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## Structure Reports

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Tetraaqualithium(I) bis(tropolonato- $\kappa^2O,O'$ )lithate(I)

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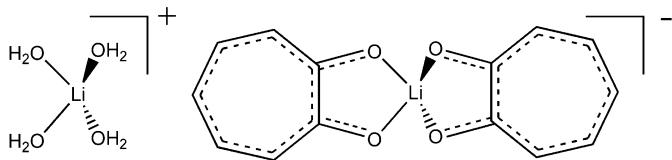
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Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(C-C) = 0.002$  Å;  $R$  factor = 0.055;  $wR$  factor = 0.157; data-to-parameter ratio = 13.0.

The title salt,  $[Li(H_2O)_4][Li(C_7H_5O_2)_2]$ , which was synthesized by reacting equimolar quantities of lithium hydroxide and tropolone in water, consists of a hydrated lithium cation whose charge is balanced by a ditropolonolite. Both Li atoms exist in a tetrahedral geometry (the cation and anion lie on different sites of 222 symmetry). Hydrogen bonds link the cation and anion into a layer structure;  $\pi$ - $\pi$  stacking [centroid-centroid distance 3.313 (2) Å] is observed with the tropolonate rings, the stacking allowing the formation of channels that facilitate the packing of the cations within them.

## Related literature

Diketonato-lithium compounds have only one diketonate group for each lithium. See, for example: Filatov *et al.* (2006); Gonçalves *et al.* (1996); Teixidor *et al.* (1985); Shiono (1961).



## Experimental

## Crystal data

$[Li(H_2O)_4][Li(C_7H_5O_2)_2]$   
 $M_r = 328.16$   
 Orthorhombic,  $Fddd$   
 $a = 9.4452$  (7) Å  
 $b = 10.0151$  (7) Å  
 $c = 32.566$  (2) Å

$V = 3080.6$  (4) Å<sup>3</sup>  
 $Z = 8$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.11$  mm<sup>-1</sup>  
 $T = 100$  (2) K  
 $0.13 \times 0.08 \times 0.06$  mm

## Data collection

Bruker X8 APEXII diffractometer  
 Absorption correction: multi-scan  
 (SADABS; Bruker, 1998)  
 $T_{min} = 0.985$ ,  $T_{max} = 0.993$

6210 measured reflections  
 844 independent reflections  
 715 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.078$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.055$   
 $wR(F^2) = 0.157$   
 $S = 1.06$   
 844 reflections  
 65 parameters  
 3 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{max} = 0.51$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.25$  e Å<sup>-3</sup>

Table 1

Selected geometric parameters (Å, °).

O01—Li2	1.9356 (12)	O1—Li1	1.9278 (12)
O1—C1	1.2894 (19)		
O01 <sup>i</sup> —Li2—O01	105.04 (8)	O1—Li1—O1 <sup>iii</sup>	84.27 (7)
O01 <sup>i</sup> —Li2—O01 <sup>ii</sup>	124.13 (8)	O1—Li1—O1 <sup>iv</sup>	132.68 (7)
O01—Li2—O01 <sup>ii</sup>	100.34 (7)	O1—Li1—O1 <sup>ii</sup>	114.95 (7)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O01—H011 $\cdots$ O1	0.847 (17)	1.967 (17)	2.8101 (16)	174 (2)

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT-Plus (Bruker, 2004); data reduction: SAINT-Plus and XPREP (Bruker, 2004); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg & Putz, 2006); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2307).

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**supplementary materials**

*Acta Cryst.* (2007). E63, m2343 [ doi:10.1107/S1600536807039657 ]

## Tetraaqualithium(I) bis(tropolonato- $\kappa^2O,O'$ )lithate(I)

G. Steyl

### Comment

The title compound, (I), is a novel example of a diketonato and lithium atom complex. To date very little data exist with lithium cation interactions with  $\alpha$ - or  $\beta$ -diketones (Filatov *et al.*, 2006; Gonçalves *et al.*, 1996; Teixidor *et al.*, 1985). The title compound is particularly interesting since the expected 1:1 ratio of an anion to cation as observed for the sodium derivative (Shiono, 1961) has been disrupted. This effect might be due to the smaller ionic radius of the lithium ion. The Li $\cdots$ O bond distances in both the independent units are nearly similar, with the Li $\cdots$ O(H<sub>2</sub>) and Li $\cdots$ O(trop), 1.9356 (12) and 1.9278 (12) Å, respectively.

The cationic and anionic parts of the title compound are linked together through O—H $\cdots$ O hydrogen bonds, see Table 2. The effect of this hydrogen bond in ordering the solid state can be observed as sheets perpendicular to the *c* axis, Figure 2. The tropolonato moieties form  $\pi$ - $\pi$  stacking units (3.313 (2) Å) in the solid state creating channels in which the solvated lithium cations can pack.

### Experimental

The title compound was obtained by mixing Tropolone (100 mg, 0.8 mmol) and LiOH (19 mg, 0.8 mmol) in 10 ml of water. The solution was stored at 4 ° C for 2 weeks, during which crystals grew suitable for X-ray crystallography. (Yield: 132 mg, 50%) NMR data: <sup>1</sup>H 6.83 (t, 9 Hz); 7.06 (d, 11 Hz); 7.31 (t, 11 Hz); <sup>7</sup>Li 0.344 (s).

### Refinement

H atoms bonded to O atoms were located in a difference map and refined with distance restraints of O—H = 0.84 (2) Å, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ . Other H atoms were positioned geometrically and refined using a riding model, with C—H = 0.95 Å and with  $U_{\text{iso}}(\text{H}) = 1.2$  times  $U_{\text{eq}}(\text{C})$ .

### Figures

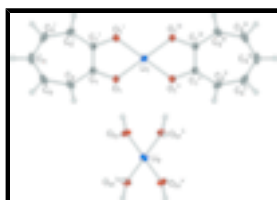


Fig. 1. The molecular structure of (I), with atom labels and 50% probability displacement ellipsoids for non-H atoms.

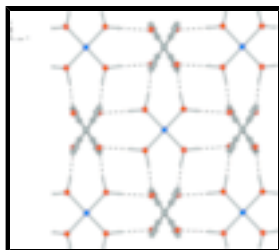


Fig. 2. The packing of (I), viewed down the *c*-axis, showing one layer of molecules connected by O—H···O hydrogen bonds (dashed lines). H atoms not involved in hydrogen bonding have been omitted.

## Tetraaqualithium(I) bis(tropolonato-κ<sup>2</sup>O,O')lithate(I)

### Crystal data

[Li(H<sub>2</sub>O)<sub>4</sub>][Li(C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>)<sub>2</sub>]

*M<sub>r</sub>* = 328.16

Orthorhombic, *Fddd*

Hall symbol: -F 2uv 2vw

*a* = 9.4452 (7) Å

*b* = 10.0151 (7) Å

*c* = 32.566 (2) Å

*V* = 3080.6 (4) Å<sup>3</sup>

*Z* = 8

*F*<sub>000</sub> = 1376

*D<sub>x</sub>* = 1.415 Mg m<sup>-3</sup>

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 2008 reflections

θ = 2.5–28.0°

μ = 0.11 mm<sup>-1</sup>

*T* = 100 (2) K

Cuboid, white

0.13 × 0.08 × 0.06 mm

### Data collection

Bruker SMART 1K CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 512 pixels mm<sup>-1</sup>

*T* = 100(2) K

φ and ω scans

Absorption correction: multi-scan (SADABS; Bruker, 1998)

*T*<sub>min</sub> = 0.985, *T*<sub>max</sub> = 0.993

6210 measured reflections

844 independent reflections

715 reflections with *I* > 2σ(*I*)

*R*<sub>int</sub> = 0.078

θ<sub>max</sub> = 27.0°

θ<sub>min</sub> = 2.5°

*h* = -12→12

*k* = -12→12

*l* = -41→41

### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.055

*wR*(*F*<sup>2</sup>) = 0.157

*S* = 1.06

844 reflections

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

*w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (0.1125*P*)<sup>2</sup> + 2.5701*P*]

where *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3

(Δ/σ)<sub>max</sub> < 0.001

Δρ<sub>max</sub> = 0.51 e Å<sup>-3</sup>

65 parameters

$$\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$$

3 restraints

Extinction correction: none

Primary atom site location: structure-invariant direct methods

### Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
O01	0.50030 (13)	0.24879 (12)	0.15285 (4)	0.0186 (4)
Li2	0.6250	0.1250	0.1250	0.0170 (11)
H011	0.520 (3)	0.3295 (18)	0.1582 (7)	0.036 (7)*
H012	0.4138 (19)	0.241 (2)	0.1578 (8)	0.039 (7)*
O1	0.54310 (12)	0.52151 (11)	0.16890 (4)	0.0150 (4)
C2	0.54144 (18)	0.49237 (18)	0.23993 (5)	0.0176 (5)
H2	0.4936	0.4110	0.2343	0.021*
C1	0.58113 (16)	0.56432 (16)	0.20457 (5)	0.0130 (4)
C3	0.5595 (2)	0.5186 (2)	0.28138 (5)	0.0231 (5)
H3	0.5209	0.4535	0.2994	0.028*
C4	0.6250	0.6250	0.30048 (7)	0.0254 (7)
H4	0.6250	0.6250	0.3296	0.030*
Li1	0.6250	0.6250	0.1250	0.0175 (11)

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O01	0.0155 (7)	0.0139 (7)	0.0264 (7)	-0.0014 (5)	0.0042 (5)	-0.0034 (5)
Li2	0.013 (2)	0.017 (3)	0.021 (3)	0.000	0.000	0.000
O1	0.0148 (7)	0.0154 (7)	0.0147 (7)	-0.0023 (5)	-0.0014 (4)	-0.0006 (4)
C2	0.0144 (9)	0.0183 (9)	0.0201 (10)	0.0029 (6)	0.0033 (6)	0.0053 (7)
C1	0.0104 (7)	0.0156 (9)	0.0130 (8)	0.0036 (6)	-0.0003 (5)	-0.0003 (6)
C3	0.0213 (10)	0.0304 (11)	0.0175 (9)	0.0113 (8)	0.0056 (7)	0.0092 (7)
C4	0.0275 (13)	0.0371 (16)	0.0116 (11)	0.0182 (12)	0.000	0.000
Li1	0.022 (3)	0.014 (3)	0.016 (3)	0.000	0.000	0.000

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

O01—Li2	1.9356 (12)	C1—Li1	2.6938 (15)
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## supplementary materials

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O01—H011	0.847 (17)	C3—C4	1.380 (2)
O01—H012	0.837 (17)	C3—H3	0.9500
Li2—O01 <sup>i</sup>	1.9356 (12)	C4—C3 <sup>iv</sup>	1.380 (2)
Li2—O01 <sup>ii</sup>	1.9356 (12)	C4—H4	0.9500
Li2—O01 <sup>iii</sup>	1.9356 (12)	Li1—O1 <sup>iv</sup>	1.9278 (12)
O1—C1	1.2894 (19)	Li1—O1 <sup>v</sup>	1.9278 (12)
O1—Li1	1.9278 (12)	Li1—O1 <sup>ii</sup>	1.9278 (12)
C2—C3	1.386 (2)	Li1—C1 <sup>iv</sup>	2.6938 (15)
C2—C1	1.409 (2)	Li1—C1 <sup>v</sup>	2.6938 (15)
C2—H2	0.9500	Li1—C1 <sup>ii</sup>	2.6938 (15)
C1—C1 <sup>iv</sup>	1.471 (3)		
Li2—O01—H011	125.2 (17)	O1 <sup>iv</sup> —Li1—O1 <sup>v</sup>	114.95 (7)
Li2—O01—H012	128.4 (17)	O1—Li1—O1 <sup>ii</sup>	114.95 (7)
H011—O01—H012	105 (2)	O1 <sup>iv</sup> —Li1—O1 <sup>ii</sup>	132.68 (7)
O01 <sup>i</sup> —Li2—O01	105.04 (8)	O1 <sup>v</sup> —Li1—O1 <sup>ii</sup>	84.27 (7)
O01 <sup>i</sup> —Li2—O01 <sup>ii</sup>	124.13 (8)	O1—Li1—C1	26.31 (5)
O01—Li2—O01 <sup>ii</sup>	100.34 (7)	O1 <sup>iv</sup> —Li1—C1	57.97 (5)
O01 <sup>i</sup> —Li2—O01 <sup>iii</sup>	100.34 (7)	O1 <sup>v</sup> —Li1—C1	140.62 (5)
O01—Li2—O01 <sup>iii</sup>	124.13 (8)	O1 <sup>ii</sup> —Li1—C1	130.83 (5)
O01 <sup>ii</sup> —Li2—O01 <sup>iii</sup>	105.04 (8)	O1—Li1—C1 <sup>iv</sup>	57.97 (5)
C1—O1—Li1	112.18 (10)	O1 <sup>iv</sup> —Li1—C1 <sup>iv</sup>	26.31 (5)
C3—C2—C1	131.78 (17)	O1 <sup>v</sup> —Li1—C1 <sup>iv</sup>	130.83 (5)
C3—C2—H2	114.1	O1 <sup>ii</sup> —Li1—C1 <sup>iv</sup>	140.62 (5)
C1—C2—H2	114.1	C1—Li1—C1 <sup>iv</sup>	31.69 (7)
O1—C1—C2	119.48 (15)	O1—Li1—C1 <sup>v</sup>	140.62 (5)
O1—C1—C1 <sup>iv</sup>	115.57 (9)	O1 <sup>iv</sup> —Li1—C1 <sup>v</sup>	130.83 (5)
C2—C1—C1 <sup>iv</sup>	124.91 (10)	O1 <sup>v</sup> —Li1—C1 <sup>v</sup>	26.31 (5)
C2—C1—Li1	160.46 (13)	O1 <sup>ii</sup> —Li1—C1 <sup>v</sup>	57.97 (5)
C1 <sup>iv</sup> —C1—Li1	74.15 (3)	C1—Li1—C1 <sup>v</sup>	162.30 (7)
C4—C3—C2	129.83 (18)	C1 <sup>iv</sup> —Li1—C1 <sup>v</sup>	153.92 (7)
C4—C3—H3	115.1	O1—Li1—C1 <sup>ii</sup>	130.83 (5)
C2—C3—H3	115.1	O1 <sup>iv</sup> —Li1—C1 <sup>ii</sup>	140.62 (5)
C3—C4—C3 <sup>iv</sup>	126.4 (2)	O1 <sup>v</sup> —Li1—C1 <sup>ii</sup>	57.97 (5)
C3—C4—H4	116.8	O1 <sup>ii</sup> —Li1—C1 <sup>ii</sup>	26.31 (5)
C3 <sup>iv</sup> —C4—H4	116.8	C1—Li1—C1 <sup>ii</sup>	153.92 (7)
O1—Li1—O1 <sup>iv</sup>	84.27 (7)	C1 <sup>iv</sup> —Li1—C1 <sup>ii</sup>	162.30 (7)
O1—Li1—O1 <sup>v</sup>	132.68 (7)	C1 <sup>v</sup> —Li1—C1 <sup>ii</sup>	31.69 (7)
Li1—O1—C1—C2	-174.11 (12)	C2—C1—Li1—O1 <sup>iv</sup>	-166.3 (4)
Li1—O1—C1—C1 <sup>iv</sup>	4.0 (2)	C1 <sup>iv</sup> —C1—Li1—O1 <sup>iv</sup>	1.94 (10)
C3—C2—C1—O1	-175.48 (17)	O1—C1—Li1—O1 <sup>v</sup>	86.96 (15)
C3—C2—C1—C1 <sup>iv</sup>	6.7 (3)	C2—C1—Li1—O1 <sup>v</sup>	102.4 (4)

C3—C2—C1—Li1	172.8 (2)	C1 <sup>iv</sup> —C1—Li1—O1 <sup>v</sup>	-89.34 (13)
C1—C2—C3—C4	-1.0 (3)	O1—C1—Li1—O1 <sup>ii</sup>	-60.69 (15)
C2—C3—C4—C3 <sup>iv</sup>	-0.82 (15)	C2—C1—Li1—O1 <sup>ii</sup>	-45.2 (4)
C1—O1—Li1—O1 <sup>iv</sup>	-1.51 (8)	C1 <sup>iv</sup> —C1—Li1—O1 <sup>ii</sup>	123.02 (11)
C1—O1—Li1—O1 <sup>v</sup>	-120.47 (11)	O1—C1—Li1—C1 <sup>iv</sup>	176.3 (2)
C1—O1—Li1—O1 <sup>ii</sup>	133.31 (11)	C2—C1—Li1—C1 <sup>iv</sup>	-168.2 (5)
C1—O1—Li1—C1 <sup>iv</sup>	-2.30 (12)	O1—C1—Li1—C1 <sup>v</sup>	53.03 (10)
C1—O1—Li1—C1 <sup>v</sup>	-157.49 (10)	C2—C1—Li1—C1 <sup>v</sup>	68.5 (4)
C1—O1—Li1—C1 <sup>ii</sup>	158.54 (8)	C1 <sup>iv</sup> —C1—Li1—C1 <sup>v</sup>	-123.26 (12)
C2—C1—Li1—O1	15.5 (3)	O1—C1—Li1—C1 <sup>ii</sup>	-39.04 (10)
C1 <sup>iv</sup> —C1—Li1—O1	-176.3 (2)	C2—C1—Li1—C1 <sup>ii</sup>	-23.5 (3)
O1—C1—Li1—O1 <sup>iv</sup>	178.23 (9)	C1 <sup>iv</sup> —C1—Li1—C1 <sup>ii</sup>	144.67 (12)

Symmetry codes: (i)  $x, -y+1/4, -z+1/4$ ; (ii)  $-x+5/4, y, -z+1/4$ ; (iii)  $-x+5/4, -y+1/4, z$ ; (iv)  $-x+5/4, -y+5/4, z$ ; (v)  $x, -y+5/4, -z+1/4$ .

Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O01—H011 $\cdots$ O1	0.847 (17)	1.967 (17)	2.8101 (16)	174 (2)

Fig. 1

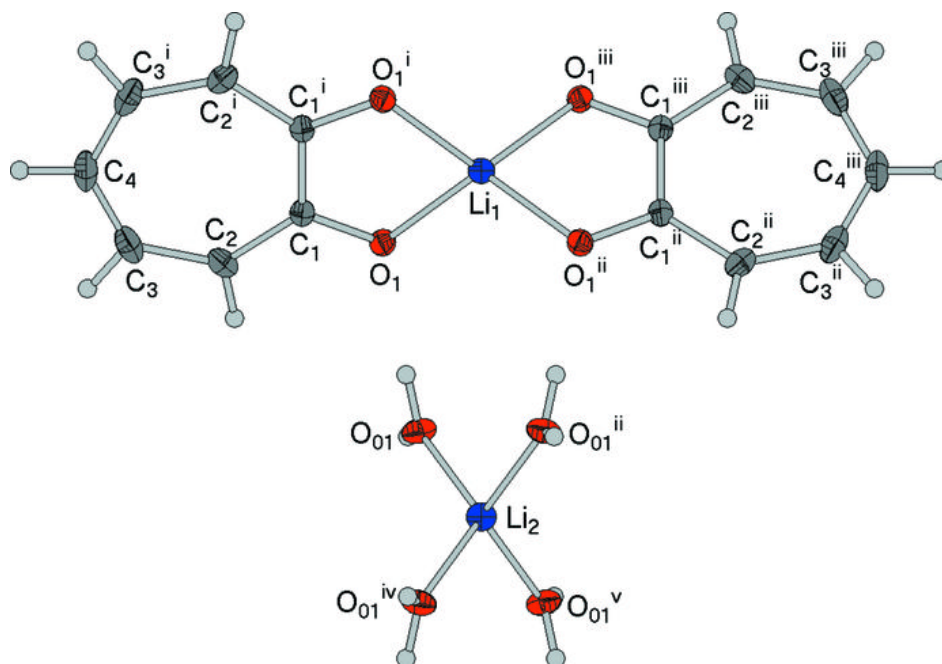




Fig. 2

