

Characterization of a Kinetically Stable, Highly Ordered, Octameric Form of Lithium *tert*-Butoxide and Its Implications Regarding Aggregate Formation

John F. Allan, Roger Nassar, Elizabeth Specht, Alicia Beatty, Nathalie Calin, and Kenneth W. Henderson*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556

Received September 9, 2003; E-mail: khenders@nd.edu

Lithium alkoxides, ROLi, enjoy a wide number of uses including precursor materials for chemical vapor deposition and sol-gel processes,¹ reagents in synthesis,² and additives polymerization reactions.³ Furthermore, alkyllithium reagents commonly contain substoichiometric amounts of lithium alkoxides, due to reaction with adventitious molecular oxygen, and these mixed-anion solutions often have significantly different reactivities as compared to the parent organolithiums.⁴ As a consequence, there has been significant interest in the structure of lithium alkoxides in the solid state, in solution, and also in the gas phase.⁵

Until very recently, a notable exception to the list of crystallographically characterized lithium alkoxides was the most widely used one, lithium *tert*-butoxide, **1**. Although the structure of the unsolvated form of **1** has been believed to be exclusively hexameric, **1₆**, for almost 40 years,⁶ as characterized by a host of techniques including cryoscopy,⁷ NMR spectroscopy,⁸ and mass spectrometry,⁷ it was only in 2002 that this aggregation state was confirmed in the literature by single-crystal X-ray diffraction.⁹ Problems associated with the crystallographic characterization of **1₆** have been cited due to poor quality, twinning, heavy disorder, or phase changes of the crystals. Herein, we present the characterization of a novel octameric form of lithium *tert*-butoxide, **1₈**, an aggregate that has never previously been detected for this common reagent despite the numerous studies regarding its identity.

Initially, **1₈** was prepared serendipitously from a complex reaction mixture containing ^tBuLi. Single-crystal X-ray analysis revealed the octameric structure shown in Figure 1. The structure of **1₈** is unusual, with sections resembling both a cubane and a cyclic hexamer. Two distinct sets of lithium centers are present, those associated with either a pair of Li₂O₂ rings and a single Li₃O₃ ring, Li(1), and those associated with a single Li₂O₂ ring and a pair of Li₃O₃ rings, Li(2). Whereas the bond lengths and angles for the hexameric form of ^tBuOLi have not been published due to substantial disorder in the structure,⁹ there are no such problems associated with the determination of **1₈** (*R* = 2.95). The Li–O bond lengths range between 1.889(2) and 1.968(1) Å, with a mean value of 1.92 Å. These distances are elongated as compared to those in the related but less sterically encumbered complexes (^tBuCH₂OLi)₈¹⁰ and [(ⁿBu)₄(ⁿBuO)₄Li₆],¹¹ where the mean Li–O bond distances are 1.89 and 1.88 Å, respectively.¹² Two sets of angles are apparent at the lithium centers, those associated with the Li₂O₂ rings (mean 99.3°) and those associated with the Li₃O₃ rings (mean 122.1°). It is noteworthy that two distinct solid-state aggregates have now been elucidated for **1**. Indeed, considering the large number of crystallographically characterized lithiated complexes, it is remarkably rare to find alternative solid-state aggregates for a single compound.⁶ This contrasts with their rich solution chemistry, where it is common for numerous aggregates to coexist.¹³

After considerable investigation, it was discovered that simply cooling a solution of the commercially supplied ^tBuLi reagent (1.6 M in pentane, Acros) to –44 °C resulted in the formation of crystals

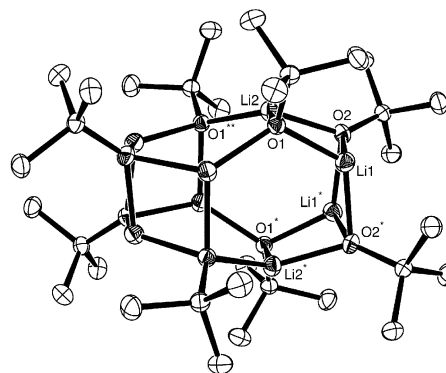


Figure 1. Molecular structure of octameric lithium *tert*-butoxide, **1₈**. Key bond lengths (Å) and angles (deg): Li(1)–O(1) 1.889(2), Li(1)–O(2) 1.918(2), Li(1)–O(2*) 1.915(2), Li(2)–O(1) 1.968(1), Li(2)–O(2) 1.906(2), Li(2)–O(1**) 1.894(2), O(1)–Li(1)–O(2) 99.87(7), O(1)–Li(1)–O(2*) 123.64(8), O(2)–Li(1)–O(2*) 100.61(7), O(1)–Li(2)–O(2) 97.49(7), O(1)–Li(2)–O(1**) 120.15(8), O(2)–Li(2)–O(1**) 129.91(8).

that were determined by X-ray diffraction to be **1₈**. Several independent batches of crystals were prepared in a similar manner, and their unit cells were checked. Furthermore, powder diffraction studies of **1₆** (freshly sublimed commercial reagent) and **1₈** were compared to their theoretical patterns to confirm the identity of the bulk samples. Investigation of the composition of the commercially purchased ^tBuLi by double titration methods indicated that it contained approximately 26% of alkalinity not associated with the highly reactive ^tBuLi.¹⁴ An alternative source of ^tBuLi (Aldrich) was determined to be essentially “pure”, and this was subsequently used to investigate the rational synthesis of **1₈**.

The octamer can reproducibly be prepared by placing hexane/pentane solutions of ^tBuLi in a Schlenk flask and either allowing the slow diffusion of air through a CaCl₂-packed drying tube or alternatively by replacing the inert gas by dry O₂. Cooling at –20 or –44 °C results in crystallization of **1₈**. In contrast, reaction of ^tBuOH or ^tBuOOH with alkyllithium reagents, or the direct reaction of lithium sand with ^tBuOH,⁷ resulted in precipitation of the hexamer, **1₆**. Solvent effects were then studied, and it was found that dissolving **1₈** in toluene followed by recrystallization resulted in formation of **1₆**. Furthermore, directly growing crystals from a ^tBuLi solution in toluene at –44 °C also gave crystals of **1₆**.

¹H, ¹³C, and ⁷Li NMR analyses of both *d*₁₄-hexane and *d*₈-toluene solutions of **1₆** and **1₈** displayed a single set of resonances with essentially identical chemical shifts over the temperature range –80 to 25 °C. Cryoscopic studies of **1₆** and **1₈** in benzene solutions proved to be more revealing.¹⁵ The hexamer behaves as expected, giving a molecular weight of 471 ± 45, over the concentration range 10.7–21.1 mmol L^{–1} (theoretical 480). Somewhat surprisingly, the octamer was also stable with a measured molecular weight of 647 ± 33, in the concentration range 5.1–16.7 mmol L^{–1} (theoretical 640). Heating a sample of **1₈** in benzene to reflux

temperature for approximately 2 h followed by a cryoscopic measurement resulted in a molecular weight of 447, which then remained unchanged on further heating. In combination, these results indicate that both the hexamer and the octamer are stable in solution but that rearrangement of **1**₈ to **1**₆ can occur. This rearrangement is also consistent with the gas-phase behavior of the aggregates, where the mass spectra (EI of a solid sample) of both **1**₆ and **1**₈ displayed no significant differences.⁵ The similar NMR data obtained for the two aggregation states must therefore be due to fast intramolecular exchange within the respective complexes.

Density functional theory calculations (geometry optimization and frequency analyses) at the B3LYP/6-311G** level were performed on the model complexes (MeOLi)₆, **I**, and (MeOLi)₈, **II**.¹⁶ From their total energies, an approximate energy of formation (ΔE_f) can be deduced according to eq 1. Unexpectedly, these calculations indicate that the octamer is substantially more stable than the hexamer. However, when the calculations (HF/6-31G* geometry optimization followed by single point B3LYP/6-311G**) were performed on the molecules (^tBuOLi)₆, **III**, and (^tBuOLi)₈, **IV**, carrying the *tert*-butoxide groups, the stabilities reverse, and the hexameric arrangement becomes favored.



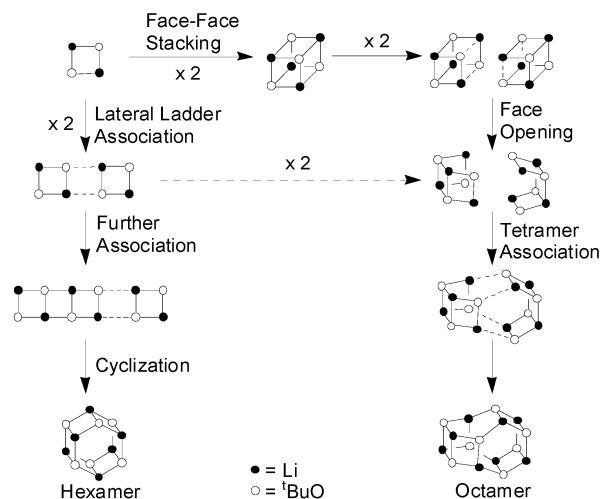
$$\text{R} = \text{Me}, \quad \Delta E_f = -8.7 \text{ kcal mol}^{-1}$$

$$\text{R} = {}^t\text{Bu}, \quad \Delta E_f = +3.4 \text{ kcal mol}^{-1}$$

These results can be rationalized by considering two issues. First, the larger octameric arrangement is more stable for the methoxide units due to a more isotropic distribution of electron density around the lithium centers, that is, a less pyramidalized geometry at lithium (average O–Li–O angles in **I** and **II** are 109.0° and 112.0°).¹⁸ Second, increasing the aggregate size results in closer packing of the alkoxide groups, and the accompanying increase in transannular strain leads to the energetic preference for **III** over **IV** (with numerous C–C distances <4 Å in **IV**). This is also evident in the mean Li–O distances, which increase from 1.915 Å in **III** to 1.936 Å in **IV**. The experimental and computational results are therefore in agreement that octamer **1**₈ is a kinetically stable form of lithium *tert*-butoxide.

We then wished to consider the factors controlling hexamer and octamer formation. ^tBuLi is a tetrameric cubane in hydrocarbon solvents, and reaction with O₂ will result in insertion into a ^tBuLi bond via a radical mechanism¹⁹ to form the peroxide ^tBuOOLi, most likely as part of a larger mixed-anion aggregate. The peroxide can then act as an electrophilic oxenoid and react with a second Li–C bond in a S_N2-type manner to form a pair of linked ^tBuOLi units.¹⁹ Further oxidation of the mixed-anion aggregate and/or ligand rearrangement must then occur to form the homoleptic complex. An intriguing scenario is that octamer assembly is controlled by the combination of two tetrameric Li₄O₄ units. This assessment is supported by the unusual connectivity found in **1**₈, which corresponds with the fusion of two face-opened cubanes or alternatively with the association of a pair of four-rung ladders (Scheme 1). The more common prismatic hexamer formation is believed to occur via face-stacking of trimeric rings or may alternatively be accomplished by the lateral association and subsequent cyclization of three dimeric Li₂O₂ rings.²⁰ Because octamer is formed by the slow reaction of O₂ with ^tBuLi in hydrocarbon solvent, this may permit the association of tetramers and stabilization of the octalithium aggregate, whereas under thermodynamic conditions, dissociation into dimers (or trimers) results in assembly into the more stable hexameric aggregation state. This model is also consistent

Scheme 1



with the noted solvent effects (hexamer formation in toluene), because aggregate dissociation is significantly enhanced in arene as compared to hydrocarbon media.²¹

Finally, various forms of mixed anion tetramers, ^tBu_n(^tBuO)_{4–n}Li₄, and hexamers, ^tBu_n(^tBuO)_{6–n}Li₆, have been proposed to form both in solution and in the gas phase.^{5,21,22} However, no reports of species of higher aggregation than hexamers have been disclosed. This may be a consequence of their method of preparation, but in light of the characterization of **1**₈ some reanalyses of these systems may prove valuable.

Supporting Information Available: Crystallographic, cryoscopic, and computational data (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Boyle, T. J.; Pedrotty, D. M.; Alam, T. M.; Vick, S. C.; Rodriguez, M. A. *Inorg. Chem.* **2000**, *39*, 5133.
- Lochmann, L. *Eur. J. Chem.* **2000**, 1115.
- Ko, B.-T.; Lin, C.-C. *J. Am. Chem. Soc.* **2001**, *123*, 7973.
- McGarrrity, J. F.; Ogle, C. A.; Brich, Z.; Loosli, H.-R. *J. Am. Chem. Soc.* **1985**, *107*, 1815.
- Kahn, J. D.; Haag, A.; Schleyer, P. v. R. *J. Phys. Chem.* **1988**, *92*, 212.
- Huml, K. *Czech. J. Phys.* **1965**, *15*, 699.
- Chisholm, M. H.; Drake, S. R.; Naiini, A. A.; Streib, W. E. *Polyhedron* **1991**, *10*, 337.
- Thomas, R. D.; Bott, S. G.; Gravelle, P. W.; Nguyen, H. D. *Abstracts of Papers*; 215th ACS National Meeting, Dallas, 1998; Part 1, INOR 291.
- Nekola, H.; Olbrich, F.; Behrens, U. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2067.
- Boyle, T. J.; Alam, T. M.; Peters, K. P.; Rodriguez, M. A. *Inorg. Chem.* **2001**, *40*, 6281.
- Marsch, M.; Harms, K.; Lochmann, L.; Boche, G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 308.
- A similar octameric amino chelated lithium alkoxide has also been characterized: Andrews, P. C.; MacLellan, J. G.; Mulvey, R. E.; Nichols, P. J. *J. Chem. Soc., Dalton Trans.* **2002**, 1651.
- Lucht, B. L.; Collum, D. B. *Acc. Chem. Res.* **1999**, *32*, 1035.
- Schlosser, M. *Organometallic Chemistry*. In *Organometallics in Synthesis*; Schlosser, M., Ed.; John Wiley & Sons: New York, 2002; p 295 for a review of titration methods.
- Experiments in Physical Chemistry*, 5th ed.; Shoemaker, D. P., Garland, C. W., Nibler, J. W., Eds.; McGraw-Hill: New York, 1989.
- (a) Becke, D. A. *J. Chem. Phys.* **1993**, *98*, 5648. (b) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.
- (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (b) Hariharan, P. C.; Pople, J. A. *J. Chem. Phys.* **1973**, *28*, 213.
- Armstrong, D. R.; Carstairs, A.; Henderson, K. W. *Organometallics* **1999**, *18*, 3589.
- Boche, G.; Lohrenz, J. C. W. *Chem. Rev.* **2001**, *101*, 697.
- Armstrong, D. R.; Barr, D.; Clegg, W.; Hodgson, S. M.; Mulvey, R. E.; Reed, D.; Snaith, R.; Wright, D. S. *J. Am. Chem. Soc.* **1989**, *111*, 4719.
- Darensbourg, M. Y.; Kimura, B. Y.; Hartwell, G. E.; Brown, T. L. *J. Am. Chem. Soc.* **1970**, *92*, 1236.
- DeLong, G. T.; Pannell, D. K.; Clarke, M. T.; Thomas, R. D. *J. Am. Chem. Soc.* **1993**, *115*, 7013.

JA038420M