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A triclinic polymorph of octa-*tert*-butoxytetralithiumtetrasodium

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Key indicators

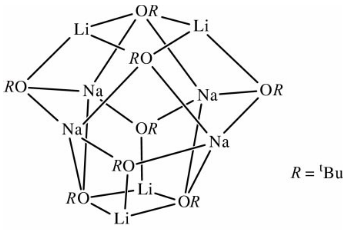
Single-crystal X-ray study
T = 160 K
Mean σ(C–C) = 0.003 Å
R factor = 0.036
wR factor = 0.094
Data-to-parameter ratio = 16.4

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

The title compound, tetra-μ_3-*tert*-butoxy-tetra-μ_4-*tert*-butoxytetralithiumtetrasodium, $[Li_4Na_4(C_4H_9O)_8]$, has been obtained in a second, triclinic, modification, with three crystallographically independent molecules in the asymmetric unit. All three molecules, as well as the two independent molecules of a previously reported monoclinic polymorph, have essentially the same structure, in which the *tert*-butoxy ligands are either triply or quadruply bridging, Li^+ cations have trigonal pyramidal coordination, and Na^+ cations have irregular fourfold coordination. The molecules have no crystallographic symmetry, but approximate to $\overline{4}2m$ (D_{2d}) symmetry.

Comment

We recently reported the structures of the complete series of compounds $[Li_4M_4(^tBuO)_8]$, where M is Na, K, Rb and Cs (Clegg *et al.*, 1999; Armstrong *et al.*, 2000). Despite the differences in atomic size of the four heavier alkali metals, all the compounds have the same basic molecular structure, which is a tetramer with a 'breastplate-like' appearance, having a planar and essentially square arrangement of four M^+ ions sandwiched between two $\{(^tBuO)_4Li_2\}^{2-}$ dianions, the overall molecular symmetry being $\overline{4}2m$ (D_{2d}). This common structure for all the compounds contrasts with the variety found for the homometallic *tert*-butoxides: those of K, Rb and Cs are tetrameric (Weiss *et al.*, 1967, 1968; Chisholm *et al.*, 1991; Mann & Jansen, 1994), the Li compound is hexameric (Thomas *et al.*, 1998), and the Na compound is both hexameric and nonameric in the same crystal structure (Davies *et al.*, 1982); none of them has an octanuclear structure. There appears to be no precedent for a complete set of homologous alkali metal complexes with the same molecular architecture, and these compounds are unusual in metal alkoxide chemistry generally (Bradley *et al.*, 2001).



(I)

During experiments to confirm the reproducibility of the syntheses of these compounds, preparation of the mixed lithium–sodium complex by essentially the same route as

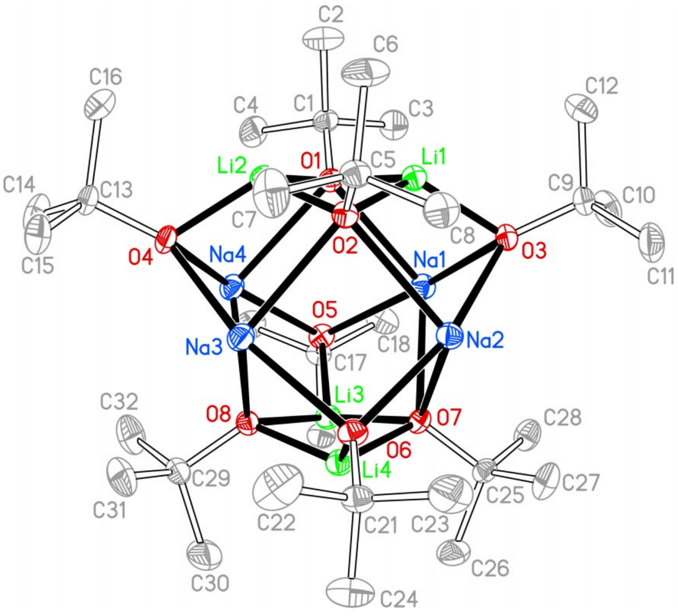


Figure 1

The structure of molecule *A*, with generic atom labels and 50% probability ellipsoids. H atoms have been omitted. Partially obscured atoms C19 and C20 are not labelled.

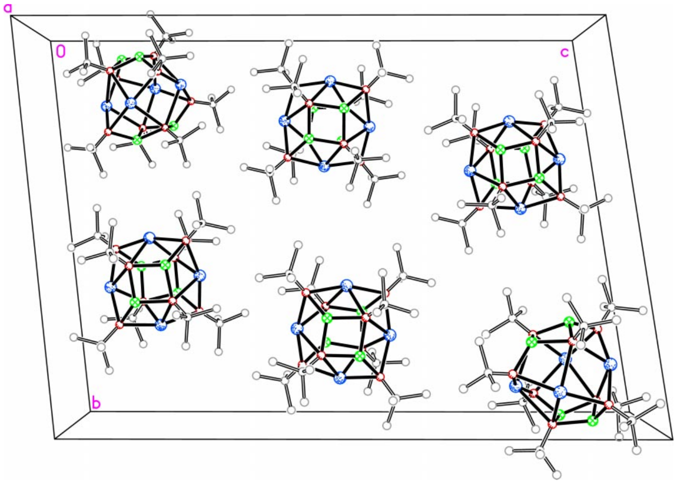


Figure 2

The six molecules (three inversion-related pairs) in the unit cell.

Table 1

Selected geometric parameters (Å, °).

Na1*A*—O1*A*	2.5184 (13)	Na4*B*—O5*B*	2.3481 (13)
Na1*A*—O3*A*	2.3200 (12)	Na4*B*—O8*B*	2.4916 (13)
Na1*A*—O5*A*	2.3104 (12)	Li1*B*—O1*B*	1.890 (3)
Na1*A*—O7*A*	2.5205 (13)	Li1*B*—O2*B*	1.902 (3)
Na2*A*—O2*A*	2.5289 (13)	Li1*B*—O4*B*	1.824 (3)
Na2*A*—O3*A*	2.3320 (13)	Li2*B*—O1*B*	1.903 (3)
Na2*A*—O6*A*	2.3136 (13)	Li2*B*—O2*B*	1.895 (3)
Na2*A*—O7*A*	2.5100 (12)	Li2*B*—O3*B*	1.828 (3)
Na3*A*—O2*A*	2.5000 (13)	Li3*B*—O5*B*	1.828 (3)
Na3*A*—O4*A*	2.3285 (13)	Li3*B*—O7*B*	1.897 (3)
Na3*A*—O6*A*	2.3426 (13)	Li3*B*—O8*B*	1.907 (3)
Na3*A*—O8*A*	2.5341 (12)	Li4*B*—O6*B*	1.827 (3)
Na4*A*—O1*A*	2.5125 (13)	Li4*B*—O7*B*	1.892 (3)
Na4*A*—O4*A*	2.3177 (13)	Li4*B*—O8*B*	1.913 (3)
Na4*A*—O5*A*	2.3071 (13)	Na1*C*—O1*C*	2.5776 (13)
Na4*A*—O8*A*	2.5151 (13)	Na1*C*—O3*C*	2.2890 (13)
Li1*A*—O1*A*	1.897 (3)	Na1*C*—O5*C*	2.2704 (13)
Li1*A*—O2*A*	1.906 (3)	Na1*C*—O8*C*	2.5882 (13)
Li1*A*—O3*A*	1.839 (3)	Na2*C*—O2*C*	2.5332 (13)
Li2*A*—O1*A*	1.887 (3)	Na2*C*—O4*C*	2.3113 (13)
Li2*A*—O2*A*	1.892 (3)	Na2*C*—O6*C*	2.3137 (13)
Li2*A*—O4*A*	1.846 (3)	Na2*C*—O7*C*	2.5628 (13)
Li3*A*—O5*A*	1.843 (3)	Na3*C*—O2*C*	2.5041 (13)
Li3*A*—O7*A*	1.896 (3)	Na3*C*—O3*C*	2.3574 (13)
Li3*A*—O8*A*	1.895 (3)	Na3*C*—O6*C*	2.3526 (13)
Li4*A*—O6*A*	1.834 (3)	Na3*C*—O8*C*	2.4887 (13)
Li4*A*—O7*A*	1.898 (3)	Na4*C*—O1*C*	2.4985 (13)
Li4*A*—O8*A*	1.896 (3)	Na4*C*—O4*C*	2.3276 (13)
Na1*B*—O1*B*	2.5372 (14)	Na4*C*—O5*C*	2.3395 (13)
Na1*B*—O3*B*	2.2895 (14)	Na4*C*—O7*C*	2.4934 (12)
Na1*B*—O5*B*	2.3059 (14)	Li1*C*—O1*C*	1.893 (3)
Na1*B*—O7*B*	2.6030 (15)	Li1*C*—O2*C*	1.908 (3)
Na2*B*—O2*B*	2.5735 (13)	Li1*C*—O3*C*	1.833 (3)
Na2*B*—O3*B*	2.3178 (14)	Li2*C*—O1*C*	1.893 (3)
Na2*B*—O6*B*	2.3112 (14)	Li2*C*—O2*C*	1.899 (3)
Na2*B*—O7*B*	2.5375 (14)	Li2*C*—O4*C*	1.824 (3)
Na3*B*—O2*B*	2.4986 (13)	Li3*C*—O5*C*	1.836 (3)
Na3*B*—O4*B*	2.3491 (13)	Li3*C*—O7*C*	1.896 (3)
Na3*B*—O6*B*	2.3449 (13)	Li3*C*—O8*C*	1.893 (3)
Na3*B*—O8*B*	2.4775 (13)	Li4*C*—O6*C*	1.827 (3)
Na4*B*—O1*B*	2.4955 (13)	Li4*C*—O7*C*	1.898 (3)
Na4*B*—O4*B*	2.3251 (13)	Li4*C*—O8*C*	1.901 (3)

previously reported led to crystals with a noticeably different habit. Preliminary X-ray diffraction indicated a different unit cell, and so we determined the crystal structure in full. The result is a second polymorphic modification of the compound. Like the previously reported form, it is unsolvated. This structure is triclinic, with three molecules in the asymmetric unit, whereas the other is monoclinic, with two molecules in the asymmetric unit. One molecule of the triclinic form is shown in Fig. 1, with generic atom labels; atoms of the three independent molecules are identified by a suffix *A*, *B* or *C*. Bond distances for the metal ions are given in Table 1.

There are no chemically significant differences among the three crystallographically independent molecules of this triclinic polymorph, or indeed within the whole set of molecules of both polymorphs. In each case, Li^+ cations are coordinated by three *tert*-butoxy ligands in a trigonal pyramidal arrangement, and Na^+ cations have a highly distorted fourfold coordination geometry. Half the ligands are triply bridging (to one Li^+ and two Na^+) and half are quadruply bridging (to two Li^+ and two Na^+). Li—O bond lengths range from 1.824 (3) to 1.913 (3) Å, while Na—O bond lengths cover the rather wider range 2.2704 (13)–2.6030 (15) Å, each Na^+ ion having two shorter and two longer bonds, to μ_3- and μ_4-O atoms, respectively. In the homometallic *tert*-butoxy oligomers, all ligands are triply bridging. Further details of the molecular structures, together with theoretical calculations for comparison, are discussed by Armstrong *et al.* (2000).

There are no significant intermolecular interactions. The molecules are effectively covered by a sheath of H atoms and are essentially close packed (Fig. 2).

Experimental

The compound was prepared as described by Armstrong *et al.* (2000), but essentially the same procedure and conditions on this occasion produced a different polymorph.

Acta Cryst. (2003). E**59**, m64–m66 William Clegg *et al.* • $[Li_4Na_4(C_4H_9O)_8]$ **m65**

Crystal data

$[Li_4Na_4(C_4H_9O)_8]$
$M_r = 704.62$
Triclinic, $P\bar{1}$
$a = 11.1917\ (8)$ Å
$b = 21.0007\ (14)$ Å
$c = 29.450\ (2)$ Å
$\alpha = 82.560\ (2)^\circ$
$\beta = 89.492\ (2)^\circ$
$\gamma = 82.033\ (2)^\circ$
$V = 6796.8\ (8)$ Å^3
$Z = 6$
$D_x = 1.033$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 28018 reflections
$\theta = 2.3$–28.1°
$\mu = 0.10$ mm^{-1}
$T = 160\ (2)$ K
Block, colourless
0.82 × 0.80 × 0.80 mm

Data collection

Bruker SMART 1K CCD diffractometer
Fine-slice ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
$T_{\min} = 0.890$, $T_{\max} = 0.950$
32571 measured reflections
22410 independent reflections
15221 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\max} = 25.0^\circ$
$h = -13 \rightarrow 12$
$k = -24 \rightarrow 24$
$l = -33 \rightarrow 35$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.094$
$S = 0.92$
22410 reflections
1370 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.00064 (9)

H atoms were placed geometrically and refined with a riding model (including free rotation about C—C bonds), and with $U_{\rm iso} = 1.5U_{\rm eq}$(C).

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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