

## Communications to the Editor

### Butyllithium Cubane Tetramers Linked by Li-TMEDA-Li Bridges in an Infinite, Zig-Zag Chain Arrangement: First Crystallographic Study of a Simple Butyl Compound of an Early Main Group Element

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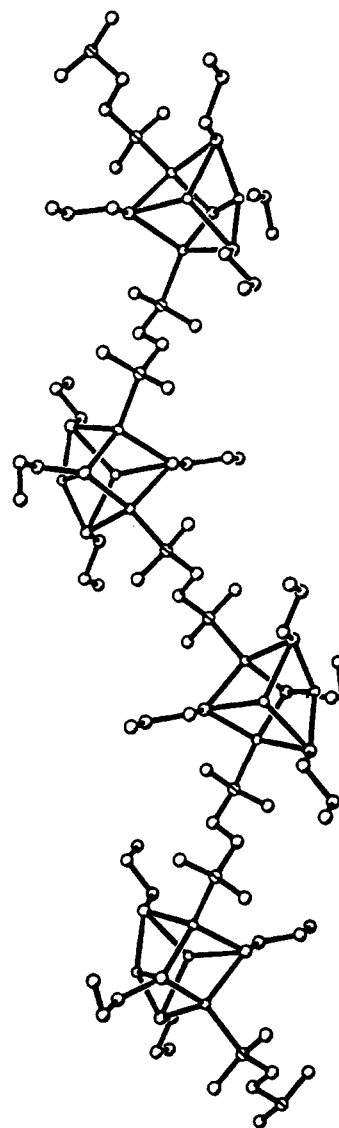
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Herein we report the structure of the crystalline alkyllithium complex  $[(\text{Bu}^n\text{Li})_4\text{TMEDA}]_n$  ( $\text{Bu}^n\text{Li}$ , *n*-butyllithium; TMEDA, *N,N,N',N'*-tetramethylethylenediamine) which, to the best of our knowledge, is the first crystal structure of a simple butyl derivative of a group 1 (Li, Na, etc.) or a group 2 (Be, Mg, etc.) metal (i.e. of formula " $\text{Bu}^n\text{M}$ " or " $\text{Bu}_2\text{M}$ ").  $\text{Bu}^n\text{Li}$  is much in demand in both chemical synthesis<sup>1</sup> and polymer synthesis<sup>2</sup> due to its ability to function efficiently either as a base or as a nucleophile. The complex " $\text{Bu}^n\text{Li}\cdot\text{TMEDA}$ " is also an effective in situ deprotonating reagent. Compositions of variable  $\text{Bu}^n\text{Li}:\text{TMEDA}$  ratios have been isolated from solution by Langer.<sup>3</sup> He found the 1:1 complex to be a yellow oil but the 2:1 and 4:1 complexes to be crystalline, though identification was limited to elemental analyses and cryoscopic molecular mass measurements.

We prepared a batch of  $\text{Bu}^n\text{Li}\cdot\text{TMEDA}$  with the intention of employing it in a metalation process. Precipitation occurred almost immediately on adding the Lewis base (1.66 mmol) to a chilled solution of  $\text{Bu}^n\text{Li}$  (10 mmol in hexane) under argon cover gas. Gentle heating to about 30 °C proved necessary to form the desired homogeneous metalating solution, but upon standing overnight, the solution deposited a large crop of colorless hexagonal blocks,<sup>4</sup> which were collected by conventional vacuum filtration techniques. Their superb quality, coupled with the knowledge that no solid-state structure of *n*-butyllithium<sup>5</sup> or a *n*-butyllithium-donor complex<sup>6</sup> had yet been elucidated, prompted us to examine them by X-ray crystallography.

This study revealed a zig-zag, polymeric chain structure (Figure 1) of TMEDA-linked  $(\text{Bu}^n\text{Li})_4$  tetramers (Figure 2).<sup>7</sup> The repeating tetrameric skeletal core brings together four  $\text{Li}^+$  cations



**Figure 1.** Crystal structure of  $[(\text{Bu}^n\text{Li})_4\text{TMEDA}]_n$  showing the polymeric, zig-zag chain arrangement. Hydrogen atoms are omitted for clarity.

and the four  $\alpha$ -C atoms of the butyl anions in a distorted cubane arrangement which has become a trademark of the structural chemistry of organolithium and other lithium compounds.<sup>8</sup> Butyl

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(2) For examples of its use in polymerization initiation, see: Morton, M. *Anionic Polymerization: Principles and Practice*; Academic Press: London, 1983. Young, R. N.; Quirk, R. P.; Fetters, L. J. *Adv. Polym. Sci.* **1984**, *56*, 1.

(3) *Polyamine-Chelated Alkali Metal Compounds*; Langer, A. W., Jr., Ed.; American Chemical Society: Washington, DC, 1974. Langer, A. W., Jr. U.S. Patent 3,541,149, 1970.

(4)  $[(\text{Bu}^n\text{Li})_4\text{TMEDA}]_n$ : sensitive to moisture and oxygen; mp 83–84 °C. Anal. ( $\text{C}_{22}\text{H}_{52}\text{Li}_4\text{N}_2$ ) C, H, Li, N.

(5) However, the solution nature of *n*-butyllithium has been probed. For example, see: Bywater, S.; Lachance, P.; Worsfold, D. J. *J. Phys. Chem.* **1975**, *79*, 2148. Seebach, D.; Hässig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 308. Heinzer, J.; Oth, J. F. M.; Seebach, D. *Helv. Chim. Acta* **1985**, *68*, 1848. McGarrity, J. F.; Ogle, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 1805. McGarrity, J. F.; Ogle, C. A.; Brich, Z.; Loosli, H.-R. *J. Am. Chem. Soc.* **1985**, *107*, 1810. Bauer, W.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1987**, *109*, 970.

(6) A crystal structure is known for the mixed alkyllithium–lithium alkoxide complex  $(\text{Bu}^n\text{Li}\cdot\text{Bu}^n\text{OLi})_4$ : Marsch, M.; Harms, K.; Lochmann, L.; Boche, G. *Angew. Chem.* **1990**, *102*, 334; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 308.

(7) Crystal data:  $\text{C}_{22}\text{H}_{52}\text{Li}_4\text{N}_2$ ,  $M = 372.42$ , orthorhombic, *Pnma*,  $a = 8.336(2)$  Å,  $b = 16.157(3)$  Å,  $c = 20.836(4)$  Å,  $V = 2806.3(12)$  Å<sup>3</sup>,  $Z = 4$ ,  $d_{\text{calcd}} = 0.881$  g·cm<sup>-3</sup>,  $\lambda$  (Cu K $\alpha$ ) = 1.54184 Å,  $\mu = 0.339$  mm<sup>-1</sup>,  $F(000) = 840$ . Measurements were made at 200 K on a Stoe-Siemens diffractometer with an Oxford Cryostream cooler from a crystal of size 0.75 × 0.46 × 0.27 mm. All 2163 independent reflections were used for least-squares refinement on  $F^2$ . H atoms were constrained and other atoms assigned anisotropic displacement parameters. Positional disorder in the  $\text{Bu}^n$  group C(4) to C(43) refined with linked partial occupancies and some restraints. For 1324 reflections with  $I > 2\sigma(I)$ ,  $R = 0.0917$ ,  $wR(\text{all data}) = [(\sum w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2)^2)]^{1/2} = 0.2725$ , and goodness of fit = 1.06 for 162 parameters. All features in a final difference map were within  $\pm 0.45$  e·Å<sup>-3</sup>. Sheldrick, G. M. SHELXL-92, program for crystal structure refinement, University of Göttingen, Germany, 1992.

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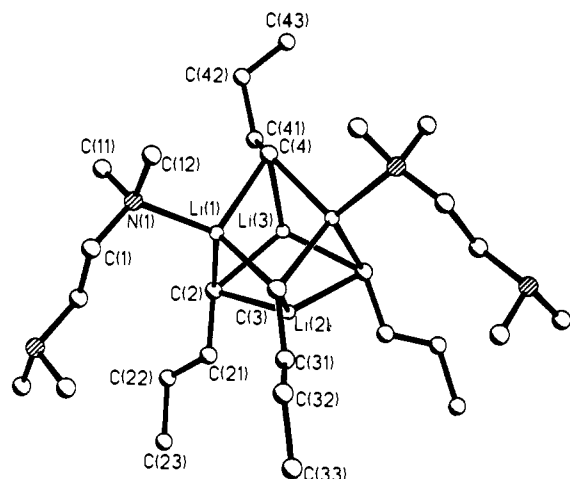


Figure 2. Closeup view of the bis-complexed tetrameric repeating unit within the structure.

Table I. Selected Bond Lengths (Å) and Angles (deg)

Li(1)-N(1)	2.131(8)	Li(1)-C(4)	2.314(8)
Li(1)-C(2)	2.321(8)	Li(1)-C(3)	2.326(8)
Li(2)-C(3)	2.166(11)	Li(2)-C(2)	2.210(7)
Li(3)-C(4)	2.145(11)	Li(3)-C(2)	2.164(7)
N(1)-Li(1)-C(4)	108.9(3)	N(1)-Li(1)-C(2)	121.2(4)
C(4)-Li(1)-C(2)	101.7(3)	N(1)-Li(1)-C(3)	109.8(3)
C(4)-Li(1)-C(3)	110.8(3)	C(2)-Li(1)-C(3)	104.1(3)
C(3)-Li(2)-C(2)	113.7(3)	C(2)-Li(2)-C(2')	107.4(5)
C(4)-Li(3)-C(2)	113.0(3)	C(2)-Li(3)-C(2')	110.7(5)
Li(3)-C(2)-Li(2)	64.6(3)	Li(3)-C(2)-Li(1)	67.4(3)
Li(2)-C(2)-Li(1)	66.4(3)	Li(2)-C(3)-Li(1)	67.0(3)
Li(1)-C(3)-Li(1')	67.6(4)	Li(3)-C(4)-Li(1)	67.8(3)
Li(1)-C(4)-Li(1')	68.0(4)		

chains protrude from the (CLi)<sub>4</sub> core in orientations which allow room for two of the four metal centers [Li(1) and its symmetry relation] to be ligated by TMEDA molecules. This additional N-Li bonding raises the coordination numbers of Li(1) and Li(1') to four (three C-Li bonds, one N-Li bond) while uncomplexed Li(2) and Li(3) remain only three-coordinate. The two TMEDA molecules each bridge two (Bu<sup>n</sup>Li)<sub>4</sub> tetramers, thereby interacting with one Li<sup>+</sup> center per tetramer in a monodentate manner, giving an overall Bu<sup>n</sup>Li:TMEDA ratio of 4:1, not 4:2. Normally TMEDA adopts a didentate chelating mode toward Li<sup>+</sup> cations, but occasionally, as here, a monodentate, bridging role is preferred.<sup>9</sup> Clear similarities exist between this crystal structure and that of [(MeLi)<sub>4</sub>·(TMEDA)<sub>2</sub>]<sub>n</sub><sup>10</sup> since both have (CLi)<sub>4</sub> pseudo-cubane units connected by Li-TMEDA-Li bridges. Significantly, however, the smaller steric demands of the methyl groups permit all four Li<sup>+</sup> cations within the tetrameric clusters to be complexed by TMEDA molecules, resulting in an infinite, three-dimensional array rather than an infinite, zig-zag chain structure.

Table I lists important bond lengths and bond angles in the title structure. An examination reveals that the three-coordinate metal centers form noticeably shorter C-Li bonds [mean lengths: Li(2), 2.194 Å; Li(3), 2.158 Å] than the four-coordinate ones (mean length, 2.320 Å; cf. 2.262 Å in the methyl analogue<sup>10</sup>). Furthermore, the N-Li bonds between tetramers are only marginally shorter than corresponding ones in the methyl analogue [2.131(8) Å; cf. 2.214(5) Å<sup>10</sup>] even though the connectivity of the (Bu<sup>n</sup>Li)<sub>4</sub> tetramers is half that of the (MeLi)<sub>4</sub> tetramers (2 vs 4). These

nitrogen-attached Li<sup>+</sup> centers occupy distorted tetrahedral sites (mean angle at Li<sup>+</sup>, 109.4°) with distortion most pronounced at N(1)Li(1)C(2) [121.2(4)°] to offset butyl-TMEDA repulsions. The mean bond angle at the three-coordinate, pyramidal Li<sup>+</sup> centers is 111.9°. Atoms connected to the Li<sup>+</sup> centers, the butyl α-carbons and the TMEDA nitrogens, are six- and four-coordinate, respectively.

In conclusion, the failure of TMEDA to break down the tetrameric cluster and to assume its preferred chelating role in the butyllithium solid described herein adds further support to the recent claim that TMEDA is not a particularly effective ligand for the Li<sup>+</sup> cation.<sup>11</sup>

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**Supplementary Material Available:** Details of the X-ray analysis and tables of atomic coordinates, bond lengths and angles, and thermal parameters (5 pages); listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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### Palladium(II)-Directed Assembly of Macrocyclic Dinuclear Complexes Composed of (en)Pd<sup>2+</sup> and Bis(4-pyridyl)-Substituted Bidentate Ligands. Remarkable Ability for Molecular Recognition of Electron-Rich Aromatic Guests

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Self-assembly phenomena have been utilized recently for the construction of highly organized structures.<sup>1</sup> Application of these phenomena to macrocyclization<sup>2</sup> is quite attractive since cyclization

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