New Dodecameric *n*-Propyllithium/Lithium *n*-Propoxide Mixed Aggregate. Evidence for the First Cuboctahedral Lithium Aggregate

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Lithium alkoxides formed in less than stoichiometric amounts from alkyllithium compounds can produce mixed alkyllithium/lithium alkoxide aggregates.[1] The alkyllithium components of these mixed aggregates often have different reactivity than the original alkyllithium compound. This likely explains differences in reactivity of alkyllithium compounds in the presence of selected alkoxides.[2] The mixed complexes are also precursors to hydrocarbon soluble lithium hydrides.[3]

The mixed alkyllithium/lithium alkoxide aggregates are of special interest, since they likely exist even in solutions of "pure" alkyllithiums from reaction with ethers or molecular oxygen. Of interest in this regard are possible mixed complexes of the widely used *n*-butyllithium. Unfortunately, due to the inability to observe $^{13}C-^{6}Li$ coupling in most *n*-butyllithium compounds, these are difficult to study in solution by standard NMR techniques. However, *n*-propyllithium serves as a useful model compound for *n*-butyllithium.

We now report on the solution structure of a new cuboctahedral mixed complex, $(n\text{-Pr})_8(n\text{-PrO})_4Li_{12}$, in which the alkyl groups are bonded to triangular faces of three lithium atoms, but the propoxide groups are bonded to faces of four lithium atoms. This is, to our knowledge, the first cuboctahedral lithium aggregate and the first evidence for alkoxide groups bonded to a square face of lithium atoms.

Addition of 0.42 mmol of *n*-propyl alcohol to 2.1 mmol of *n*-propyllithium-^{6}Li in cyclopentane solution produces evolution of gas, presumably *n*-propane.[4] The ^{13}C NMR spectrum[5] of the resulting solution shows the presence of *n*-propane at 16.60 and 16.38 ppm and new alkoxide resonances at 64.79 (C-1), 28.86 (C-2), and 9.84 (C-3) ppm. This is as expected (eq 1, R = *n*-propyl). There are also new propyl resonances at 16.5 (C-1), 23.29 (C-2), and 23.21 (C-3) ppm.

$$RLi + ROH \rightarrow ROLi + RH \qquad (1)$$

As the temperature of the sample is dropped, multiple ^{13}C NMR resonances are resolved for multiple *n*-propyllithium aggregates. In particular are the three multiplets at 15.7, 17.5, and 18.6 ppm. These were first identified by Fraenkel as the α-carbons of hexameric, octameric, and nonameric *n*-propyllithium, respectively.[6] In this sample, there is also a new multiplet at 16.5 ppm. ^{6}Li decoupling causes a collapse of the multiplet, confirming that the multiplicity is due to $^{13}C-^{6}Li$ coupling. Since such coupling is only observed for direct carbon–lithium bonding,[7] the newly formed lithium propoxide exists as a mixed aggregate of the form $R_a(RO)_bLi_{a+b}$.

The ^{13}C NMR resonance for the new α-carbon at 16.5 ppm shows temperature-dependent behavior (Figure 1). At room temperature the resonance is a single broad peak. As the temperature is lowered to approximately −25 °C, the peak separates into a multiplet with coupling of 2.25 Hz. The multiplet corresponds very well with the 25-line multiplet expected for coupling to 12 equivalent ^{6}Li nuclei ($I = 1$), Figure 2.[8] Coupling to 12 equivalent lithium nuclei indicates a fluxional dodecameric aggregate.

Further lowering of the temperature again causes a broadening of the ^{13}C NMR peak. Finally, below −70 °C, the peak resolves into a multiplet with a complex coupling pattern.

The ^{6}Li spectrum for this compound also shows temperature-dependent behavior. At higher temperatures, there is a single peak ($w_{1/2} \approx 1.4$ Hz) at −0.94 ppm. This broadens as the temperature is lowered and eventually separates into two sharp peaks at −0.49 and −1.98 ppm ($w_{1/2} \approx 0.7$ Hz), with relative intensities of 2:1.

The temperature dependence of both spectra indicates a lithium aggregate that is rapidly fluxional at higher temperatures, but is static on the NMR time scale at lower temperatures. Static organolithium aggregates larger than tetramers are rare. Study of this species in the slow fluxional exchange limit provides an unusual opportunity to determine the solution state structure of such a large lithium aggregate.

Selective irradiation of the upfield (less abundant) ^{6}Li resonance causes the ^{13}C multiplet at 16.5 ppm to collapse to a 1:2:3:2:1 five-line multiplet ($J = 8.1$ Hz), indicating coupling to two ^{6}Li nuclei. This is consistent with the ^{13}C satellites observed for the downfield ^{6}Li peak with a splitting of 8.2 Hz. Irradiation of the downfield (more abundant) ^{6}Li resonance produces a 1:1:1 ^{13}C triplet ($J = 3.3$ Hz), indicating coupling to one ^{6}Li nucleus. Neither the upfield ^{6}Li peak nor the higher temperature ^{6}Li peak show satellites, consistent with the expected couplings of 3.3 and 2.25 Hz, respectively, which are less than the baseline width of these peaks.
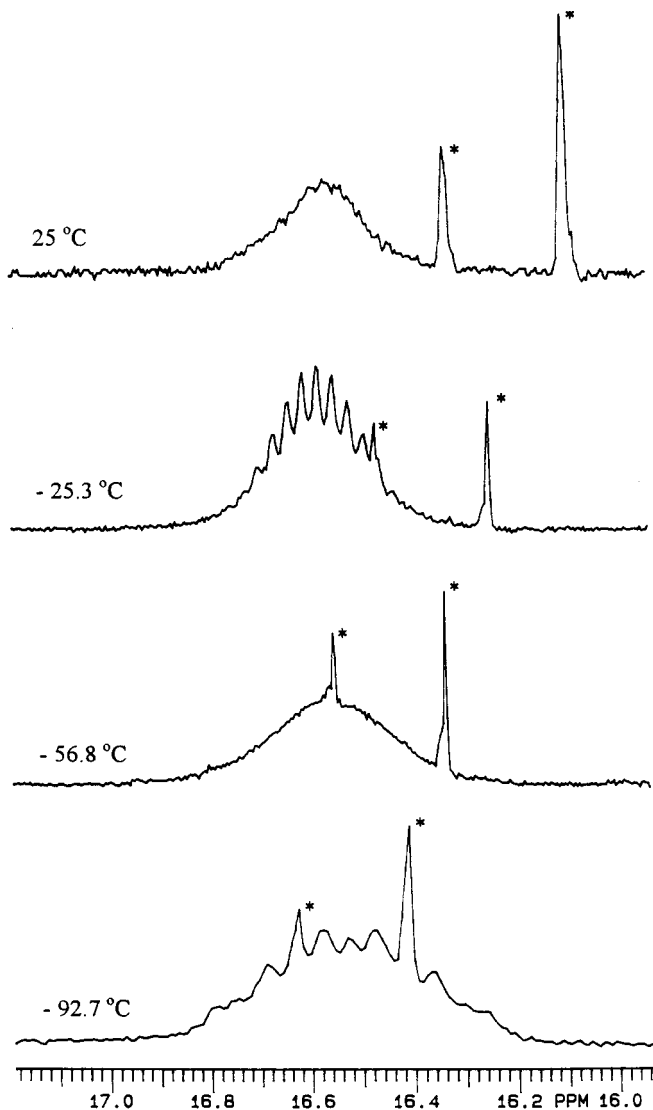
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(4) *n*-Propyllithium-^{6}Li was synthesized by reaction of excess ^{6}Li metal (94.5% isotopic abundance) with bis-*n*-propylmercury in cyclopentane. The mixed aggregate was prepared by slow addition of a cyclopentane solution of *n*-PrOH to 2.1 mmol of *n*-Pr^{6}Li in 0.6 mL of cyclopentane at room temperature in an argon-filled glovebox. In most cases, the solvent was then removed on the vacuum line to also remove *n*-propane. All solvents were predried over LiAlH$_4$ and distilled on the vacuum line.

(5) NMR spectra were run on a Varian VXR-300 NMR spectrometer at 75 and 44 MHz, respectively, for ^{13}C and ^{6}Li. The solvent was a mixture of 8% d^{10}-cyclopentane in protonated cyclopentane. ^{13}C chemical shifts are referenced to TMS by assigning the protonated cyclopentane peak to 25.89 ppm. ^{6}Li chemical shifts are relative to $(t\text{-BuLi})_4$ at 0.0 ppm. ^{6}Li decoupling was done using a custom-built decoupler.[12]

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Figure 1. Variable-temperature ^{13}C NMR spectra of the α-carbon of $(n\text{-Pr})_8(n\text{-PrO})_4Li_{12}$, prepared by addition of 0.63 mmol of *n*-propyl alcohol to 2.1 mmol of *n*-propyllithium-^{6}Li in 8% d^{10}-cyclopentane/protonated cyclopentane. The asterisks denote *n*-propane.
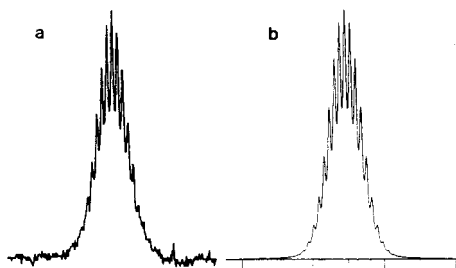
Figure 2. (a) Experimental ^{13}C NMR spectrum at −24.5 °C of the α-carbon of $(n\text{-Pr})_8(n\text{-PrO})_4Li_{12}$, prepared by addtion of 1.2 mmol of *n*-propyl alcohol to 2.1 mmol of *n*-propyllithium in cyclopentane. (b) Simulated NMR spectrum for a carbon bonded to 12 equivalent ^{6}Li nuclei ($I = 1$), $J = 2.25$ Hz; line width = 1.45 Hz.

To determine the relative ratio of propyl to propoxide groups, corresponding carbon peaks and corresponding proton peaks for the two groups were compared. Integration indicated a propyl-
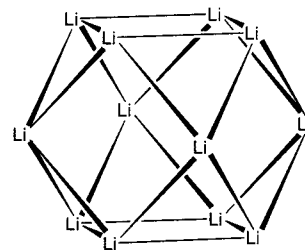
Figure 3. Cuboctahedral arrangement of lithium atoms. The propyl groups, which bond to the triangular faces, and the propoxide groups, which bond to four of the square faces, are removed for clarity.

to-propoxide ratio of 2:1. The propyl protons and the propoxide protons both correlated to the same ^{6}Li resonance in a ^{6}Li−^{1}H 2D heteronuclear NOE NMR experiment (HOESY), confirming that both of the groups were in the same aggregate.

Taken collectively, these data indicate a dodecameric aggregate, with eight equivalent propyl groups and four equivalent propoxide groups, $(n\text{-Pr})_8(n\text{-PrO})_4Li_{12}$. At higher temperatures, the aggregate is fluxional, making all lithium nuclei equivalent in the NMR spectrum. At the slow exchange limit, the lithium nuclei are split into two groups of eight and four nuclei, respectively. Each propyl group is bonded to three lithium atoms, two of one type and one of another type.

These data are best explained by a structure with a cuboctahedral arrangement of lithium atoms (Figure 3). The propyl groups are bonded to four of the six square faces. Two trans square faces remain open, analogous to the trans open triangular faces in alkyllithium hexamers. The eight lithium atoms around the two open square faces are equivalent and correspond to the downfield ^{6}Li NMR resonance.

Calculations at the B3LYP/6-31G level for the model compound $(Me)_8(MeO)_4Li_{12}$ indicate the cuboctahedral structure is at an energy minimum. Although bonding of the alkoxide group to a face of four lithium atoms had been unexpected, the Li−O bond lengths in the energy-minimized structure of the model compound are approximately 1.93 Å. This is identical with observed Li−O bond lengths (1.85−1.93 Å) in the X-ray crystal structure of hexameric lithium *tert*-butoxide,[9] and actually less than the longest Li−O bond (1.98 Å) in hexameric LiOCMe$_2$-Ph.[10] Likewise, the predicted Li−Li distances in the calculated structure are comparable to those in hexameric alkyllithium and lithium alkoxide structures.

The data do not prove the existence of the cuboctahedral structure, but the unprecedented detail from the NMR spectra allows for elimination of many other potential structures. For example, there are 10 convex geometric shapes which can be constructed from regular polygons that have 12 vertexes.[11] The cuboctahedral arrangement of lithiums is the only one of the 10 that is consistent with the NMR data.

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