

An alkoxide cluster with 18 Li⁺ ions encapsulating two borate anions, [(^tBuO)₁₂Li₁₈(BO₃)₂]

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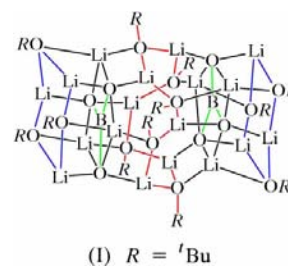
The title compound, bis(borato)dodeca(*tert*-butoxo)octadecalithium, [Li₁₈(BO₃)₂(C₄H₉O)₁₂], is formulated conveniently as [(^tBuOLi)₃(Li₃BO₃)₂(^tBuOLi)₆]. A central 12-membered ring and two outer six-membered rings are formed by alternating Li⁺ cations and alkoxide O atoms. Sandwiched between the central ring and each of the outer rings is a planar array of three further Li⁺ cations surrounding a [BO₃]³⁻ anion. Thus, the molecule consists of a cationic [Li₁₈(O^tBu)₁₂]⁶⁺ cage encapsulating two borate anions. This compound is the first example of a structurally characterized polynuclear lithium borate, and a rare case of a lithium alkoxide cage with nuclearity greater than eight. All the alkoxide ligands are triply bridging, and the lithium ions have trigonal-planar, trigonal-pyramidal and fourfold coordination, all with major distortions from regular coordination geometry.

Comment

There has been growing interest in the borates of alkali and alkaline earth metals, owing to their potential applications as optical materials. In particular, β-BaB₂O₄ (β-barium borate, BBO), discovered by Chen *et al.* (1985), is an excellent non-linear optical material, possessing many advantageous characteristics, such as a high damage threshold, good optical homogeneity, mechanical strength and chemical stability (Nikogosyan, 1991; Eimerl *et al.*, 1987). Lithium borates are also important materials for non-linear optical applications, for example, LiB₃O₅ (lithium triborate; Chen *et al.*, 1989). This compound contains a continuous network of B₃O₇ groups and Li atoms. Two B₃O₇ groups share one O atom and are connected to form endless chains running parallel to one axis. The compound is stable and not hygroscopic, with good chemical properties. Recent investigations of lithium triborate

as a non-linear medium for optical parametric oscillators showed that it is relevant for low-pump energy sources (< 3 mJ), such as in miniature solid-state systems (Withers *et al.*, 1993).

Much of the current interest in metal alkoxides arises from their use as precursors to metal oxide materials. In recent years, significant effort has been devoted to the synthesis of heterometallic alkoxides as potential single-source precursors to mixed-metal oxide ceramics, catalysts and glasses, since the well defined stoichiometries and solubilities of these alkoxides offer significant advantages for the production of single-phase materials by methods such as sol-gel, chemical vapour deposition and spray pyrolysis (Caulton & Hubert-Pfalzgraf, 1990). We have been investigating the synthesis of single-source precursors for the production of metal borates (Errington *et al.*, 1999) and report here the structure of a unique molecular species containing trigonal [BO₃]³⁻ units, viz. the title compound, (I).



The reaction between Li metal and ^tBuOH, with subsequent addition of B(O^tBu)₃ in toluene, yielded pale-yellow crystalline (I) after removal of the solvent and crystallization of the residue. The product contained crystals of various types and was not analytically pure. Mass spectral analysis was hampered by the facile decomposition of the butoxide groups. The compound is volatile and is soluble in methanol and toluene.

The molecular structure of (I) is shown in Fig. 1, with a view along the crystallographic threefold rotation axis; the central core, with alkyl substituents omitted, is shown in Fig. 2. The molecule has crystallographic $\bar{3}$ symmetry. The formula can be rewritten conveniently as [(^tBuOLi)₃(Li₃BO₃)₂(^tBuOLi)₆], to illustrate the way in which the molecule is constructed from simple units, and these units are emphasized by the different colours employed in the *Scheme* representing the structural formula in the online version of this journal. A total of 18 lithium cations and 12 alkoxide anions encapsulate two borate anions. In the centre of the molecule, six Li⁺ and six alkoxide ions form a 12-membered ring (red in the *Scheme*); this structure resembles that of [Li₆(C₄₃H₆₁O₃)₂], a lithium complex of a tridentate ligand that effectively enforces such a geometric arrangement (Dinger & Scott, 2000), but seems to be otherwise unknown in lithium alkoxide chemistry. Each end of the molecule is formed by a chair-shaped Li₃O₃ ring of three cations and three alkoxide anions (blue in the *Scheme*), which is a common motif in lithium alkoxide and amide structural chemistry. Sandwiched between the central ring and each end ring is a planar borate anion (green in the *Scheme*),

with three charge-balancing Li^+ cations bridging pairs of borate O atoms. As a result, 12 of the cations have threefold coordination (pyramidal for Li1 in the end rings, and essentially planar for Li3 in the centre ring), and the other six cations, linking the end and centre rings, have a distorted fourfold coordination (Li2), all bonds to lithium being from the O atoms of alkoxide and borate anions. All 12 alkoxide ligands are triply bridging, while the borate O atoms coordinate to four lithium ions each, as well as being bonded to B atoms, and thus have a high coordination number for O atoms. Nevertheless, the B—O bonds are not unusually long (Table 1). Li—O bond lengths range from 1.862 (5) to 2.194 (5) Å, both the shortest and the longest being for Li2, which can be regarded as having a primary twofold coordination, with its shortest bonds being to the end and centre lithium alkoxide rings, and two weaker interactions with a borate anion. This structure reinforces the view of the molecule as a cationic $[\text{Li}_{18}(\text{O}'\text{Bu})_{12}]^{6+}$ cage encapsulating two intact and recognizable borate anions.

The molecular structure of (I) is unusual in a number of ways. High-nuclearity lithium alkoxides are rare; heteroleptic lithium complexes of simple alkoxides and aryloxides are usually small cage or ring oligomers with up to eight lithium centres, and incorporation of neutral auxiliary ligands generally reduces the nuclearity, with four-membered ring dimers and pseudo-cubanes being common [a search of the Cambridge Structural Database (Version 5.24, update of February 2003; Allen, 2002) gives about 30 relevant structures]. An exception is the polymeric chain structure of lithium phenolate (Dinnebier *et al.*, 1997). Lithium alkoxides of higher nuclearity are found only with additional bridging ligands, such as in $[\text{Li}_{33}\text{H}_{17}(\text{O}'\text{Bu})_{16}]$ (Hoffmann *et al.*, 1998) and $[\text{Li}_{16}(\text{OH})_6(\text{O}'\text{Bu})_{10}]$ (Lambert *et al.*, 1995); the homoleptic $[\text{Li}_{12}(\text{OO}'\text{Bu})_{12}]$ peroxide complex is dodecanuclear (Boche *et al.*, 1996).

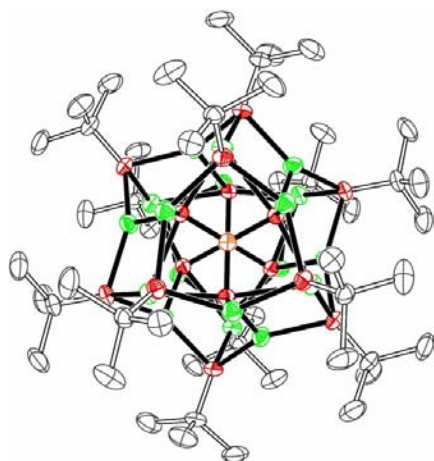


Figure 1
A view of the molecule of (I) along the c axis, showing the $\bar{3}$ symmetry. Bonds to C atoms are hollow and other bonds are filled. Displacement ellipsoids are shown at the 30% probability level and H atoms have been omitted.

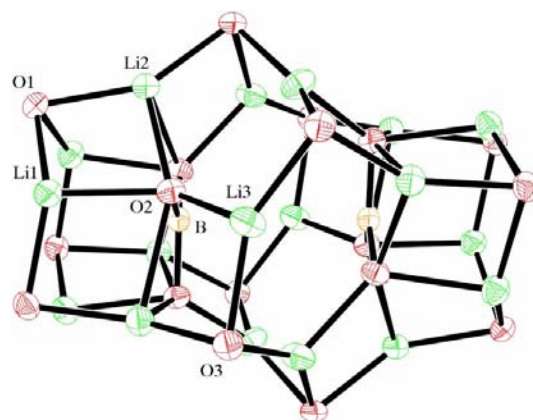


Figure 2
The core of the molecule of (I), with *tert*-butyl substituents omitted. Atoms of the asymmetric unit are labelled.

As far as we are aware, there are no previously reported polynuclear lithium borate complexes. Only one example is known of a $[\text{BO}_3]^{3-}$ anion coordinated to three metal atoms, *viz.* $[\text{BO}_3(\text{SnPh}_3)_3]$ (Ferguson *et al.*, 1995), analogous to the corresponding silicon compound, $[\text{BO}_3(\text{SiPh}_3)_3]$, which is known in two solvate forms (Murphy *et al.*, 1993; Beckett *et al.*, 1998).

Experimental

A solution of $\text{B}(\text{O}'\text{Bu})_3$ (1.91 ml, 6.75 mmol) in toluene (15 ml) was added to $\text{LiO}'\text{Bu}$ (0.54 g, 6.75 mmol). The mixture was heated to dissolve the reactants, and the resulting solution was filtered and the solvent removed *in vacuo*. Recrystallization from toluene (10 ml), with cooling to 243 K, gave a large crop of crystals over a period of two months.

Crystal data

$[\text{Li}_{18}(\text{BO}_3)_2(\text{C}_4\text{H}_9\text{O})_{12}]$
 $M_r = 1119.88$
 Trigonal, $R\bar{3}$
 $a = 19.917(3)$ Å
 $c = 15.608(3)$ Å
 $V = 5362.0(16)$ Å³
 $Z = 3$
 $D_x = 1.040$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 1806 reflections
 $\theta = 2.7\text{--}25.6^\circ$
 $\mu = 0.07$ mm⁻¹
 $T = 200(2)$ K
 Block, colourless
 $0.28 \times 0.26 \times 0.20$ mm

Data collection

Bruker SMART 1K CCD diffractometer
 Narrow-frame ω scans
 6484 measured reflections
 2682 independent reflections
 1502 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.070$
 $\theta_{\text{max}} = 28.5^\circ$
 $h = -12 \rightarrow 26$
 $k = -16 \rightarrow 24$
 $l = -19 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.078$
 $wR(F^2) = 0.153$
 $S = 1.13$
 2682 reflections
 136 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0283P)^2 + 9.227P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.17$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.18$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Li1—O1	1.906 (5)	Li3—O2	1.901 (5)
Li1—O1 ⁱ	1.890 (5)	Li3—O3	1.942 (5)
Li1—O2	2.006 (5)	Li3—O3 ⁱⁱⁱ	1.900 (5)
Li2—O1	1.913 (4)	O1—C1	1.421 (3)
Li2—O2	1.989 (5)	O2—B	1.3799 (16)
Li2—O2 ⁱⁱ	2.194 (5)	O3—C3	1.414 (3)
Li2—O3 ⁱⁱ	1.862 (5)		
O1—Li1—O1 ⁱ	133.2 (3)	O2—Li2—O3 ⁱⁱ	114.1 (2)
O1—Li1—O2	95.3 (2)	O2 ⁱⁱ —Li2—O3 ⁱⁱ	94.96 (19)
O1 ⁱ —Li1—O2	101.5 (2)	O2—Li3—O3	102.5 (2)
O1—Li2—O2	95.7 (2)	O2—Li3—O3 ⁱⁱⁱ	111.4 (2)
O1—Li2—O2 ⁱⁱ	94.38 (19)	O3—Li3—O3 ⁱⁱⁱ	145.8 (3)
O1—Li2—O3 ⁱⁱ	150.2 (3)	O2—B—O2 ⁱⁱ	119.86 (3)
O2—Li2—O2 ⁱⁱ	69.44 (16)		

Symmetry codes: (i) $1 - y, 1 + x - y, z$; (ii) $-x + y, 1 - x, z$; (iii) $y - \frac{1}{3}, \frac{1}{3} - x + y, \frac{4}{3} - z$.

Cooling the crystals to below 200 K led to fragmentation, presumably as a result of a phase transition. At 200 K, high-angle data are relatively weak because of the high displacement of atoms of the alkyl groups, leading to a structure of only moderate precision. H atoms were located from a difference map, and were then positioned geometrically and refined with a riding model, including free methyl rotation about C—C bonds, with $U_{\text{iso}}(\text{H})$ values equal to $1.5U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Bruker, 2001); cell refinement: local programs; data reduction: *SAINTE* (Bruker, 2001); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1167). Services for accessing these data are described at the back of the journal.

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