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## Structure Reports

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Poly[ $\mu_6$ -(naphthalene-2,6-dicarboxylato)-bis(aqualithium)]

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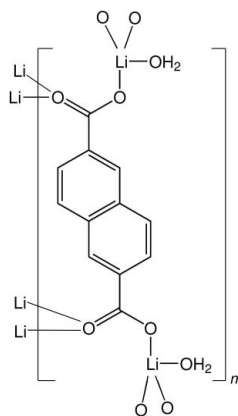
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.043;  $wR$  factor = 0.109; data-to-parameter ratio = 14.0.

The title compound,  $[\text{Li}_2(\text{C}_{12}\text{H}_6\text{O}_4)(\text{H}_2\text{O})_2]_n$ , crystallizes with one half of the molecular entities in the asymmetric unit. The second half is generated by inversion symmetry. The crystal structure has a layered arrangement built from distorted edge-sharing  $\text{LiO}_3(\text{OH})_2$  tetrahedra parallel to (100), with naphthalenedicarboxylate bridging the  $\text{LiO}_3(\text{OH})_2$  layers along the [100] direction. Hydrogen bonding between the water molecule and adjacent carboxylate groups consolidates the packing.

## Related literature

For the synthesis and crystal structure of 2,6-naphthalenedicarboxylic acid, see Kaduk & Golab (1999). For the synthesis and crystal structure of dilithium-2,6-naphthalene dicarboxylate  $[\text{Li}_2(2,6\text{-NDC})]$ , see: Banerjee *et al.* (2009*a*). For related compounds, see: Banerjee *et al.* (2009*b*).  $[\text{Li}_2(2,6\text{-NDC})]$  was recently reported to exhibit good electrochemical performance, see: Fédèle *et al.* (2014).



## Experimental

## Crystal data

$[\text{Li}_2(\text{C}_{12}\text{H}_6\text{O}_4)(\text{H}_2\text{O})_2]$   
 $M_r = 132.04$   
 Monoclinic,  $C2/c$   
 $a = 23.5695$  (18) Å  
 $b = 6.8115$  (5) Å  
 $c = 7.5327$  (6) Å  
 $\beta = 90.325$  (3)°

$V = 1209.31$  (16) Å<sup>3</sup>  
 $Z = 8$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.11$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.12 \times 0.05 \times 0.03$  mm

## Data collection

Bruker D8 Venture diffractometer  
 Absorption correction: multi-scan  
 (*SADABS*; Bruker, 2007)  
 $T_{\min} = 0.707$ ,  $T_{\max} = 0.746$

12848 measured reflections  
 1388 independent reflections  
 1032 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.050$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$   
 $wR(F^2) = 0.109$   
 $S = 1.06$   
 1388 reflections  
 99 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.23$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.24$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O2}-\text{H1W}\cdots\text{O1}^i$	0.81 (3)	2.10 (3)	2.905 (2)	176 (3)
$\text{O2}-\text{H2W}\cdots\text{O3}^{ii}$	0.89 (3)	2.01 (3)	2.883 (2)	169 (3)

Symmetry codes: (i)  $x, -y + 1, z + \frac{1}{2}$ ; (ii)  $-x, -y + 2, -z + 1$ .

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINTE* (Bruker, 2007); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL* (Hübschle *et al.*, 2011); molecular graphics: *VESTA* (Momma & Izumi, 2011); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: PJ2011).

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## supporting information

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**Poly[ $\mu_6$ -(naphthalene-2,6-dicarboxylato)-bis(aqualithium)]****Lionel Fédèle, Frédéric Sauvage, Matthieu Becuwe and Jean-Noël Chotard****S1. Comment**

For the last 30 years, inorganic compounds involving at least one transition metal as a redox center (such as  $\text{LiCoO}_2$  or  $\text{LiFePO}_4$ ) have been the traditional electrodes for Li-ion batteries. While they exhibit good performances in terms of cyclability, output voltage capacity, main drawbacks such as toxicity, sustainability and eco-conception still remain. In this context, organic based electrodes for Li-ion batteries recently regained attention. Among them, the dilithium 2,6-naphthalene dicarboxylate ( $\text{Li}_2$ -2,6-NDC) was recently reported to exhibit good electrochemical performances (Fédèle *et al.* 2014). The title compound (dilithium 2,6-naphthalene dicarboxylate dihydrate) is the hydrated form of the  $\text{Li}_2$ -2,6-NDC. In the former, pairs of edge-sharing  $\text{LiO}_4$  tetrahedra are connected to each other by corners (Banerjee *et al.* 2009a). In the hydrated form, the corner sharing arrangement is no longer possible as one oxygen is replaced by a water molecule. Edge-sharing  $\text{LiO}_3(\text{OH}_2)$  tetrahedra are connected into sheets that extend in the  $yz$  plane. These are linked by the naphthalene dicarboxylate into a 3-D array. Crystal data, data collection and structure refinement details are summarized in Table 1.

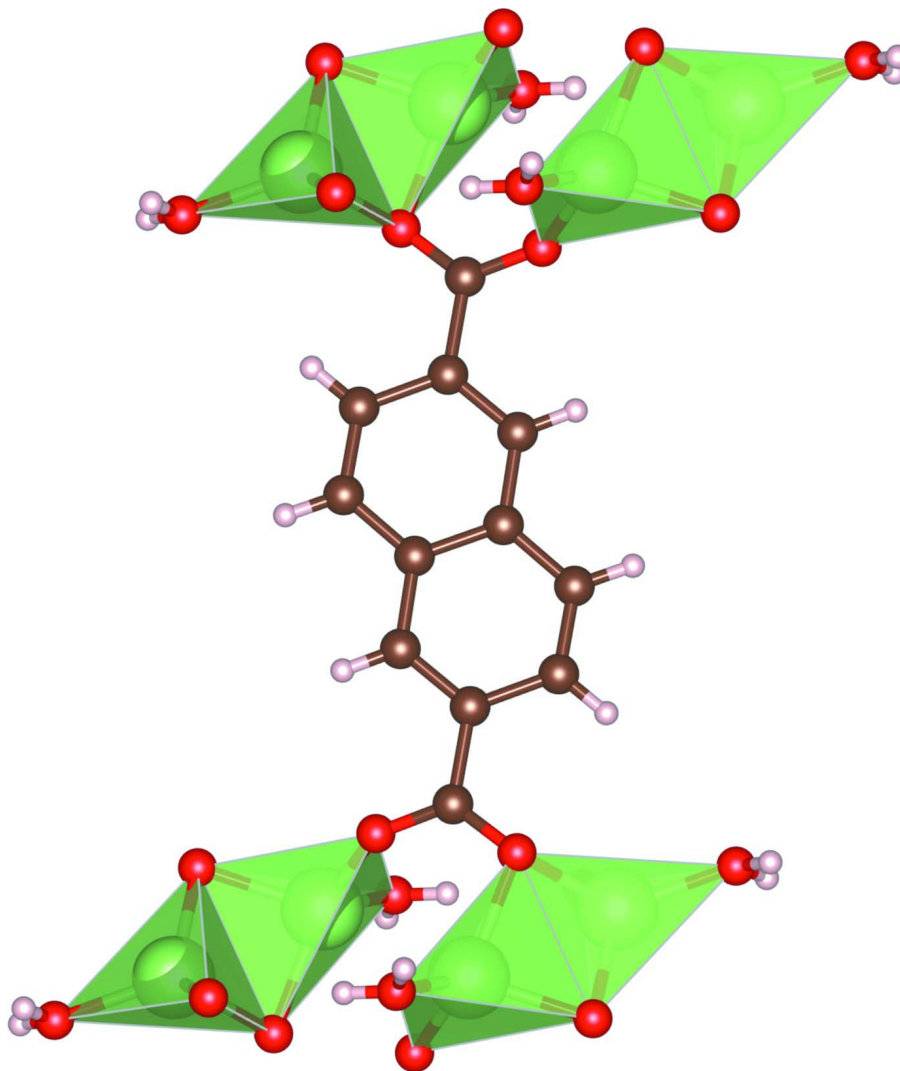
**S2. Experimental**

**Reagent and chemicals.** The 2,6 naphthalene dicarboxylic acid (98+%) and lithium hydroxide were purchased from Alfa Aesar and Sigma-Aldrich, respectively. They were used as received without further purification. De-ionized water was utilized for the synthesis of the di-lithium salt.

**Hydrothermal Lithiation procedure.** 1 g of 2,6-naphthalene dicarboxylic acid (4.6 mmol) was added into 10 ml de-ionized water and added to a 23 ml autoclave. Two equivalents of anhydrous lithium hydroxide (222 mg, 9.3 mmol) were incorporated with the naphthalene derivative. The autoclave was then placed into a temperature controlled oven set at 150°C for 12 h duration before to be cooled down to room temperature with a ramp of 10°C/h. The resulting green solution was poured into a 50 ml beaker while the excess water was slowly evaporated under ambient conditions to form the colorless single crystals of the di-lithium-2,6-naphthalene dicarboxylate dihydrate.

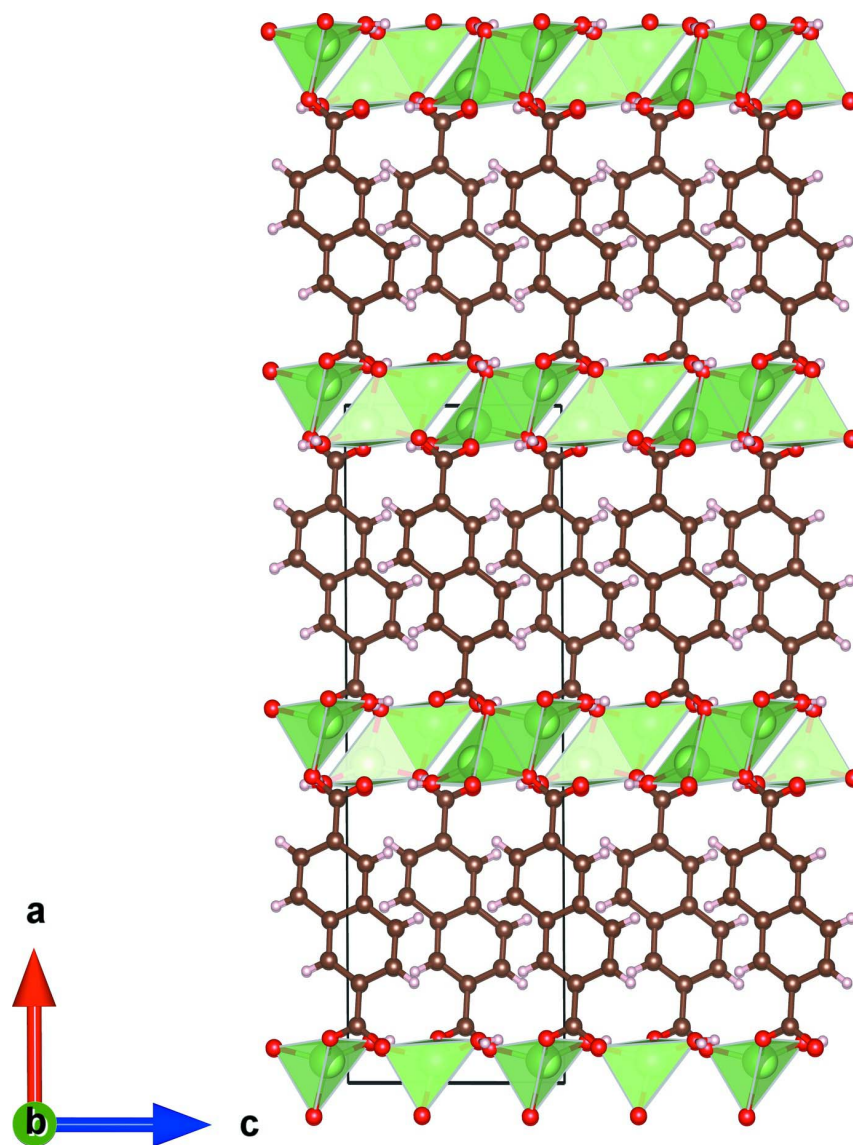
**S3. Refinement**

All H-atoms were positioned geometrically and refined using a riding model with  $\text{C—H} = 0.90\text{--}0.93 \text{ \AA}$  and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The H atoms of the aqua ligand (H1W and H2W) were found by Fourier difference map and further refined without any constrains.



**Figure 1**

Molecular view of the title compound. Li, O, C, and H atoms are represented by light green, red, brown and white spheres respectively



**Figure 2**

Crystal structure of the title compound view along the  $b$  axis. Layers of  $\text{LiO}_3(\text{OH}_2)$  edge-sharing tetrahedra in the  $(yz)$  plane are connected *via* naphthalene dicarboxylate molecules.

**Poly[ $\mu_6$ -(naphthalene-2,6-dicarboxylato)-bis(aqualithium)]**

*Crystal data*

$[\text{Li}_2(\text{C}_{12}\text{H}_6\text{O}_4)(\text{H}_2\text{O})_2]$

$M_r = 132.04$

Monoclinic,  $C2/c$

Hall symbol:  $-C\ 2yc$

$a = 23.5695$  (18) Å

$b = 6.8115$  (5) Å

$c = 7.5327$  (6) Å

$\beta = 90.325$  (3)°

$V = 1209.31$  (16) Å<sup>3</sup>

$Z = 8$

$F(000) = 544$

$D_x = 1.450$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

$\mu = 0.11$  mm<sup>-1</sup>

$T = 293$  K

Prism, colourless

$0.12 \times 0.05 \times 0.03$  mm

Data collection

Bruker D8 Venture  
diffractometer  
Radiation source: fine-focus sealed tube  
Multilayer optics monochromator  
phi scan  
Absorption correction: multi-scan  
(SADABS; Bruker, 2007)  
 $T_{\min} = 0.707$ ,  $T_{\max} = 0.746$

12848 measured reflections  
1388 independent reflections  
1032 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.050$   
 $\theta_{\text{max}} = 27.5^\circ$ ,  $\theta_{\text{min}} = 3.1^\circ$   
 $h = -30 \rightarrow 29$   
 $k = -8 \rightarrow 8$   
 $l = -9 \rightarrow 9$

Refinement

Refinement on  $F^2$   
Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.043$   
 $wR(F^2) = 0.109$   
 $S = 1.06$   
1388 reflections  
99 parameters  
0 restraints  
Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map  
Hydrogen site location: inferred from  
neighbouring sites  
H atoms treated by a mixture of independent  
and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 1.0165P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.010$   
 $\Delta\rho_{\text{max}} = 0.23 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.24 \text{ e } \text{\AA}^{-3}$

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. A single gross outlier (reflection 3 3 3) was omitted from the final refinement.

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

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.06322 (5)	0.42265 (18)	0.41860 (17)	0.0357 (3)
H1W	0.0611 (12)	0.761 (5)	0.695 (4)	0.082 (10)*
H2W	0.0553 (11)	0.949 (5)	0.635 (4)	0.089 (10)*
O2	0.05985 (7)	0.8245 (3)	0.6045 (2)	0.0496 (4)
O3	-0.05040 (4)	0.75789 (19)	0.34106 (15)	0.0323 (3)
C1	0.08206 (6)	0.3193 (2)	0.5432 (2)	0.0252 (4)
C2	0.14481 (6)	0.2809 (2)	0.5548 (2)	0.0251 (4)
C3	0.17876 (6)	0.3237 (2)	0.4137 (2)	0.0261 (4)
H3	0.1627	0.3764	0.3112	0.031*
C4	0.23825 (6)	0.2893 (2)	0.4209 (2)	0.0245 (4)
C5	0.22574 (7)	0.1697 (3)	0.7239 (2)	0.0300 (4)
H4	0.2412	0.1206	0.8288	0.036*
C6	0.16892 (7)	0.2010 (3)	0.7120 (2)	0.0303 (4)
H5	0.1457	0.1700	0.8074	0.036*
Li1	0.03075 (12)	0.6849 (4)	0.4040 (4)	0.0305 (6)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0262 (6)	0.0378 (7)	0.0432 (7)	0.0097 (5)	-0.0039 (5)	0.0041 (6)
O2	0.0714 (11)	0.0404 (9)	0.0367 (8)	-0.0102 (8)	-0.0102 (7)	-0.0003 (7)
O3	0.0197 (5)	0.0452 (7)	0.0322 (6)	-0.0007 (5)	0.0075 (5)	-0.0052 (6)
C1	0.0190 (7)	0.0253 (8)	0.0313 (9)	0.0018 (6)	0.0016 (6)	-0.0084 (7)
C2	0.0180 (7)	0.0241 (8)	0.0333 (9)	0.0019 (6)	0.0022 (6)	-0.0009 (7)
C3	0.0208 (8)	0.0285 (8)	0.0290 (8)	0.0037 (7)	-0.0011 (6)	0.0035 (7)
C4	0.0215 (8)	0.0236 (8)	0.0283 (8)	0.0021 (6)	0.0010 (6)	0.0023 (7)
C5	0.0241 (8)	0.0365 (9)	0.0293 (9)	0.0035 (7)	0.0005 (6)	0.0096 (8)
C6	0.0239 (8)	0.0366 (9)	0.0304 (9)	0.0016 (7)	0.0063 (6)	0.0053 (7)
Li1	0.0275 (14)	0.0337 (15)	0.0302 (14)	0.0016 (12)	-0.0007 (11)	0.0021 (12)

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

O1—C1	1.253 (2)	C3—C4	1.422 (2)
O1—Li1	1.946 (3)	C3—H3	0.9300
O2—Li1	1.910 (3)	C4—C5 <sup>iii</sup>	1.414 (2)
O2—H1W	0.81 (3)	C4—C4 <sup>iii</sup>	1.417 (3)
O2—H2W	0.89 (3)	C5—C6	1.359 (2)
O3—C1 <sup>i</sup>	1.265 (2)	C5—C4 <sup>iii</sup>	1.414 (2)
O3—Li1 <sup>ii</sup>	1.969 (3)	C5—H4	0.9300
O3—Li1	2.030 (3)	C6—H5	0.9300
C1—O3 <sup>i</sup>	1.265 (2)	Li1—O3 <sup>ii</sup>	1.969 (3)
C1—C2	1.504 (2)	Li1—C1 <sup>i</sup>	2.691 (3)
C1—Li1 <sup>i</sup>	2.691 (3)	Li1—Li1 <sup>ii</sup>	2.728 (6)
C2—C3	1.365 (2)	Li1—Li1 <sup>i</sup>	3.250 (6)
C2—C6	1.419 (2)		
C1—O1—Li1	134.09 (14)	C5—C6—C2	120.35 (15)
Li1—O2—H1W	114 (2)	C5—C6—H5	119.8
Li1—O2—H2W	129.8 (19)	C2—C6—H5	119.8
H1W—O2—H2W	107 (3)	O2—Li1—O1	105.84 (15)
C1 <sup>i</sup> —O3—Li1 <sup>ii</sup>	133.11 (14)	O2—Li1—O3 <sup>ii</sup>	122.04 (16)
C1 <sup>i</sup> —O3—Li1	107.22 (13)	O1—Li1—O3 <sup>ii</sup>	100.98 (14)
Li1 <sup>ii</sup> —O3—Li1	86.02 (13)	O2—Li1—O3	113.35 (15)
O1—C1—O3 <sup>i</sup>	122.81 (14)	O1—Li1—O3	127.43 (16)
O1—C1—C2	119.05 (14)	O3 <sup>ii</sup> —Li1—O3	86.88 (12)
O3 <sup>i</sup> —C1—C2	118.13 (14)	O2—Li1—C1 <sup>i</sup>	103.83 (13)
O1—C1—Li1 <sup>i</sup>	76.73 (11)	O1—Li1—C1 <sup>i</sup>	111.74 (13)
O3 <sup>i</sup> —C1—Li1 <sup>i</sup>	46.09 (10)	O3 <sup>ii</sup> —Li1—C1 <sup>i</sup>	112.28 (13)
C2—C1—Li1 <sup>i</sup>	164.10 (13)	O3—Li1—C1 <sup>i</sup>	26.69 (6)
C3—C2—C6	119.84 (14)	O2—Li1—Li1 <sup>ii</sup>	149.25 (11)
C3—C2—C1	119.89 (14)	O1—Li1—Li1 <sup>ii</sup>	104.78 (10)
C6—C2—C1	120.27 (14)	O3 <sup>ii</sup> —Li1—Li1 <sup>ii</sup>	47.92 (9)
C2—C3—C4	121.15 (15)	O3—Li1—Li1 <sup>ii</sup>	46.06 (9)
C2—C3—H3	119.4	C1 <sup>i</sup> —Li1—Li1 <sup>ii</sup>	66.74 (11)

C4—C3—H3	119.4	O2—Li1—Li1 <sup>i</sup>	101.12 (15)
C5 <sup>iii</sup> —C4—C4 <sup>iii</sup>	119.35 (17)	O1—Li1—Li1 <sup>i</sup>	55.92 (10)
C5 <sup>iii</sup> —C4—C3	122.30 (14)	O3 <sup>ii</sup> —Li1—Li1 <sup>i</sup>	136.12 (18)
C4 <sup>iii</sup> —C4—C3	118.35 (17)	O3—Li1—Li1 <sup>i</sup>	82.63 (12)
C6—C5—C4 <sup>iii</sup>	120.93 (15)	C1 <sup>i</sup> —Li1—Li1 <sup>i</sup>	58.82 (9)
C6—C5—H4	119.5	Li1 <sup>ii</sup> —Li1—Li1 <sup>i</sup>	98.18 (13)
C4 <sup>iii</sup> —C5—H4	119.5		
Li1—O1—C1—O3 <sup>i</sup>	71.7 (2)	C1—O1—Li1—O2	24.8 (2)
Li1—O1—C1—C2	-109.69 (19)	C1—O1—Li1—O3 <sup>ii</sup>	152.87 (15)
Li1—O1—C1—Li1 <sup>i</sup>	72.46 (19)	C1—O1—Li1—O3	-112.6 (2)
O1—C1—C2—C3	-13.1 (2)	C1—O1—Li1—C1 <sup>i</sup>	-87.6 (2)
O3 <sup>i</sup> —C1—C2—C3	165.63 (15)	C1—O1—Li1—Li1 <sup>ii</sup>	-158.04 (16)
Li1 <sup>i</sup> —C1—C2—C3	159.3 (4)	C1—O1—Li1—Li1 <sup>i</sup>	-68.08 (18)
O1—C1—C2—C6	166.67 (15)	C1 <sup>i</sup> —O3—Li1—O2	-73.79 (18)
O3 <sup>i</sup> —C1—C2—C6	-14.6 (2)	Li1 <sup>ii</sup> —O3—Li1—O2	152.12 (13)
Li1 <sup>i</sup> —C1—C2—C6	-21.0 (5)	C1 <sup>i</sup> —O3—Li1—O1	61.0 (2)
C6—C2—C3—C4	0.2 (3)	Li1 <sup>ii</sup> —O3—Li1—O1	-73.05 (18)
C1—C2—C3—C4	179.88 (14)	C1 <sup>i</sup> —O3—Li1—O3 <sup>ii</sup>	162.48 (11)
C2—C3—C4—C5 <sup>iii</sup>	179.28 (16)	Li1 <sup>ii</sup> —O3—Li1—O3 <sup>ii</sup>	28.40 (17)
C2—C3—C4—C4 <sup>iii</sup>	-0.5 (3)	Li1 <sup>ii</sup> —O3—Li1—C1 <sup>i</sup>	-134.08 (16)
C4 <sup>iii</sup> —C5—C6—C2	-1.7 (3)	C1 <sup>i</sup> —O3—Li1—Li1 <sup>ii</sup>	134.08 (16)
C3—C2—C6—C5	1.0 (3)	C1 <sup>i</sup> —O3—Li1—Li1 <sup>i</sup>	25.18 (15)
C1—C2—C6—C5	-178.74 (15)	Li1 <sup>ii</sup> —O3—Li1—Li1 <sup>i</sup>	-108.90 (8)

Symmetry codes: (i)  $-x, -y+1, -z+1$ ; (ii)  $-x, y, -z+1/2$ ; (iii)  $-x+1/2, -y+1/2, -z+1$ .

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

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O2—H1 <i>W</i> $\cdots$ O1 <sup>iv</sup>	0.81 (3)	2.10 (3)	2.905 (2)	176 (3)
O2—H2 <i>W</i> $\cdots$ O3 <sup>v</sup>	0.89 (3)	2.01 (3)	2.883 (2)	169 (3)

Symmetry codes: (iv)  $x, -y+1, z+1/2$ ; (v)  $-x, -y+2, -z+1$ .