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Acta Cryst. (1984). **C40**, 372–374

Structure of Tetrakis[μ_3 -(4-methoxy-2-butyl)-O, μ_3 -C²]tetralithium, [Li₄(C₅H₁₁O)₄]

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(Received 26 July 1983; accepted 1 November 1983)

Abstract. $M_r = 376.33$, tetragonal, $P\bar{4}b2$, $a = 12.389$ (3), $c = 8.218$ (1) Å, $U = 1261.4$ (5) Å³, $Z = 2$, $D_x = 0.991$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 4.3$ cm⁻¹, $F(000) = 416$, $T = 295$ K, $R = 0.046$ for 664 observed reflections with $I > 2.5\sigma(I)$. 3-Lithio-1-methoxybutane crystallizes from pentane as chelated *meso* tetramers with 4 site symmetry. The four Li atoms form a slightly distorted tetrahedron.

Introduction. Any attempt to understand the enhanced reactivity exhibited by Lewis-base adducts of alkyl-lithium tetramers in certain reactions – Wurtz coupling (Eastham & Gibson, 1963), iodine–lithium exchange (Appelquist & O'Brien, 1963), bromine–lithium exchange (Rogers & Houk, 1982), ethylenation reaction (Bartlett, Goebel & Weber, 1969) – requires the knowledge of structure and bonding in these species. So far ⁷Li NMR has revealed the tetrahedral nature of alkyl-lithiums dissolved in diethyl ether (Brown, 1970; McKeever, 1972). More detailed information about the structure of alkyl-lithium etherates has remained unavailable due to the failure to obtain crystalline materials from these solutions. We now report the crystal structure of the intramolecularly etherated title compound that was obtained from the corresponding Hg derivative by reaction with Li in pentane (Geurink,

1982). A preliminary discussion of the results has been given previously (Klumpp, Geurink, Spek & Duisenberg, 1983).

Experimental. Enraf–Nonius CAD-4F diffractometer, block-shaped (~0.5 × 0.5 × 0.5 mm) transparent colourless crystal mounted under vacuum in a Lindemann-glass capillary [$\theta < 70^\circ$, $\omega/2\theta$ scan, $+h, +k, +l: k > h$; Cu $K\alpha$ (Ni-filtered)]. 868 reflections collected and corrected for Lorentz–polarization effects and for long- and short-term instabilities as monitored by four reference reflections ($322, \bar{3}2\bar{2}, \bar{3}2\bar{2}, 3\bar{2}\bar{2}$): max. correction 2%, no indication of decay, 752 unique reflections. The observed extinctions for $0kl$ ($k = 2n + 1$) did not fix the space group uniquely. The correct symmetry was deduced *via* the successful structure determination and refinement in space group $P\bar{4}b2$. Solution by direct methods, refinement by full-matrix least-squares techniques on F : all non-hydrogen atoms with anisotropic thermal parameters and the H atoms with one overall isotropic thermal parameter, and all positional parameters; H-atom positions from a difference Fourier map. Final $R = 0.0457$, $wR = 0.0459$ [$w = 1$, 664 reflections with $I > 2.5\sigma(I)$]; $(\Delta/\sigma)_{\text{max}} = 0.4$; 74 parameters; minimum and maximum residual densities $-0.11, 0.13$ e Å⁻³.

Scattering factors from Cromer & Mann (1968). All calculations carried out on either the Cyber-175 of the University of Utrecht with programs of the *MULTAN80* (Main *et al.*, 1980), *APOLLO* (data reduction by ALS) and *EUCLID* (Spek, 1982) packages or on the in-house *ECLIPSE-S/230* mini-computer with a locally adapted version of the *SHELX76* package (Sheldrick, 1976).*

Discussion. The final parameters are given in Table 1. The crystal structure of the title compound consists of discrete tetrameric units, located at positions with $\bar{4}$ site symmetry (Fig. 1). The four Li atoms form a slightly distorted tetrahedron. To each face a 1-methoxybutane moiety is attached by four-centre bonding *via* a chiral carbon atom [C(2)]. In addition, each Li atom is coordinated intramolecularly by one of the O atoms. Each tetramer contains two molecules with the *R* configuration and two with the *S* configuration. The molecular geometry is similar to that found in the related structure of $[2-(\text{CH}_2\text{NMe}_2)-\text{C}_6\text{H}_4\text{Li}]_4$ (Jastrzebski, van Koten, Konijn & Stam, 1982). The somewhat larger torsion angle O—C(4)—C(3)—C(2), $61.6(3)^\circ$, in the present study as compared to the corresponding angles N(8)—C(7)—C(2)—C(1), 48.2 and 52.0° , in $[2-(\text{CH}_2\text{NMe}_2)-\text{C}_6\text{H}_4\text{Li}]_4$ reflects *inter*

* Lists of structure factors, anisotropic thermal parameters and bond distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39001 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

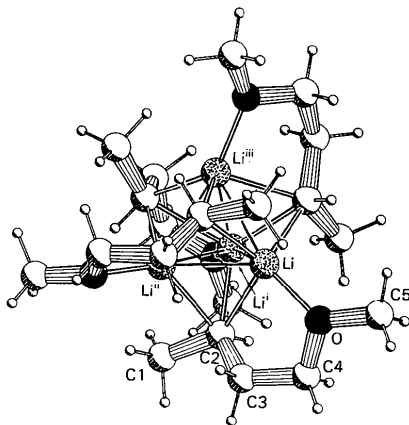


Fig. 1. Drawing of the tetrameric 3-lithio-1-methoxybutane molecule along with the adopted numbering scheme. The symmetry codes i, ii and iii are explained in Table 2. The crystallographic $\bar{4}$ axis passes through the midpoints of the two opposing central Li tetrahedral edges $\text{Li}^i, \text{Li}^{ii}$ and $\text{Li}^i, \text{Li}^{iii}$ respectively. The lines within and to the Li nucleus represent short distances rather than simple bonds.

Table 1. *Final coordinates and equivalent isotropic thermal parameters*

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
O	-0.0122 (2)	0.2184 (2)	0.7450 (2)	0.0676 (6)
Li	-0.0340 (4)	0.0939 (4)	0.6092 (6)	0.0585 (9)
C(1)	0.2271 (2)	-0.0475 (2)	0.6810 (4)	0.0693 (8)
C(2)	0.1484 (2)	0.0480 (2)	0.6560 (4)	0.0580 (7)
C(3)	0.1363 (3)	0.1039 (2)	0.8225 (4)	0.0629 (7)
C(4)	0.0939 (2)	0.2191 (2)	0.8154 (4)	0.0686 (8)
C(5)	-0.0592 (3)	0.3237 (3)	0.7378 (5)	0.0910 (8)
H(1)	0.1863 (2)	-0.1116 (2)	0.7455 (4)	0.089 (2)
H(2)	0.2961 (2)	-0.0210 (2)	0.7506 (4)	0.089 (2)
H(3)	0.2535 (2)	-0.0767 (2)	0.5638 (4)	0.089 (2)
H(4)	0.2142 (3)	0.1041 (2)	0.8813 (4)	0.089 (2)
H(5)	0.0801 (3)	0.0573 (2)	0.8944 (4)	0.089 (2)
H(6)	0.1473 (2)	0.2670 (2)	0.7408 (4)	0.089 (2)
H(7)	0.0908 (2)	0.2527 (2)	0.9366 (4)	0.089 (2)
H(8)	0.190 (2)	0.105 (1)	0.593 (2)	0.089 (2)
H(9)	-0.1387 (3)	0.3183 (3)	0.6846 (5)	0.089 (2)
H(10)	-0.0092 (3)	0.3758 (3)	0.6643 (5)	0.089 (2)
H(11)	-0.0653 (3)	0.3563 (3)	0.8593 (5)	0.089 (2)

Table 2. *Relevant data on the geometry of $(\text{C}_5\text{H}_{11}\text{OLi})_4$*

Bond distances (Å)			
Li—Li ⁱ	2.506 (7)	Li ⁱ —C(2)	2.288 (6)
Li—Li ⁱⁱ	2.474 (7)	Li ⁱⁱ —C(2)	2.291 (6)
Li—O	1.923 (5)	O—C(4)	1.436 (4)
Li—C(2)	2.362 (6)	O—C(5)	1.429 (4)
C(1)—C(2)	1.546 (4)	C(2)—C(3)	1.541 (4)
C(3)—C(4)	1.523 (4)		
Bond angles (°)			
O—Li—Li ⁱ	124.4 (3)	Li ⁱ —C(2)—Li ⁱⁱ	66.4 (2)
O—Li—Li ⁱⁱ	135.0 (3)	Li ⁱ —Li—Li ⁱⁱ	60.4 (2)
O—Li—Li ⁱⁱⁱ	164.6 (3)	Li ⁱ —Li—Li ⁱⁱⁱ	59.2 (2)
O—Li—C(2)	88.0 (2)	C(1)—C(2)—C(3)	106.7 (3)
O—Li—C(2 ⁱⁱ)	127.2 (3)	C(2)—C(3)—C(4)	114.9 (3)
O—Li—C(2 ⁱⁱⁱ)	109.1 (2)	O—C(4)—C(3)	109.0 (2)
Li—C(2)—Li ⁱ	65.2 (2)	C(5)—O—C(4)	112.6 (2)
Li—C(2)—Li ⁱⁱ	64.2 (2)		
Torsion angles (°)			
C(1)—C(2)—C(3)—C(4)	160.5 (3)	C(2)—C(3)—C(4)—O	61.6 (3)
C(3)—C(4)—O—C(5)	178.4 (3)		

Symmetry code: (i) $y, -x, 1 - z$; (ii) $-x, -y, z$; (iii) $-y, x, 1 - z$.

alia the difference in the hybridization at the C atoms that partake in the four-centre bonding and the ones that are directly bonded to them, *i.e.* sp^3 and sp^2 respectively. The perpendicular C to Li-triangle distance [$1.809(17)$ Å] in the title compound is significantly greater than the average value 1.747 Å in $[2-(\text{CH}_2\text{NMe}_2)-\text{C}_6\text{H}_4\text{Li}]_4$, whereas the average Li—Li distance $2.490(7)$ Å is significantly smaller than the corresponding average $2.566(11)$ Å. Table 2 lists additional data on the geometry.

The investigations were supported in part (ALS) by the Netherlands Foundation for Chemical Research (SON) with financial aid from The Netherlands Organization for Advancement of Pure Research (ZWO).

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Acta Cryst. (1984). **C40**, 374–376

Structure of Lead(II) D-Gluconate, $Pb[C_6H_{11}O_7]_2$

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(Received 22 March 1983; accepted 4 November 1983)

Abstract. $M_r = 597.5$, trigonal, $P3_221$, $a = 5.498$ (5), $c = 47.28$ (5) Å, $V = 1238$ Å³, $Z = 3$, $D_x = 2.40$, $D_m = 2.40$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 10.2$ mm⁻¹, $F(000) = 864$, $T = 293$ K. Final $R = 0.037$ for 838 non-zero reflexions. The Pb atom lies on the twofold axis and is surrounded by six O atoms from four gluconate ligands; each Pb atom is chelated by the α -hydroxyl O atom at 2.48 (2) Å and a carboxylate O atom at 2.43 (2) Å forming a five-membered ring. The second carboxylate O atom (from another gluconate anion) is bonded at 2.71 (2) Å. Thus the carboxylate groups bridge two Pb atoms forming two-dimensional nets parallel to (001). The gluconate ligands have the zig-zag, nearly planar carbon-chain conformation with their long molecular axis approximately parallel to c .

Introduction. This work is a continuation of investigations into the crystal structures of metal gluconate salts. The compounds of Pb^{II} in acidic and basic solutions have been investigated by some authors who found that in water the Pb^{2+} ions may coordinate with different numbers of gluconate ligands and with different numbers of O atoms from carboxylate or hydroxyl groups forming mono- or polynuclear complexes (Pecsok & Juvet, 1956; Sawyer & Brannan, 1966; Coccioli & Vicedomini, 1978). Preliminary X-ray data for lead(II) D-gluconate were given by Pepinsky (1942), but no attempt has been made to determine the full crystal structure.

Experimental. Title compound prepared by heating an equimolar ratio of $PbCO_3$ and δ -gluconolactone in water until all $PbCO_3$ dissolved. After slow evaporation of water (at room temperature) platy trigonal crystals appeared. Analysis: calculated for $C_{12}H_{22}O_{14}Pb$: C 24.1, H 3.7, Pb 34.7%; found C 24.1, H 3.6, Pb 34.7%. Weissenberg and oscillation photographs showed crystals to be trigonal. Extinctions for 00 l reflexions if $l \neq 3n$. For a few investigated crystals the c axis was similar to that reported by Pepinsky (1942) but a was, however, half Pepinsky's value. It may be suggested that the crystal investigated by Pepinsky was twinned. An almost hexagonal platy crystal, approximately $0.2 \times 0.2 \times 0.07$ mm selected. D_m measured pycnometrically in 1,2-dibromoethane/ CH_2Br_2 . Syntex $P2_1$ diffractometer, Mo $K\alpha$ radiation, graphite monochromator, ω -scan technique. 15 reflexions in range $15 \leq 2\theta \leq 30^\circ$ used for measuring lattice parameters. 1685 reflexions measured up to $2\theta = 65^\circ$, range of hkl : $-6 \leq h \leq 6$, $-3 \leq k \leq 2$, $-48 \leq l \leq 49$ ($|h| > |k|$). Two standards, variation $\pm 1.5\%$. Empirical absorption corrections from φ -scan data. Pb atoms found from Patterson map, which also showed $P3_121$ (or $P3_221$) space group; all other non-H atoms from difference syntheses and correct enantiomer believed to have $P3_221$ space group; C-bonded H atoms included in calculated positions at 1.0 Å and fixed. Least-squares refinement on F (Pb, C, O anisotropic, H isotropic) led to final $R = 0.037$, $R_w = 0.031$, $S = 1.812$ for 838