

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

catena-Poly[[*(*6-carboxypyrazine-2-carboxylato)lithium]- $\mu$ -aqua]

Wojciech Starosta and Janusz Leciejewicz\*

Institute of Nuclear Chemistry and Technology, ul. Dorodna 16, 03-195 Warszawa, Poland

Correspondence e-mail: j.leciejewicz@ichtj.waw.pl

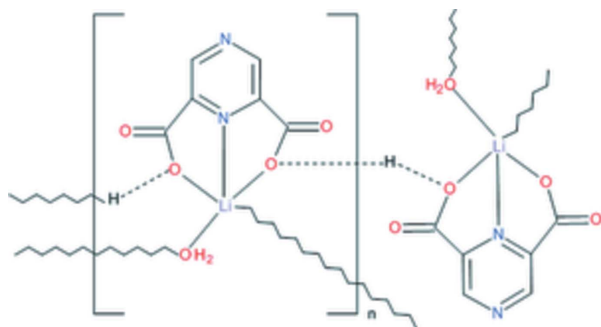
Received 27 October 2011; accepted 2 November 2011

Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.054;  $wR$  factor = 0.171; data-to-parameter ratio = 14.7.

The asymmetric unit of the title compound,  $[\text{Li}(\text{C}_6\text{H}_3\text{N}_2\text{O}_4)(\text{H}_2\text{O})]_n$ , contains an  $\text{Li}^{\text{I}}$  ion with a distorted trigonal-bipyramidal coordination environment. It is chelated by a singly protonated ligand molecule *via* its heterocyclic N atom, by two O atoms, each donated by an adjacent carboxylate group, and is further coordinated by a water O atom which acts as a bridge, forming a molecular ribbon. A proton attached to one of the carboxylate O atoms is situated on an inversion centre and forms a short centrosymmetric hydrogen bond, generating molecular layers parallel to the *ac* plane. These layers are held together by weak  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds in which the coordinated water molecules act as donors, whereas carboxylate O atoms are acceptors.

## Related literature

For the structures of three lithium complexes with pyrazine-2,3-dicarboxylate and water ligands, see: Tombul *et al.* (2008); Tombul & Guven (2009); Starosta & Leciejewicz (2011*b*). For the structure of a  $\text{Li}^{\text{I}}$  complex with a pyrazine-2,5-dicarboxylate ligand, see: Starosta & Leciejewicz (2011*a*) and for the structure of a  $\text{Li}^{\text{I}}$  complex with pyrazine-2,3,5,6-tetracarboxylate, see: Starosta & Leciejewicz (2010). The structure of pyrazine-2,6-dicarboxylate acid dihydrate has been also reported, see: Ptasiwicz-Bąk & Leciejewicz (2003).



## Experimental

## Crystal data

$[\text{Li}(\text{C}_6\text{H}_3\text{N}_2\text{O}_4)(\text{H}_2\text{O})]$   
 $M_r = 192.06$   
 Monoclinic,  $P2_1/m$   
 $a = 3.5346$  (7) Å  
 $b = 12.519$  (3) Å  
 $c = 8.3583$  (17) Å  
 $\beta = 97.86$  (3)°

$V = 366.37$  (13) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.15$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.31 \times 0.22 \times 0.08$  mm

## Data collection

Kuma KM-4 four-circle diffractometer  
 Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2008)  
 $T_{\text{min}} = 0.954$ ,  $T_{\text{max}} = 0.973$   
 1262 measured reflections

1106 independent reflections  
 729 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.027$   
 3 standard reflections every 200 reflections  
 intensity decay: 1.3%

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$   
 $wR(F^2) = 0.171$   
 $S = 1.09$   
 1106 reflections  
 75 parameters  
 2 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.38$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.31$  e Å<sup>-3</sup>

Table 1

Selected bond lengths (Å).

N1—Li1	2.115 (7)	O3—Li1 <sup>i</sup>	2.085 (7)
O1—Li1	2.271 (2)	Li1—O1 <sup>ii</sup>	2.271 (2)
O3—Li1	1.950 (7)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O3—H31 <sup>iii</sup> ⋯O2 <sup>iii</sup>	0.83 (2)	2.24 (2)	2.9987 (19)	152 (3)
O1—H1 <sup>iii</sup> ⋯O1 <sup>iii</sup>	1.23 (1)	1.23 (1)	2.455 (3)	180 (1)

Symmetry code: (iii)  $-x + 1, -y + 1, -z$ .

Data collection: *KM-4 Software* (Kuma, 1996); cell refinement: *KM-4 Software*; data reduction: *DATAPROC* (Kuma, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2364).

## References

- Kuma (1996). *KM-4 Software*. Kuma Diffraction Ltd, Wrocław, Poland.  
 Kuma (2001). *DATAPROC*. Kuma Diffraction Ltd, Wrocław, Poland.  
 Oxford Diffraction (2008). *CrysAlis RED*. Oxford Diffraction Ltd, Yarnton, England.  
 Ptasiwicz-Bąk, H. & Leciejewicz, J. (2003). *J. Coord. Chem.* **56**, 173–180.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
 Starosta, W. & Leciejewicz, J. (2010). *Acta Cryst.* **E66**, m1561–m1562.

Starosta, W. & Leciejewicz, J. (2011*a*). *Acta Cryst.* **E67**, m50–m51.  
Starosta, W. & Leciejewicz, J. (2011*b*). *Acta Cryst.* **E67**, m1133–m1134.

Tombul, M. & Guven, K. (2009). *Acta Cryst.* **E65**, m1704–m1705.  
Tombul, M., Güven, K. & Büyükgüngör, O. (2008). *Acta Cryst.* **E64**, m491–m492.

## supporting information

*Acta Cryst.* (2011). E67, m1708–m1709 [https://doi.org/10.1107/S1600536811046198]

**catena-Poly[[[(6-carboxypyrazine-2-carboxylato)lithium]- $\mu$ -aqua]****Wojciech Starosta and Janusz Leciejewicz****S1. Comment**

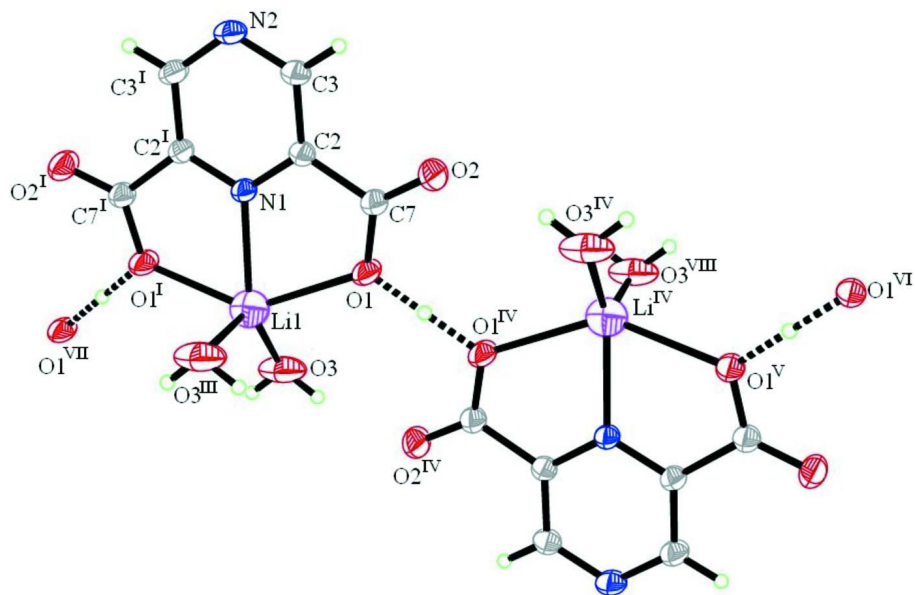
The asymmetric unit of the title compound consists of a Li<sup>i</sup> ion, a singly deprotonated pyrazine-2,6-dicarboxylate ligand molecule and a coordinated water molecule (Fig. 1). The coordination environment of the Li1 ion is composed of five atoms: ligand carboxylate O1, O1<sup>i</sup>, hetero-ring N1, aqua O3 and O3<sup>iii</sup> atoms. The coplanar Li1, N1, O3 and O3<sup>iii</sup> form the base of a distorted trigonal bipyramid with O1 and O1<sup>i</sup> atoms at its apices. [Symmetry code: <sup>i</sup>  $x, -y + 3/2, z$ ; <sup>ii</sup>  $x + 1, y, z$ , <sup>iii</sup>  $x - 1, y, z$ , <sup>iv</sup>  $1 - x, 1 - y, -z$ ]. The observed Li—O and Li—N bond distances (Table 1) are typical for Li<sup>i</sup> complexes with diazine carboxylate ligands, see, for example: Tombul & Guven, (2009); Starosta & Leciejewicz, (2010); Starosta & Leciejewicz, (2011*b*). Coordinated aqua O3 atom bridges Li1 with Li<sup>ii</sup> ion to form molecular ribbons which propagate in the crystal along [001] direction (Fig. 2). The carboxylato O1 atom remains protonated and maintains the charge balance. This proton, located at an inversion centre, forms a short centrosymmetric O1—H1<sup>iii</sup>⋯O1<sup>iv</sup> hydrogen bond of 2.455 (3) Å<sup>o</sup> which links adjacent ribbons to form molecular layers. The pyrazine ring is planar with r.m.s of 0.0024 (1) Å. The C7/O1/O2 and C7<sup>i</sup>/O1<sup>i</sup>/O2<sup>i</sup> carboxylic groups make with it dihedral angles of 3.0 (1)<sup>o</sup>. Bond distances and bond angles within the ligand molecule do not differ from those reported in the structure of pyrazine-2,6-dicarboxylic acid dihydrate (Ptasiewicz-Bąk & Leciejewicz, 2003). The layers are held together by weak hydrogen bonds in which the coordinated water molecules act as donors and carboxylate O atoms and hetero-ring N atoms from adjacent layers are as acceptors (Table 2). Protonated ligand carboxylate groups have been observed in the structures of Li<sup>i</sup> complexes with pyrazine-2,3-carboxylate (Tombul *et al.*, 2008, Starosta & Leciejewicz, 2011*b*) and pyrazine-2,5-dicarboxylate (Starosta & Leciejewicz, 2011*a*) ligands and in the structure of a Li<sup>i</sup> complex with pyrazine-2,3,5,6-tetracarboxylate ligand (Starosta & Leciejewicz, 2010). In the above structures, protons participate in short hydrogen bonds in which O atoms from adjacent intra-ligand carboxylate groups are donors and acceptors.

**S2. Experimental**

Hot aqueous solutions of 1 mmol of pyrazine-2,6-dicarboxylic acid dihydrate and 1 mmol of lithium hydroxide (Aldrich) were mixed and boiled under reflux with constant stirring for 6 h. Left for evaporation at room temperature, after a couple of days small single-crystal plates of the title complex were obtained. Crystals were washed with cold ethanol and dried in air.

**S3. Refinement**

Pyrazine ring H atoms were placed in calculated positions with C—H = 0.93 and 0.96 Å and treated as riding on the parent atoms with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$ . Water H atoms were found in Fourier map and refined isotropically.

**Figure 1**

The asymmetric unit of the title compound with atom labelling scheme and 50% probability displacement ellipsoids.

Symmetry code: <sup>i</sup>  $x, -y + 3/2, z$ ; <sup>ii</sup>  $x + 1, y, z$ ; <sup>iii</sup>  $x - 1, y, z$ ; <sup>iv</sup>  $1 - x, 1 - y, -z$ ; <sup>v</sup>  $1 - x, -1/2 + y, -z$ ; <sup>vi</sup>  $x, 1/2 - y, z$ ; <sup>vii</sup>  $1 - x, 1/2 + y, -z$ ; <sup>viii</sup>  $2 - x, 1 - y, -z$ .

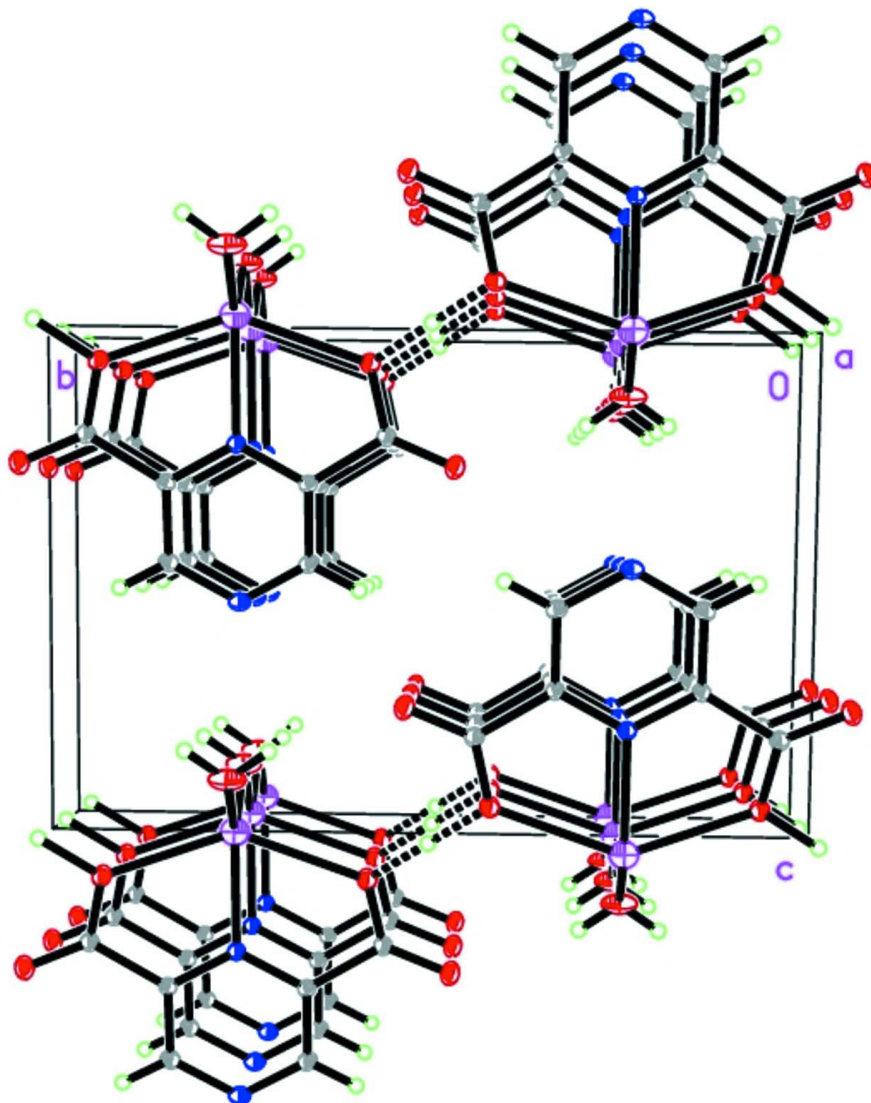


Figure 2

The alignment of the ribbons viewed along the axis *a*.

**catena-Poly[[6-carboxypyrazine-2-carboxylato]lithium]- $\mu$ -aqua]**

*Crystal data*

[Li(C<sub>6</sub>H<sub>3</sub>N<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O)]

*M<sub>r</sub>* = 192.06

Monoclinic, *P*2<sub>1</sub>/*m*

Hall symbol: -P 2yb

*a* = 3.5346 (7) Å

*b* = 12.519 (3) Å

*c* = 8.3583 (17) Å

$\beta$  = 97.86 (3)°

*V* = 366.37 (13) Å<sup>3</sup>

*Z* = 2

*F*(000) = 196

*D<sub>x</sub>* = 1.741 Mg m<sup>-3</sup>

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

Cell parameters from 25 reflections

$\theta$  = 6–15°

$\mu$  = 0.15 mm<sup>-1</sup>

*T* = 293 K

Plates, colourless

0.31 × 0.22 × 0.08 mm

*Data collection*

Kuma KM-4 four-circle  
diffractometer  
Radiation source: fine-focus sealed tube  
Graphite monochromator  
Profile data from  $\omega/2\theta$  scans  
Absorption correction: analytical  
(*CrysAlis RED*; Oxford Diffraction, 2008)  
 $T_{\min} = 0.954$ ,  $T_{\max} = 0.973$   
1262 measured reflections

1106 independent reflections  
729 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.027$   
 $\theta_{\max} = 30.1^\circ$ ,  $\theta_{\min} = 3.0^\circ$   
 $h = 0 \rightarrow 4$   
 $k = -17 \rightarrow 0$   
 $l = -11 \rightarrow 11$   
3 standard reflections every 200 reflections  
intensity decay: 1.3%

*Refinement*

Refinement on  $F^2$   
Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.054$   
 $wR(F^2) = 0.171$   
 $S = 1.09$   
1106 reflections  
75 parameters  
2 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  
 $w = 1/[\sigma^2(F_o^2) + (0.1039P)^2 + 0.0995P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.38 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$

*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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.2901 (6)	0.7500	0.2305 (2)	0.0216 (4)
O1	0.4179 (5)	0.57853 (10)	0.07619 (15)	0.0333 (4)
C2	0.2425 (5)	0.65866 (13)	0.30619 (19)	0.0216 (4)
N2	0.0883 (7)	0.7500	0.5385 (2)	0.0297 (5)
O2	0.2587 (5)	0.47052 (12)	0.27081 (17)	0.0371 (4)
C3	0.1409 (5)	0.65888 (14)	0.4618 (2)	0.0269 (4)
H3	0.1092	0.5942	0.5130	0.032*
C7	0.3068 (5)	0.55822 (14)	0.2144 (2)	0.0245 (4)
O3	0.8304 (9)	0.7500	-0.1306 (3)	0.0572 (8)
Li1	0.3902 (17)	0.7500	-0.0132 (8)	0.0456 (13)
H31	0.866 (12)	0.6976 (8)	-0.186 (4)	0.092 (14)*
H1	0.5000	0.5000	0.0000	0.10 (2)*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.0281 (10)	0.0194 (9)	0.0187 (8)	0.000	0.0084 (7)	0.000
O1	0.0561 (9)	0.0228 (7)	0.0254 (6)	0.0003 (6)	0.0216 (6)	-0.0014 (5)
C2	0.0253 (8)	0.0206 (7)	0.0198 (7)	-0.0006 (6)	0.0059 (5)	0.0012 (6)
N2	0.0404 (12)	0.0314 (12)	0.0196 (9)	0.000	0.0124 (8)	0.000
O2	0.0584 (10)	0.0223 (7)	0.0340 (7)	0.0004 (6)	0.0186 (6)	0.0037 (5)
C3	0.0348 (9)	0.0261 (9)	0.0217 (7)	0.0000 (7)	0.0109 (6)	0.0031 (6)
C7	0.0300 (8)	0.0223 (7)	0.0225 (7)	0.0009 (6)	0.0080 (6)	0.0002 (6)
O3	0.0642 (18)	0.084 (2)	0.0247 (10)	0.000	0.0122 (10)	0.000
Li1	0.039 (3)	0.053 (3)	0.046 (3)	0.000	0.007 (2)	0.000

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

N1—C2 <sup>i</sup>	1.3287 (18)	O2—C7	1.216 (2)
N1—C2	1.3287 (18)	C3—H3	0.9300
N1—Li1	2.115 (7)	O3—Li1	1.950 (7)
O1—C7	1.295 (2)	O3—Li1 <sup>ii</sup>	2.085 (7)
O1—Li1	2.271 (2)	O3—H31	0.825 (17)
O1—H1	1.2275 (13)	Li1—O3 <sup>iii</sup>	2.085 (7)
C2—C3	1.396 (2)	Li1—O1 <sup>i</sup>	2.271 (2)
C2—C7	1.506 (2)	Li1—Li1 <sup>iii</sup>	3.5346 (7)
N2—C3 <sup>i</sup>	1.334 (2)	Li1—Li1 <sup>ii</sup>	3.5346 (7)
N2—C3	1.334 (2)		
C2 <sup>i</sup> —N1—C2	118.8 (2)	O3—Li1—N1	137.3 (3)
C2 <sup>i</sup> —N1—Li1	120.51 (10)	O3 <sup>iii</sup> —Li1—N1	100.4 (3)
C2—N1—Li1	120.51 (10)	O3—Li1—O1 <sup>i</sup>	99.45 (16)
C7—O1—Li1	118.33 (19)	O3 <sup>iii</sup> —Li1—O1 <sup>i</sup>	98.65 (16)
C7—O1—H1	115.31 (13)	N1—Li1—O1 <sup>i</sup>	71.83 (16)
Li1—O1—H1	126.08 (17)	O3—Li1—O1	99.45 (16)
N1—C2—C3	120.51 (16)	O3 <sup>iii</sup> —Li1—O1	98.65 (16)
N1—C2—C7	115.98 (14)	N1—Li1—O1	71.84 (16)
C3—C2—C7	123.52 (15)	O1 <sup>i</sup> —Li1—O1	141.9 (3)
C3 <sup>i</sup> —N2—C3	117.5 (2)	O3—Li1—Li1 <sup>iii</sup>	150.10 (19)
N2—C3—C2	121.34 (16)	O3 <sup>iii</sup> —Li1—Li1 <sup>iii</sup>	27.79 (19)
N2—C3—H3	119.3	N1—Li1—Li1 <sup>iii</sup>	72.60 (17)
C2—C3—H3	119.3	O1 <sup>i</sup> —Li1—Li1 <sup>iii</sup>	89.89 (15)
O2—C7—O1	126.77 (16)	O1—Li1—Li1 <sup>iii</sup>	89.89 (15)
O2—C7—C2	121.16 (15)	O3—Li1—Li1 <sup>ii</sup>	29.90 (19)
O1—C7—C2	112.07 (15)	O3 <sup>iii</sup> —Li1—Li1 <sup>ii</sup>	152.21 (18)
Li1—O3—Li1 <sup>ii</sup>	122.3 (3)	N1—Li1—Li1 <sup>ii</sup>	107.40 (17)
Li1—O3—H31	119 (3)	O1 <sup>i</sup> —Li1—Li1 <sup>ii</sup>	90.11 (15)
Li1 <sup>ii</sup> —O3—H31	93 (3)	O1—Li1—Li1 <sup>ii</sup>	90.11 (15)
O3—Li1—O3 <sup>iii</sup>	122.3 (3)	Li1 <sup>iii</sup> —Li1—Li1 <sup>ii</sup>	179.999 (1)

Symmetry codes: (i)  $x, -y+3/2, z$ ; (ii)  $x+1, y, z$ ; (iii)  $x-1, y, z$ .

*Hydrogen-bond geometry (Å, °)*

<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>
O3—H31 $\cdots$ O2 <sup>iv</sup>	0.83 (2)	2.24 (2)	2.9987 (19)	152 (3)
O1—H1 $\cdots$ O1 <sup>iv</sup>	1.23 (1)	1.23 (1)	2.455 (3)	180 (1)

Symmetry code: (iv)  $-x+1, -y+1, -z$ .