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The first solid-state structure of a mixed-anion ROLi/LiOH compound: $(^t\mathrm{BuOLi})_{10}\cdot(\mathrm{LiOH})_6$

Christoph Lambert [a,b,*], Frank Hampel [a], Paul von Ragé Schleyer [a], Matthew G. Davidson [b], Ronald Snaith [b]

[a] *Institut für Organische Chemie der Universität Erlangen-Nürnberg, Henkestrasse 42, 91054 Erlangen, Germany*
[b] *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK*

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Abstract

X-Ray analysis of the title compound $(^t\mathrm{BuOLi})_{10}\cdot(\mathrm{LiOH})_6$ (**1**) which was obtained by prolonged exposure of a concentrated ^{t}BuOLi/hexane solution to moist air, has revealed a mixed-anion aggregate structure comprised of two hexagonal $(^t\mathrm{BuO})_5(\mathrm{OH})\mathrm{Li}_6$ subaggregates and a crossed LiOH ladder structure.

Keywords: Lithium; Alkoxide; Hydroxide; Mixed anion aggregate; X-ray diffraction

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1. Introduction

Mixed-anion alkali metal compounds $(\mathrm{RLi})_m\cdot(\mathrm{XLi})_n$, with R = alkyl and X = halide or alkoxide are synthetically useful reagents since their reactivity is often enhanced compared to that of the "pure" organolithium species, RLi. A number of solid-state structures are known [1]. However, mixed-anion compounds derived from a lithium alkoxide and lithium hydroxide have not been observed hitherto [2]. The X-ray analysis of $(^t\mathrm{BuOLi})_{10}\cdot(\mathrm{LiOH})_6$ (**1**) is the subject of this report.

2. Results and discussion

The solid-state structures of lithiated organic CH, NH, and OH acids complexed with R′OH ligands [4] can be regarded as models for the species which may occur, as the first reaction step, during hydrolysis of organolithium base solutions with alcohols (R′ = alkyl) or water which leads subsequently to the formation of lithium hydroxide precipitate [see Eqn. (1) for R′ = H]. However, in principle soluble mixed-anion compounds of the lithiated organic acid RLi (R = R''_3C, R''_2N, R″O) and the resulting lithium hydroxide may result from incomplete hydrolysis [Eqn. (2)] [5].

$$\mathrm{RLi} + \mathrm{H_2O} \longrightarrow \mathrm{RLi}\cdot\mathrm{OH_2} \longrightarrow \mathrm{RH} + \mathrm{LiOH} \qquad (1)$$

$$\mathrm{RLi} + \mathrm{LiOH} \longrightarrow (\mathrm{RLi})_m\cdot(\mathrm{LiOH})_n \qquad (2)$$

Exploring this possibility, prolonged but slow exposure of a concentrated ^{t}BuOLi/hexane solution to moist air over three months (in a loosely closed Schlenk tube) allowed isolation of a few crystals which were identified as a mixed-anion species, $(^t\mathrm{BuOLi})_{10}\cdot(\mathrm{LiOH})_6$ (**1**) by X-ray analysis [3] [Fig. 1(a)]. Although we could not locate the OH hydrogens in the structure, O(1), O(7) and O(8) as well as their symmetry equivalents must belong to OH groups due to the stoichiometry.

Fig. 1(b) shows **1** to be a centrosymmetric dimer of two hexagonal $(^t\mathrm{BuO})_5(\mathrm{OH})\mathrm{Li}_6$ aggregates (black framework) linked by a crossed LiOH ladder structure (open framework). Although the hexagons are comprised of five ^{t}BuOLi units and one LiOH [Li(6), O(1)] unit, the hexagonal prismatic geometry is only little affected by this substitution. The cross-like LiOH ladder moiety is fused to the two hexagons by sharing Li(6), O(1)H and Li(6a), O(1a)H (dashed bonds) with the hexagons. In addition, Li(7) and Li(7a) cap the hexagonal faces.

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[*] Corresponding author.

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Table 1
Selected Li–O distances of **1** (Å)

Li(1)–O(6)	1.877(10)	Li(1)–O(2)	1.964(9)
Li(2)–O(1)	1.964(10)	Li(8a)–O(1)	2.020(11)
Li(2)–O(2)	1.874(11)	Li(3)–O(4)	1.895(11)
Li(4)–O(3)	1.922(10)	Li(4)–O(5)	1.938(9)
Li(5)–O(4)	1.909(10)	Li(5)–O(6)	1.845(11)
Li(6)–O(5)	2.022(11)	Li(6)–O(6)	1.910(10)
Li(8)–O(1a)	2.020(10)	Li(1)–O(1)	1.905(11)
Li(8)–O(1)	1.951(10)	Li(7)–O(1)	1.968(10)
Li(6)–O(1)	2.066(10)	Li(2)–O(3)	1.967(11)
Li(3)–O(2)	1.852(11)	Li(3)–O(3)	2.040(10)
Li(7)–O(3)	2.063(9)	Li(4)–O(4)	1.837(10)
Li(5)–O(5)	2.023(10)	Li(7)–O(5)	1.994(10)
Li(6)–O(8)	2.345(11)	Li(7)–O(7)	2.260(11)
Li(8)–O(8)	2.260(12)	Li(8)–O(7a)	2.291(12)

Due to this capping, the mean Li–O distance (see Table 1) in the O(1)–Li(2)–O(3)–Li(4)–O(5)–Li(6) ring is 0.090 Å longer (1.980 Å; 1.922–2.066 Å range) than in the Li(1)–O(2)–Li(3)–O(4)–Li(5)–O(6) ring (1.890 Å; 1.845–1.964 Å range). The mean Li–O distance of the Li–O bonds connecting the two hexagonal faces is intermediate (1.932 Å; 1.837–2.040 Å range). The Li–O–Li angles in the Li(1)–O(2)–Li(3)–O(4)–Li(5)–O(6) ring are 98.0–101.7° and the O–Li–O angles are 133.2–136.2°. These angles are similar to those in hexameric $(PhMe_2COLi)_6$ which also shows small Li–O–Li angles (110.3–112.4°) and wide O–Li–O angles (123.9–126.3°) [6] However, the angle ranges are reversed in the O(1)–Li(2)–O(3)–Li(4)–O(5)–Li(6) ring of **1**: here the Li–O–Li angles are wider (128.5–129.6°) and the O–Li–O angles are smaller (100.1–108.2°). This also is due to the ring capping by Li(7) which draws the O(1), O(3) and O(5) oxygen atoms together and thus gives rise to smaller angles around Li and wider angles around oxygen.

The Li–O separations within the crossed LiOH ladder are distinctly longer (2.145 Å; 1.951–2.345 Å range) than those in the hexagons. While all Li cations of the ladder substructure are tetrahedrally coordinated by four oxygens, the O(1)H ion is six-fold coordinated but the O(7)H and O(8)H ions only two-fold.

The solid state structure of ^{t}BuOLi itself is not known exactly due to crystallographic problems with disordered tert-butyl groups but it is very likely to be a hexamer [7] as it is in the gas phase (by mass spectrometry) [8] and in benzene solution (by a thermoelectric method) [9]. In contrast, crystals of ^{t}BuONa contain nonameric and hexameric aggregates [10]. Although ladder arrangements are quite common in lithium amide structures [11] there are no examples of such an arrangement for alkali metal hydroxides. In particular, a crossed ladder structure has never been observed before, regardless of the anion. In fact, the LiOH ladder arrangement in **1** is a part of the solid-state layer structure of pure LiOH: [12] all the Li cations lie in a plane [in **1**, Li(6), Li(7), Li(8) and their symmetry equivalents] and are tetrahedrally surrounded while the OH anions are situated above [in **1**, O1(H), O(7a)H and O(8a)H] and below [in **1**, O(1a)H, O(7)H and O(8)H] the plane and are four-fold coordinated from one side.

In this manner **1** provides a unique example of a mixed-anion lithium structure which is built up from structural domains of the "pure" ^{t}BuOLi and LiOH components. Moreover, the solid-state structure of **1**

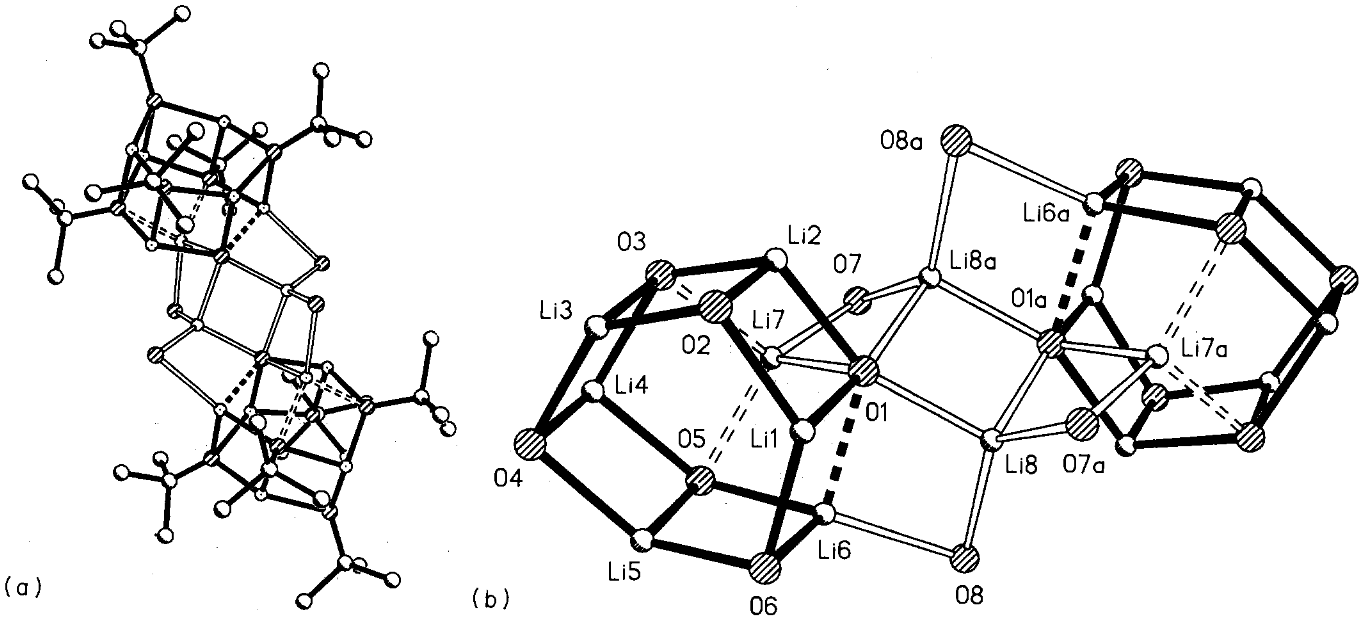

Fig. 1. (a) The structure of **1** in the solid state; hydrogen atoms are omitted for clarity; (b) the Li–O framework of **1**; the ^{t}Bu groups are omitted for clarity.

demonstrates that incomplete hydrolysis of lithium bases can yield mixed-anion hydroxide co-complexes rather than simply a conglomerate of the nonhydrolysed lithium base (in **1**, ^{t}BuOLi) and LiOH. We are currently investigating the specific and more practical conditions under which similar mixed-anion LiOH complexes can be formed.

An interesting implication is that commercially supplied or laboratory prepared "pure" RLi reagents (organometallic, R = alkyl, as well as metallated organic ones, R = amide, alkoxide) may themselves contain mixed-anion (RLi · LiOH) species due to partial (and essentially unavoidable) atmospheric hydrolysis although a white LiOH precipitate cannot be seen.

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[2] However, a mixed aggregate comprised of four molecules lithium tert-butoxide, four molecules potassium pinacolate and one molecule potassium hydroxide has been characterized by X-ray crystallography, see P.G. Williard and G.J. Mac Ewan, *J. Am. Chem. Soc., 111* (1989) 7671.

[3] Crystal data: $C_{40}H_{96}Li_{16}O_{16}$, $M = 944.2$, orthorhombic, space group *Pbca*, $a = 17.726(4)$, $b = 18.293(4)$, $c = 20.265(4)$ Å, $V = 6571(2)$ Å^3, $Z = 4$, $D_c = 0.948$ Mg m^{-3}, 13119 collected ($14.00° < 2\Theta < 54.16°$) and 7049 independent reflections and 354 parameters. $R_1 = 0.1163$ and $wR_2 = 0.2836$ $[I > 2\sigma(I)]$ for 1429 reflections. $R_1 = 0.3241$ and $wR_2 = 0.4407$ for all reflections The data were collected on a Nicolet-R3m/V four-circle diffractometer at 200(2) K using Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refinement was based on F^2 (SHELX 93), G.M. Sheldrick, Göttingen 1993) All nonhydrogen atoms were refined anisotropically, the hydrogen atoms of the ^{t}Bu groups isotropically in idealized positions. Four of the five ^{t}Bu groups show disorder which was resolved. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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