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X-Ray Structural Analysis of a Novel Lithium Hydride/Lithium *tert*-Butoxide Superaggregate: $Li_{33}H_{17}(OtBu)_{16}$[**]

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The high lattice energy of lithium hydride drastically reduces its reactivity and is responsible for its insolubility in organic solvents.[1, 2] Consequently, any form of lithium hydride, whether complexed by ligands or uncomplexed, is an amorphous solid. Crystal structures of lithium hydride or of mixed aggregates containing lithium hydride have not been reported. We have recently provided evidence that the photochemical and thermal decomposition[3] of *tert*-butyllithium/lithium *tert*-butoxide mixtures[4] (molar ratio 3:7) in cyclopentane leads to highly reactive, hydrocarbon-soluble LiH[5] in the form of mixed LiH/LiO*t*Bu aggregates.[6] Precipitation of amorphous lithium hydride from such mixtures is apparently prevented by the excess of lithium *tert*-butoxide, which assists in solubilizing the LiH by incorporating it in mixed aggregates.[7, 8] Previous NMR spectroscopic studies revealed that the photochemical decomposition product is the decamer $Li_{10}H(OtBu)_9$, while the thermal decomposition product is dodecameric $Li_{12}H(OtBu)_{11}$.[6] It is noteworthy that these mixed aggregates form only at high alcoholate:alkyllithium ratios (ROLi:RLi $\geq$ 7:3), that is, when a large excess of *tert*-butoxide ligands is present. At lower ROLi:RLi ratios, amorphous lithium hydride precipitates from solution.

X-ray structural analyses of crystals grown from photolyzed *t*BuOLi/*t*BuLi mixtures (ca. 7:3) showed the presence of the hydride-rich superaggregate $Li_{33}H_{17}(OtBu)_{16}$ (**1**, Figure 1).[9] The synthesis is reproducible and, under the conditions chosen, exclusively yields crystals of **1**. To our knowledge, this is the largest lithium-containing aggregate so far known. The structural framework consists of fused cubic subunits (Figure 2), whose arrangement to form an infinite lattice is disrupted by the incorporation of the sterically demanding *tert*-butoxide groups. The inner core of the aggregate is hydride-rich, while in the outer shell *tert*-butoxide ligands are

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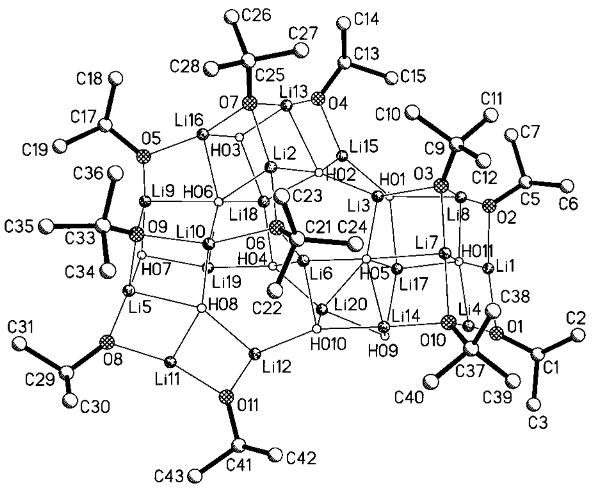

Figure 1. Asymmetric unit of **1**: Li–H distances 181(4)–224(4) pm; Li–O distances 185.1(11)–203.5(8) pm.

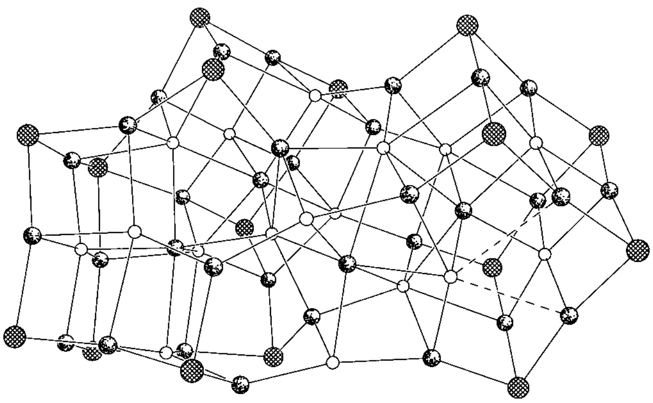

Figure 2. The Li–H–O framework of **1** (*tert*-butyl groups are omitted for clarity). Empty, shaded, and hatched circles represent hydrogen, lithium, and oxygen atoms, respectively. The two dashed lines represent long-range electrostatic Li ··· H interactions.

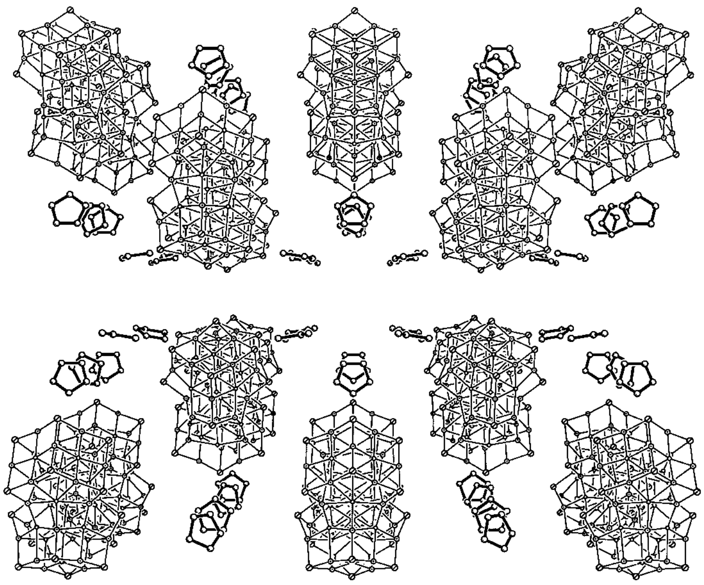

Figure 3. View of the packing of **1** in the lattice illustrating the incorporation of uncoordinated cyclopentane solvent molecules in channels between isolated aggregates (*tert*-butyl groups are omitted for clarity).

abundant. The *tert*-butoxide ligands at the periphery provide a nonpolar cover, which makes the aggregate highly hydrocarbon-soluble. Similar lipophilically wrapped polyion aggregates were recently discussed by Bock et al.[10] The arrangement of **1** within the lattice provides channels in which solvent molecules (cyclopentane) are incorporated (Figure 3).

Figure 2 shows the Li–H–O framework of **1** without the *tert*-butyl groups. It has C_s symmetry and is generated from the asymmetric unit by a mirror plane (the plane of the page in Figure 1). Among the numerous atoms in special positions are Li1, Li11, Li15, and Li17–Li20. The lithium cations exhibit a variety of coordination modes (Figure 2) that range from three- and four-coordinate to six-coordinate. The four three-coordinate lithium cations (Li4, Li12, and their symmetry equivalents) are located at the periphery of the aggregate where the fused cubic cells are disrupted; these cations are surrounded by one hydride ion and two *tert*-butoxide ligands or by two hydride ions and one *tert*-butoxide ligand. The abundant four-coordinate lithium cations at the periphery of the cluster (Li1–Li16 and their symmetry equivalents, except Li4 and Li12 and their symmetry equivalents) are surrounded by two hydride ions and two *tert*-butoxide ligands or by three hydride ions and one *tert*-butoxide group. The six-coordinate lithium cations (Li17–Li20) are located in the core of the aggregate and are exclusively encapsulated by hydride ions in a distorted octahedral arrangement. With the exception of H09 and H010, which are four-coordinate, all other hydride ions are surrounded by five or six lithium cations.

A wide range of Li–H distances (181(4)–224(4) pm) is found in **1**. The shortest Li-H distance (Li3–H05 181(4) pm) in **1** is slightly longer than that in $[\{(Me_3Si)_2NAlH_3Li \cdot 2Et_2O\}_2]$ (177.7 pm)[11] and significantly shorter than those in the LiH lattice (204.0 pm),[12] $LiAlH_4$ (188–216 pm),[13] and $[LiAlH(NEt_2)_3 \cdot n THF]$ (195.1 pm).[14] Shorter Li–H distances are known for $(tBu_3AlHLi)_2$ (168 pm)[15] and for molecular LiH[16] in the gas phase (159.6 pm). The Li–O distances range between 185.1(11) and 203.5(8) pm, values typical of lithium alkoxides and lithium enolates in which three cations are μ^3-bridged by an oxygen anion.[17]

Aggregates such as **1** result when lithium hydride is trapped in its nascent state by self-assembly with lithium *tert*-butoxide. The energetically favorable, largely ionic $Li^{\delta+} \cdots H^{\delta-}$ and $Li^{\delta+} \cdots O^{\delta-}$ interactions contribute to the stability of the cluster. Further growth of the superaggregate is presumably prevented by van der Waals interaction of the *tert*-butyl groups in the lipophilic hydrocarbon shell.

Complexes such as **1** can be regarded as models of superbasic mixtures or "unimetal superbases" ("complex bases").[5d, 18] Solutions of LiH/LiO*t*Bu react smoothly with 3,3-dimethyl-2-butanone (pinacolone) to give the corresponding enolate and hydrogen gas, whereas commercially available lithium hydride is completely unreactive.[5a, b] The ease of preparation of this system offers considerable advantages over other superactive lithium hydrides.[5a–c] Mixtures of *tert*-butyllithium with protic amines or silazanes may yield the corresponding LiH/amide or LiH/silazide aggregates upon photolysis. The strategy used to synthesize **1** could provide a general, facile route to a variety of superactive, hydrocarbon-soluble lithium hydride reagents. This is currently under investigation.

Experimental Section

1: All manipulations were performed by standard Schlenk and needle/septum techniques under an argon atmosphere. All solvents were dried over Na/K alloy and freshly distilled before use.

At −40 °C, *tert*-butyllithium (26 mL, 1.5 M in pentane, 39 mmol) was added dropwise to a solution of *tert*-butanol (2.5 mL, 26.5 mmol; dried over $MgSO_4$) in cyclopentane (10 mL). The reaction mixture was allowed to warm to room temperature and then irradiated for 7 h with a medium-pressure Hanovia Hg-vapor lamp (purchased from ACE). Ice water was used as an external coolant. The resulting pale yellow solution was concentrated in vacuo and layered with *n*-pentane. Crystals suitable for X-ray analysis were obtained after several weeks at −90 °C. The crystals are extremely temperature-sensitive and rapidly disintegrate when handled outside the mother liquor.

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