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Tetrakis(μ_3-phenoxo-acetonitrilelithium), a tetrameric lithium aryloxide with a cubane core

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The title compound, $(CH_3CNLiOC_6H_5)_4$ or $[Li_4(C_6H_5O)_4(C_2H_3N)_4]$, is tetrameric with a distorted Li_4O_4 cube core. The molecule has crystallographic $\overline{4}$ symmetry. Each Li atom has distorted tetrahedral coordination, with bonds to three triply bridging phenoxo ligands and a terminal acetonitrile ligand derived from the solvent in the synthesis.

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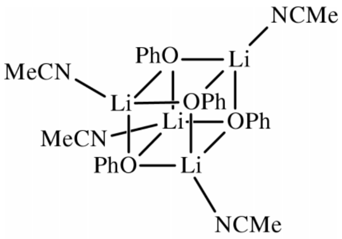
Key indicators

Single-crystal X-ray study
T = 160 K
Mean σ(C–C) = 0.002 Å
R factor = 0.042
wR factor = 0.102
Data-to-parameter ratio = 18.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

In recent years, metal alkoxides have been intensively studied and have generated much interest owing to their use as precursors in thin-film metal oxide production *via* sol-gel and chemical vapour deposition processes (Bradley, 1989; Herrmann *et al.*, 1995). Particular attention has been given to metal alkoxides for their potential applications as precursors to fine ceramic materials, for the possibility of creating novel structures, for the formation of oxoalkoxides by hydrolysis or other reactions, for the production of molecular heterometallic alkoxides, and for the considerable catalytic activity of these compounds (Mehrotra *et al.*, 1994*a*). Alkoxide compounds of some elements have attracted increasing interest in the glass, ceramics, and composite materials industries (American Ceramic Society, 1993); alkoxides of Si, Al, B and Li are used in glass production, and those of Ti, Zr, Ba, Nb, Sr, and Mg are used for electronic ceramics.



(I)

Among alkali metal alkoxides, derivatives of lithium are found to have the greatest degree of covalency, as demonstrated by their solubility in common organic solvents (Mehrotra *et al.*, 1994*b*). The stability of lithium alkoxides increases in the order LiOEt < LiO^{i}Pr < LiO^{t}Bu, and in the same order they become less polymeric and more volatile. There have been numerous publications in the area of lithium phenolate compounds. Various lithium phenolates having dimeric (Matilainen *et al.*, 1995), trimeric (van der Schaaf *et al.*, 1992) and hexameric (van der Schaaf *et al.*, 1993) structures have been reported. Among lithium compounds structurally characterized to date, the most common coordination number is four, though occasionally coordination numbers of three and two are found.

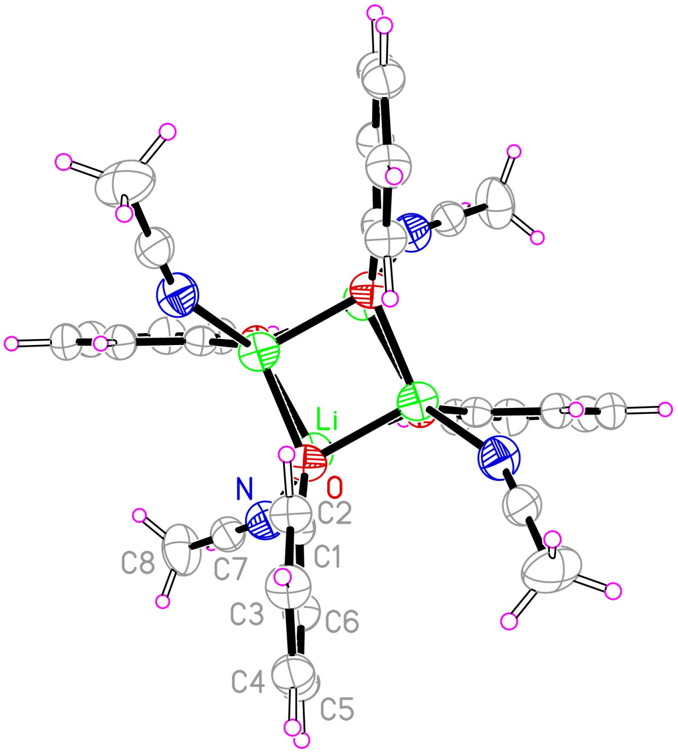


Figure 1
The molecular structure of (I) with 50% probability ellipsoids for non-H atoms. The view is along the crystallographic $\overline{4}$ axis, and only non-H atoms of the asymmetric unit are labelled.

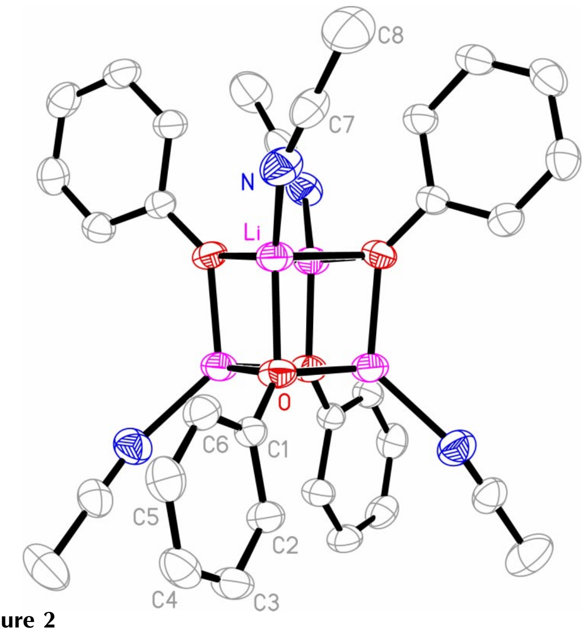


Figure 2
An alternative view of the molecule, without H atoms, highlighting the Li_4O_4 distorted cubane core.

A reaction between LiOPh and $B(O^tBu)_3$, in an attempt to produce a boron-containing lithium phenolate, resulted in a colourless solution, with THF, toluene, diethyl ether and acetonitrile as solvents. From THF, we obtained a crystalline product, but this was identified as the known hexamer $[(THF)Li(OPh)_6]$ (Jackman *et al.*, 1993), $B(O^tBu)_3$ remaining in solution. From acetonitrile as solvent, we obtained the title compound, (I), $B(O^tBu)_3$ again remaining unchanged in solution. The previously unreported structure of the product is presented here (Figs. 1 and 2).

Incorporation of acetonitrile as a ligand converts the hexameric starting material into a tetrameric molecule. Distorted cubane-like M_4X_4 clusters occur as a frequent structural motif in both main-group and transition metal chemistry, with over 1800 reported crystal structures containing such a fragment. The Cambridge Structural Database (Version 5.23, November 2002; Allen, 2002) contains 42 examples with an Li_4O_4 core. Most of these have ligands X that are chelating as well as triply bridging, so that Li is additionally coordinated by another group in the same ligand. Only seven reported structures have no chelating function for X, and have a single additional ligand on each Li atom, as in the title compound. These include alkoxides, enolates, and a phosphine oxide complex (Seebach *et al.*, 1985; Pospisil *et al.*, 1992; Hoskin & Stephan, 1999; Boyle *et al.*, 2000). The mean Li—O bond length in these structures is 1.970 Å, with a range of 1.900–2.046 Å; eight of the 12 Li—O bonds in (I) lie towards the lower end of this range, while the other four are near the upper end (Table 1). No simple pattern is discernible in the distribution of Li—O bonds in these molecules. The crystallographic symmetry of the tetrameric molecule of (I) is $\overline{4}$, which is the approximate symmetry of the other compounds. In all cases, the angular distortion of the Li_4O_4 core from a perfect cube is similar, with O—Li—O angles a few degrees above, and Li—O—Li angles correspondingly below, 90°.

The coordination of each Li is distorted tetrahedral, with bonds to three triply bridging phenoxo ligands and to a terminal acetonitrile ligand. This ligand is somewhat bent at N, but essentially linear at the nitrile C atom (Table 1).

There are no unusual intermolecular interactions, the molecular packing involving only van der Waals forces.

Experimental

LiOPh (0.6 g, 6 mmol) was dissolved in 10 ml of THF. To this solution, $B(O^tBu)_3$ (1.7 ml, 6 mmol) was added dropwise with a syringe, resulting in the formation of a colourless solution. This was filtered, and the solvent was removed *in vacuo* to give a white powder. The powder was dissolved in acetonitrile; cooling to 243 K produced a large crop of crystals (yield: 1.12 g).

Crystal data

$[Li_4(C_6H_5O)_4(C_2H_3N)_4]$
$M_r = 564.38$
Tetragonal, $I4_1/a$
$a = 14.1961\ (19)$ Å
$c = 15.869\ (2)$ Å
$V = 3198.0\ (7)$ Å^3
$Z = 4$
$D_x = 1.172$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 6123 reflections
$\theta = 1.9–28.6°$
$\mu = 0.08$ mm^{-1}
$T = 160\ (2)$ K
Block, colourless
0.40 × 0.32 × 0.28 mm

Data collection

Bruker SMART 1K CCD diffractometer
Narrow-frame ω scans
Absorption correction: none
9983 measured reflections
1918 independent reflections

1645 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 28.6°$
$h = -18 \rightarrow 15$
$k = -11 \rightarrow 18$
$l = -21 \rightarrow 21$

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.102$
$S = 1.11$
1918 reflections
102 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0353P)^2 + 1.6883P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0022 (5)

Table 1
Selected geometric parameters (Å, °).

Li—O	1.924 (2)	O—C1	1.3290 (13)
Li—O^{i}	1.923 (2)	N—C7	1.1310 (17)
Li—O^{ii}	2.034 (2)	C7—C8	1.448 (2)
Li—N	2.018 (2)		
O—Li—O^{i}	96.60 (9)	Li^{ii}—O—Li^{i}	83.97 (10)
O^{i}—Li—O^{ii}	95.91 (10)	Li—O—Li^{i}	83.35 (9)
O—Li—O^{ii}	93.01 (9)	Li—O—C1	136.34 (10)
O—Li—N	127.85 (12)	Li^{ii}—O—C1	131.97 (9)
O^{i}—Li—N	127.02 (11)	Li^{i}—O—C1	115.85 (9)
O^{ii}—Li—N	107.25 (10)	Li—N—C7	157.42 (13)
Li—O—Li^{ii}	86.39 (9)	N—C7—C8	179.01 (16)

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

After confirming their location in a difference map, H atoms were positioned geometrically and refined with a riding model (including free methyl rotation about C—C bonds), and with $U_{\rm iso}$ values constrained to be 1.2 (1.5 for methyl groups) times $U_{\rm eq}$ of the carrier atom.

Data collection: *SMART* (Bruker, 2001); cell refinement: local programs; data reduction: *SAINT* (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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