes is that they may exist as aggregates and their nuclearity is determined by several factors: the ligand's steric hindrance and denticity, the coordinating ability of the solvent or available Lewis base, the ratio of Li to Lewis base, etc. However, there are some puzzling cases such as lithium bis(isopropylamide) (LDA), which upon treatment with TMEDA (=*N,N,N',N'*-tetramethylethylenediamine) may be isolated both as an unsolvated helical polymer[7] and as a solvated dimer with bridging amides.[8]

Recently, we have been using a tetralithium salt of the macrocycle *meso*-octaethylcalix-[4]-pyrrole (OEC-4-$\mathrm{PLi_4}$)[9] and the lithium salt of bis(cyclohexylamine) $[\mathrm{Cy_2NLi}]_n$ as starting materials for studying low- and medium-valent early transition metals and lanthanides.[10] Since the amount of THF or other Lewis bases available to these systems plays an important role in determining the reaction pathways, the non-THF-containing salts of both OEC-4-$\mathrm{PH_4}$ and $\mathrm{Cy_2NH}$ were synthesized in hexane.[10a,b] In this paper, we describe the isolation and crystal structures of a solvent-free tetralithium salt of *meso*-octaethylcalix-[4]-pyrrole as a *t*-BuLi adduct and of the tetrameric $(\mathrm{Cy_2NLi})_4$.

Experimental Section

All operations were performed under inert atmosphere in a nitrogen-filled drybox (Vacuum Atmospheres) or by using standard Schlenk techniques. *meso*-Octaethylcalix-[4]-pyrrole was prepared according a literature procedure.[9] $\mathrm{Cy_2NH}$ (Aldrich) was dried over molten K and distilled prior to use. NMR spectra were recorded on a Varian Gemini 200 and on a Bruker AMX-500 spectrometer by using vacuum-sealed samples prepared in a drybox. Solvents for NMR spectroscopy were dried over the appropriate drying agents, vacuum-transferred into appropriate ampules, and stored inside a drybox. Infrared spectra were recorded on a Mattson 9000 FTIR instrument from Nujol mulls prepared in a drybox. Elemental analyses were carried out with a Perkin-Elmer PE 2400 CHN analyzer.

Synthesis of {[OEC-4-P]$\mathbf{Li_4}$}(*t*-BuLi)$_2$ (1). *tert*-Butyllithium (8.8 mL, 1.7 M solution, 14.96 mmol) was added via syringe to a stirred suspension of OEC-4-$\mathrm{PH_4}$ (2.03 g, 3.75 mmol) in freshly distilled anhydrous hexane (110 mL). When addition was complete, stirring was discontinued and the solution was allowed to stand at room temperature overnight. White rhomboidal crystals of **1** formed (1.12 g, 45%) that were suitable for X-ray diffraction analysis. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 6.17 (s, 8H, pyrrole β-H), 1.98 (q, 16H, $\mathrm{CH_3C}H_2$), 0.85 (m, overlap of 24H $\mathrm{C}H_3\mathrm{CH_2}$ and 18H of 2 *t*-Bu). IR (Nujol, cm^{-1}): ν 1649 m, 1316 s, 1275 m, 1197 m, 1155 m, 1047 s, 989 m, 987 m, 973 m, 925 m, 886 m, 844 s, 779 s, 748 s, 697 m, 669 m, 565 w, 530 w, 517 s, 454 s. Anal. Calcd (found) for $\mathrm{C_{22}H_{33}N_2Li_3}$: C, 76.29 (76.12); H, 9.60 (9.51); N, 8.09 (8.00).

Synthesis of $(\mathbf{Cy_2NLi})_4$ (2). A solution of *n*-BuLi in hexane (1.92 M, 52 mL, 100 mmol) was added dropwise to a cold solution (−30 °C) of cyclohexylamine (20 mL, 100 mmol) in the same solvent. A white solid separated almost immediately, and stirring was continued overnight at room temperature. The suspension was then refluxed for 2 h without stirring. Colorless crystalline **2** was obtained in 94% yield (17.6 g). ^{7}Li NMR ($\mathrm{C_6D_6}$, 24.7 °C, 194.3 MHz): δ 0.32 (s, $\nu_{1/2} = 71$ Hz). ^{1}H NMR ($\mathrm{C_6D_6}$, 24.7 °C, 500 MHz): δ 2.78 (tt, 1H), 2.59 (tt, 1H), 2.16–0.95 (m, 20H). ^{13}C NMR ($\mathrm{C_6D_6}$, 24.7 °C, 125.73 MHz):

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Table 1. Crystal Data and Structural Analysis Results

complex	**1**	**2**
formula	$C_{22}H_{33}N_2Li_3$	$C_{48}H_{88}Li_4N_4$
formula weight	346.34	749.01
crystal system	triclinic	monoclinic
space group (No.)	$P\bar{1}$ (2)	$C2$ (5)
a (Å)	11.275(2)	20.941(2)
b (Å)	11.367(2)	15.726(1)
c (Å))	10.479(2)	15.801(1)
α (deg	114.84(2)	
β (deg)	94.41(2)	111.03(1)
γ (deg)	116.55(2)	
V (Å^3)	1031(1)	4857(2)
Z	2	4
λ (Mo Kα) (Å)	0.710 69	0.710 69
T (°C)	−154	−151
$\varrho_{ca}3l_{cd}$ (g cm^{-3})	1.116	1.024
ϱ_{obsd} (g cm^{-3})	1.100	1.091
μ_{calcd} (cm^{-1})	0.58	0.53
R, R_w^{a}	0.042, 0.059	0.038, 0.045
GoF	2.85	1.72

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

δ 60.46, 58.83, 40.83, 40.00, 27.34, 27.09, 26.90, 26.72. Anal. Calcd (found) for $C_{48}H_{88}Li_4N_4$: C, 76.97 (76.90); H, 11.84 (11.81); N, 7.48 (7.39).

Synthesis of $Cy_2NLi(THF)$. Addition of 1 equiv of THF to a suspension of **2** (3.0 g, 16 mmol) in hexane (100 mL) yielded a mixture which was boiled and then filtered while hot. The hot filtrate yielded colorless crystals of $Cy_2NLi(THF)$ (3.6 g, 14 mmol, 87%) upon standing overnight at room temperature. ^{7}Li NMR (C_6D_6, 24.7 °C, 194.3 MHz): δ 0.25 (s, $\nu_{1/2}$ = 35 Hz). ^{1}H NMR (C_6D_6, 24.7 °C, 500 MHz): δ 3.58 (m, 4H), 2.82 (pseudo-t, 1H), 2.62 (tt, 1H), 1.38 (m, 4H), 2.1−0.9 (m, 20H). ^{13}C NMR (C_6D_6, 24.7 °C, 125.73 MHz): δ 67.96, 60.52, 40.75, 40.12, 27.14, 27.12, 25.67, 25.45. Anal. Calcd (found) for $C_{16}H_{30}LiNO$: C, 74.10 (74.01); H, 11.66 (11.59); N, 5.40 (5.32).

X-ray Structures. Data were collected at temperatures in the range −151 to −154 °C using the $\omega-2\theta$ scan technique in the range $3.5 < 2\theta < 50.0°$, for suitable air-sensitive crystals. The crystals were mounted on glass fibers inside a drybox and maintained under nitrogen with the aid of a specially designed glass sleeve. After the fiber was mounted on the goniometric head, the sleeve was removed, leaving the crystal under the cold nitrogen stream. Cell constants and orientation matrices were obtained from the least-squares refinement of 25 carefully centered high-angle reflections. Redundant reflections were removed from the data set. The intensities of three representative reflections were measured after every 150 reflections to monitor crystal and instrument stability. Data were corrected for Lorentz and polarization effects, but no absorption corrections were necessary. The structures were solved by either Patterson or direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were located in the difference Fourier maps but not refined. The final cycle of full-matrix least-squares refinement was based on the number of observed reflections with $I > 2.5\sigma(I)$. Neutral atom scattering factors and anomalous scattering corrections were taken from Cromer and Waber.[11] Anomalous dispersion effects were included in F_c. All calculations were performed on a Digital VAX station using the TEXSAN package. Details on data collection and structure refinement are reported in Table 1, the final atomic coordinates are given in Tables 2 and 3, and selected bond distances and angles are given in Table 4.

Results and Discussion

Addition of 4 equiv of *t*-BuLi to a hexane suspension of OEC-4-PH_4 resulted in the dissolution of the neutral ligand with subsequent reprecipitation as white rhomboidal crystals of {-[OEC-4-P]Li_4}(*t*-BuLi)$_2$, **1** (45%). (This was subsequently improved to 80% by using 6 equivalents of *t*-BuLi.[12]) Reflux of the hexane reaction mixture for a few hours resulted in the elimination of the coordinated BuLi. The ^{1}H NMR spectrum of the resulting white pyrophoric precipitate showed the complete absence of any pyrrole resonance.[13] However, addition of a small amount of THF to the NMR tube led to the nearly quantitative formation of the THF-containing tetralithium salt {[OEC-4-P]Li_4(THF)$_4$}.[10a−c]

Table 2. Atomic Coordinates and Isotropic Thermal Parameters

atom	x	y	z	B(eq)^a (Å^2)
N1	0.5164(1)	0.2924(1)	0.3938(1)	1.38(3)
N2	0.3358(1)	0.3832(1)	0.5799(1)	1.38(3)
C1	0.2460(1)	0.4367(2)	0.6085(1)	1.40(4)
C2	0.1072(1)	0.3140(2)	0.5392(2)	1.69(4)
C3	0.1101(1)	0.1789(2)	0.4670(2)	1.76(4)
C4	0.2508(1)	0.2248(1)	0.4951(1)	1.48(4)
C5	0.3124(1)	0.1238(2)	0.4478(2)	1.61(4)
C6	0.1910(2)	−0.458(2)	0.3665(2)	2.01(5)
C7	0.2337(2)	−0.1628(2)	0.3361(2)	2.67(4)
C8	0.4123(2)	0.1603(2)	0.5881(2)	1.89(5)
C9	0.3459(2)	0.1443(2)	0.7053(2)	3.00(4)
C10	0.3942(1)	0.1529(1)	0.3440(2)	1.44(4)
C11	0.3628(1)	0.0550(2)	0.1936(2)	1.76(4)
C12	0.4701(1)	0.1356(2)	0.1483(2)	1.65(4)
C13	0.5634(1)	0.2796(2)	0.2727(1)	1.38(4)
C14	0.2931(1)	0.6025(1)	0.7150(1)	1.39(4)
C15	0.1858(1)	0.6357(2)	0.6593(2)	1.58(4)
C16	0.2078(2)	0.7917(2)	0.7619(2)	2.34(5)
C17	0.296791)	0.6234(2)	0.8726(2)	1.76(4)
C18	0.1575(2)	0.5285(2)	0.8868(2)	2.48(5)
C19	0.2562(1)	0.3603(2)	0.1928(2)	1.73(4)
C20	0.1920(2)	0.4596(2)	0.2384(2)	2.20(4)
C21	0.3428(2)	0.4022(2)	0.0953(2)	2.38(5)
C22	0.1314(2)	0.1942(2)	0.0884(2)	2.71(5)
Li1	0.5384(2)	0.4514(3)	0.5946(3)	1.95(7)
Li2	0.3642(3)	0.2564(3)	0.2157(3)	2.06(7)
Li3	0.2071(3)	0.3257(3)	0.3707(3)	1.96(7)

^{a} $B(\text{eq}) = {}^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Crystals of **1** suitable for X-ray diffraction analysis were isolated from the reaction mixture. A perspective view of **1** is shown in Figure 1. The molecule is centrosymmetric and comprises a rather distorted OEC-4-P tetraanion connected to six Li cations and to two *t*-Bu groups. The four pyrrolyl rings are bonded to four lithium cations in an η^5 mode, while each of the other two lithium atoms, symmetrically placed above and below the symmetry center, is also bonded to two nitrogen atoms of two adjacent pyrrole rings. Two of the η^5-bonded lithium atoms and one η^1-bonded lithium atom are further coordinated to the central carbon atom of a *t*-Bu group, which is therefore in a formal octahedral environment.

On the basis of ^{1}H NMR data, we recently observed that [OEC-4-P]Li_4 has the ability to retain alkyllithium[10b] derivatives and other lithiated functions such as enolates[10d] and ynolates.[10a] The high Lewis acidity of the alkali cation is probably responsible for this scavenging behavior as well as for the unusual coordination geometry of the carbon atom of complex **1**. Once formed in solution, [OEC-4-P]Li_4 is strongly coordinated to any available BuLi, which severely distorts the molecule, forcing the tertiary carbon of the *tert*-butyl group into a hypercoordinated octahedral geometry. A similar forced distortion was also observed by Gade[5b] for the Li_3N_3 tripodal core of HC[$(CH_3)_2$SiN(*t*-Bu)]$_3$$Li_3$ in which considerable strain in the skeleton linking the nitrogen atoms was observed.

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[11] Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974.

[12] Same procedure as in the Experimental Section but for 9.96 g (18.42 mmol), 200 mL of hexane, and 65 mL of 1.7 M (0.11 mol, 6 equiv) *t*-BuLi. Yield of **1** was 9.80 g (80%).

[13] The reaction mixture was refluxed for 3 days, affording a white, highly pyrophoric compound. ^{1}H NMR (C_6D_6): δ 1.22 (s), 0.85 (t) in 1:1 ratio.

Table 3. Atomic Coordinates and Isotropic Thermal Parameters

atom	x	y	z	B(eq)[a] (Å^2)
N1	0.1506(1)	0.1443(1)	0.2704(1)	1.85(8)
N2	0.3500(1)	0.1151(2)	0.3959(1)	1.88(8)
N3	0.1498(1)	−0.0566(2)	0.1367(1)	1.87(8)
N4	0.3486(1)	−0.0257(2)	0.2007(1)	1.81(8)
C1	0.1183(1)	0.1453(2)	0.3392(2)	1.82(9)
C2	0.0961(1)	0.0565(2)	0.3562(2)	2.3(1)
C3	0.0617(1)	0.0562(2)	0.4263(2)	2.6(1)
C4	0.1070(1)	0.0965(2)	0.5151(2)	2.7(1)
C5	0.1289(1)	0.1853(2)	0.4999(2)	2.6(1)
C6	0.1638(1)	0.1838(2)	0.4302(2)	2.1(1)
C7	0.1460(1)	0.2274(2)	0.2265(2)	2.0(1)
C8	0.1915(1)	0.2290(2)	0.1692(2)	2.5(1)
C9	0.1907(2)	0.3148(3)	0.1236(2)	3.6(1)
C10	0.1185(2)	0.3418(3)	0.0663(2)	3.8(1)
C11	0.0724(2)	0.3415(2)	0.1222(2)	3.5(1)
C12	0.0738(1)	0.2646(2)	0.1659(2)	2.6(1)
C13	0.3815(1)	0.2002(2)	0.4127(2)	1.9(1)
C14	0.4066(1)	0.2264(2)	0.3368(2)	2.3(1)
C15	0.3083(1)	−0.0065(2)	0.4589(2)	2.4(1)
C16	0.3087(2)	−0.0545(2)	0.5429(2)	3.3(1)
C17	0.4396(1)	0.3141(2)	0.3521(2)	2.6(11)
C18	0.3673(1)	0.3572(2)	0.4415(2)	2.5(1)
C19	0.3338(1)	0.2698(2)	0.4243(2)	2.2(1)
C20	0.3536(1)	0.0728(2)	0.4809(2)	1.8(1)
C21	0.3928(1)	0.3820(2)	0.3661(2)	2.7(1)
C22	0.3807(2)	−0.0784(2)	0.6038(2)	3.4(1)
C23	0.4265(2)	0.0001(2)	0.6280(2)	3.1(1)
C24	0.4255(1)	0.0460(2)	0.5428(2)	2.4(1)
C25	0.1450(1)	−0.1400(2)	0.1768(2)	1.9(1)
C26	0.0728(1)	−0.1643(2)	0.1718(2)	2.4(1)
C27	0.0706(2)	−0.2494(2)	0.2172(2)	3.3(1)
C28	0.1180(2)	−0.2482(2)	0.3162(2)	3.4(1)
C29	0.1901(2)	−0.2252(3)	0.3238(2)	3.3(1)
C30	0.1920(1)	−0.1412(2)	0.2765(2)	2.4(1)
C31	0.1161(1)	−0.0578(2)	0.0374(2)	1.76(9)
C32	0.1227(1)	−0.0987(2)	−0.1153(2)	2.4(1)
C33	0.1600(1)	−0.0965(2)	−0.0130(2)	2.1(1)
C34	0.0995(1)	−0.0092(2)	−0.1520(2)	2.6(1)
C35	0.0574(1)	0.0319(2)	−0.1029(2)	2.3(1)
C36	0.0947(1)	0.0316(2)	−0.0001(2)	2.0(1)
C37	0.3557(1)	0.0173(2)	0.1220(2)	1.9(1)
C38	0.4287(1)	0.0482(2)	0.1369(2)	2.5(1)
C39	0.4341(2)	0.0941(2)	0.05478(2)	3.2(1)
C40	0.3846(2)	0.1688(2)	0.0272(2)	3.6(1)
C41	0.3119(2)	0.1413(2)	0.0124(2)	3.7(1)
C42	0.3080(1)	0.0941(2)	0.0947(2)	2.6(1)
C43	0.3814(1)	−0.1105(2)	0.2142(2)	1.80(9)
C44	0.4023(1)	−0.1404(2)	0.3124(2)	2.2(1)
C45	0.4389(1)	−0.2259(2)	0.3271(2)	2.4(1)
C46	0.3961(1)	−0.2938(2)	0.2635(2)	2.9(1)
C47	0.3734(1)	0.2652(2)	0.1652(2)	2.6(1)
C48	0.3371(1)	−0.1797(2)	0.1524(2)	2.2(1)
Li1	0.2504(2)	0.1338(3)	0.3371(3)	2.8(2)
Li2	0.1305(2)	0.0437(3)	0.1946(3)	2.5(2)
Li3	0.2493(2)	−0.0456(3)	0.1639(3)	2.8(2)
Li4	0.3697(2)	0.0446(3)	0.3081(3)	2.4(2)

[a] $B(\mathrm{eq}) = {}^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)\mathrm{B}(2,3)]$.

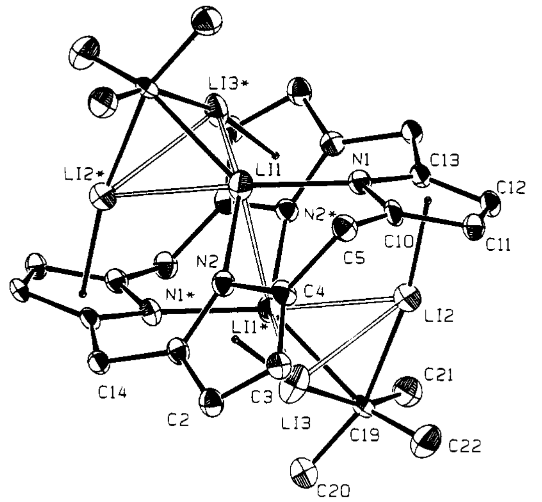

Figure 1. ORTEP plot of **1** with thermal ellipsoids drawn at the 50% probability level.

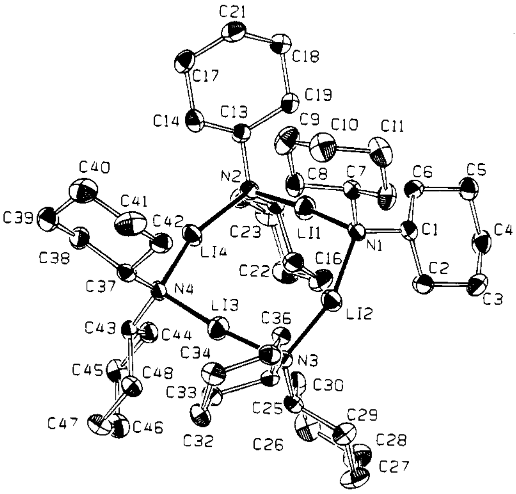

Figure 2. ORTEP plot of **2** with thermal ellipsoids drawn at the 50% probability level. Ethyl groups have been omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (deg)

1	**2**
Li1••Li2 = 2.654(4)	Li1−N1 = 1.981(5)
Li1••Li3 = 2.711(3)	Li1−N2 = 1.977(5)
Li1••Li1 = 2.887(5)	Li2−N1 = 1.937(5)
Li2••Li3 = 2.647(4)	Li2−N3 = 1.937(5)
Li1−C19 = 2.382(3)	Li3-N3 = 1.978(5)
Li2−C19 = 2.101(3)	Li3−N4 = 1.972(5)
Li3−C19 = 2.125(3)	Li4−N2 = 1.933(5)
Li2−N1 = 2.198(3)	N1−C1 = 1.472(3)
Li2−C10 = 2.218(3)	N1−C7 = 1.467(3)
Li2−C11 = 2.194(3)	N1−Li1−N2 = 174.8(3)
Li2−Cl2 = 2.143(3)	N1−Li2−N3 = 157.0(3)
Li2−Cl3 = 2.145(3)	N3−Li3−N4 = 174.0(3)
Li1−N1 = 2.020(3)	N3−Li3−N4 = 174.0(3)
Li1−N2 = 2.026(3)	N2−Li4−N4 = 156.2(3)
N1−Li1−N2 = 101.5(1)	N3−Li3−N4 = 174.0(3)
N1−Li1−Li1 = 79.1(1)	C7−N1−Li1 = 101.7(2)
Li1−Li2−Li3 = 61.52(9)	C1−N1−Li1 = 106.5(2)
Li2−Li3−Li1 = 59.37(9)	C7−N1−Li2 = 118.2(2)
Li−C19−Li2 = 72.3(1)	C1−N1−Li2 = 114.2(2)
Li2−C19−Li3 = 77.6(1)	C1−N1−C7 = 111.7(2)
Li1−C19−Li3 = 73.7(1)	

Reaction of Cy$_2$NH with 1 equiv of n-BuLi afforded the pyrophoric (Cy$_2$NLi)$_4$ (**2**), which was recrystallized from boiling hexane as colorless prisms. The solid state structure of **2** consists of a planar Li$_4$N$_4$ core, slightly skewed in a butterfly conformation (Figure 2). All of the nitrogen atoms are tetrahedral, and the two inequivalent cyclohexyl rings bonded to the nitrogen atoms are placed in the positions above and below the molecular plane. Each lithium atom is coordinated to two nitrogen atoms, forming both linear and slightly bent arrays with the two bridging nitrogens. Although the lithium complexes show an impressive variety of solid state structures,[4] the planar eight-membered-ring structure of **2** is rare. This tetrameric structure is even surprising when one considers the close chemical similarity between **2** and LDA, which is polymeric.[7] Furthermore, the projection of the helicoidal LDA structure along the axis of the helix is remarkably similar to that of **2**, showing comparable Li−N distances and angles. Steric contacts between the more bulky cyclohexyl groups probably prevent the polymeric aggregation of **2**.

The high rigidity of this cluster is probably maintained in solution. In fact, the room temperature ^{1}H NMR spectrum of complex **2** in C_6D_6 shows two different types of cyclohexyl rings which are in agreement with the solid state structure. The absence of coalescence at *T* up to +90 °C is also in line with these considerations.

Complex **2** reacts in hexane with 1 equiv of THF to yield another crystalline compound which, on the basis of the analytical and spectroscopic data, is formulated as $Cy_2NLi(THF)$. Unlike the *i*-Pr derivatives $\{[(i\text{-Pr})_2N]Li(TMEDA)\}_2$ and $\{[(i\text{-Pr})_2N]Li(THF)_2\}_2$, which are dimeric,[4,8] $Cy_2NLi(THF)$ may well have the same backbone of **2** with each Li atom bearing one THF molecule. However, other possibilities such as a cubane-like structure[14] cannot be ruled out.

Further work to clarify the structure of this compound is currently underway.

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Supplementary Material Available: Additional ORTEP diagrams and tables listing complete atomic positional parameters, crystallographic experimental details, temperature factors, torsion angles, bond angles, and bond distances (61 pages). Ordering information is given on any current masthead page.

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