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Poly[( $\mu_4$ -3-carboxypyrazine-2-carboxylato)( $\mu_4$ -nitrate)dilithium]

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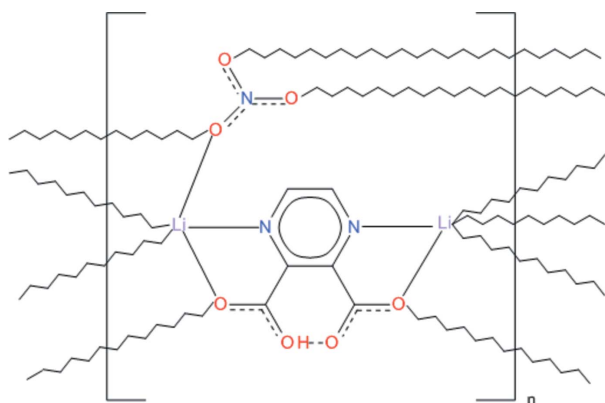
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.036;  $wR$  factor = 0.084; data-to-parameter ratio = 15.4.

In the title compound,  $[\text{Li}_2(\text{C}_6\text{H}_3\text{N}_2\text{O}_4)_2(\text{NO}_3)]_n$ , the two symmetry-independent  $\text{Li}^{\text{I}}$  ions are each in a trigonal-bipyramidal coordination and are bridged by  $N,O$ -bonding ligands, forming molecular ribbons propagating in  $[010]$ . Each  $\text{Li}^{\text{I}}$  ion is also coordinated by two O atoms from nitrate ions, connecting the ribbons into a three-dimensional network. Very strong intramolecular  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds occur between the carboxyl and the carboxylate group.

## Related literature

For three structures of lithium(I) complexes with pyrazine-2,3-dicarboxylate and water ligands, see: Tombul *et al.* (2008); Tombul & Güven (2009); Starosta & Leciejewicz (2011). For structures of calcium(II) complexes with the title ligand, see: Ptasiwicz-Bąk & Leciejewicz (1997); Starosta & Leciejewicz (2004, 2005a,b).



## Experimental

## Crystal data

 $[\text{Li}_2(\text{C}_6\text{H}_3\text{N}_2\text{O}_4)_2(\text{NO}_3)]$  $M_r = 241.99$ 

Monoclinic,  $P2_1$   
 $a = 4.6273$  (1) Å  
 $b = 15.8565$  (3) Å  
 $c = 6.1719$  (2) Å  
 $\beta = 95.598$  (2)°  
 $V = 450.69$  (2) Å<sup>3</sup>

$Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.16$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.20 \times 0.14 \times 0.12$  mm

## Data collection

Agilent SuperNova (Dual, Cu at zero, Eos) diffractometer  
 Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2011)  
 $T_{\min} = 0.936$ ,  $T_{\max} = 1.000$

4032 measured reflections  
 2572 independent reflections  
 2401 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.015$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.084$   
 $S = 1.10$   
 2572 reflections  
 167 parameters  
 1 restraint

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.21$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.20$  e Å<sup>-3</sup>

Table 1

Selected bond lengths (Å).

Li1—O1	2.086 (3)	Li2—N4	2.176 (3)
Li1—O5	2.005 (3)	Li2—O1 <sup>iii</sup>	1.989 (3)
Li1—N1	2.158 (3)	Li2—O5 <sup>iv</sup>	2.014 (3)
Li1—O7 <sup>i</sup>	1.994 (3)	Li2—O6 <sup>v</sup>	2.040 (4)
Li1—O3 <sup>ii</sup>	1.999 (3)	Li2—O3	2.086 (3)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O2}-\text{H1}\cdots\text{O4}$	1.07 (4)	1.34 (4)	2.3955 (19)	170 (4)

Data collection: CrysAlis PRO (Agilent, 2011); cell refinement: CrysAlis PRO; data reduction: CrysAlis PRO; 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: KP2442).

## References

- Agilent (2011). CrysAlis PRO. Agilent Technologies, Yarnton, England.  
 Ptasiwicz-Bąk, H. & Leciejewicz, J. (1997). *Pol. J. Chem.* **71**, 1603–1610.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
 Starosta, W. & Leciejewicz, J. (2004). *J. Coord. Chem.* **57**, 1151–1156.  
 Starosta, W. & Leciejewicz, J. (2005a). *J. Coord. Chem.* **58**, 891–898.  
 Starosta, W. & Leciejewicz, J. (2005b). *J. Coord. Chem.* **58**, 963–968.  
 Starosta, W. & Leciejewicz, J. (2011). *Acta Cryst.* **E67**, m1133–m1134.  
 Tombul, M. & Güven, K. (2009). *Acta Cryst.* **E65**, m1704–m1705.  
 Tombul, M., Güven, K. & Büyükgüngör, O. (2008). *Acta Cryst.* **E64**, m491–m492.

## supporting information

*Acta Cryst.* (2013). E69, m62 [https://doi.org/10.1107/S1600536812050738]

**Poly[( $\mu_4$ -3-carboxypyrazine-2-carboxylato)( $\mu_4$ -nitrate)dilithium]****Wojciech Starosta and Janusz Leciejewicz****S1. Comment**

Pyrazine-2,3-dicarboxylate dianion shows large versatility in forming coordination compounds with metal ions. Depending on the adopted chemical synthesis procedures, compounds with a number of different polymeric structures have been observed, as for example, in the case of the Ca(II) ion (Ptasiewicz-Bąk & Leciejewicz, 1997; Starosta & Leciejewicz, 2004, 2005*a*, 2005*b*). Polymeric structures of three Li<sup>I</sup> complexes with the title ligand have been reported (Tombul *et al.*, 2008; Tombul & Güven, 2009; Starosta & Leciejewicz, 2011). Recently we have obtained a new compound with the title ligand. The asymmetric unit of the title compound contains two symmetry independent Li<sup>I</sup> ions. Each shows a distorted trigonal-bipyramidal coordination geometry. The Li1 ion is coordinated by ligand N1, O1 bonding group, a carboxylato O3<sup>ii</sup> atom from the adjacent ligand and O5 and O7<sup>i</sup> atoms from two different nitrate ions. The O1, O5, O7<sup>i</sup> atoms form a base, the Li1 ion is 0.1572 (3) Å out of this plane; N1 and O3<sup>ii</sup> atoms are at the axial positions. The same coordination geometry shows the Li2 ion which is situated 0.3616 (3) Å out of the equatorial plane composed of N4, O1<sup>iii</sup> and O6<sup>v</sup> atoms, while the O3 and O5<sup>iv</sup> atoms form the apices. The observed Li—O and Li—N bond distances are typical of Li<sup>I</sup> complexes with diazine carboxylate ligands. Ligand carboxylate O2 and O4 atoms remain coordination inactive. Fourier maps indicate clearly, that the O2 atom is protonated acting as a donor in a low-barrier intramolecular hydrogen bond of 2.3955 (19) Å to the O4 atom suggesting a partial proton transfer (Table 2). The ligand is monovalent and with the nitrate anion maintains the charge balance in the structure. Pyrazine ring is planar with r.m.s. of 0.0051 (2) Å; carboxylate groups C7/O1/O2 and C8/O3/O4 form with it dihedral angles of 8.4 (1)° and 12.5 (1)°, respectively. Ligand molecule bridges metal ions in  $\mu_4$  mode. Li1 and Li2 ions are chelated by both N, O groups of a ligand and bidentate O1<sup>ii</sup> and O3<sup>ii</sup> atoms [Fig. 1]. A dimeric moiety Li1/O1/L2<sup>ii</sup>/O3<sup>iii</sup> constitutes a link in a bridging pathway formed by ligand molecules, giving rise to molecular ribbons propagating in the [010] direction. A nitrate anion with r.m.s. of 0.0016 (1) Å acts also in the  $\mu_4$  mode and forms the other bridging pathway: while the O6 atom coordinates the Li2<sup>v</sup> and the O7 atom - the Li1<sup>iv</sup> ion, the O5 atom acts as bidentate bridging to the Li1 and Li2<sup>iii</sup> ions giving rise to a three-dimensional framework (Fig. 2).

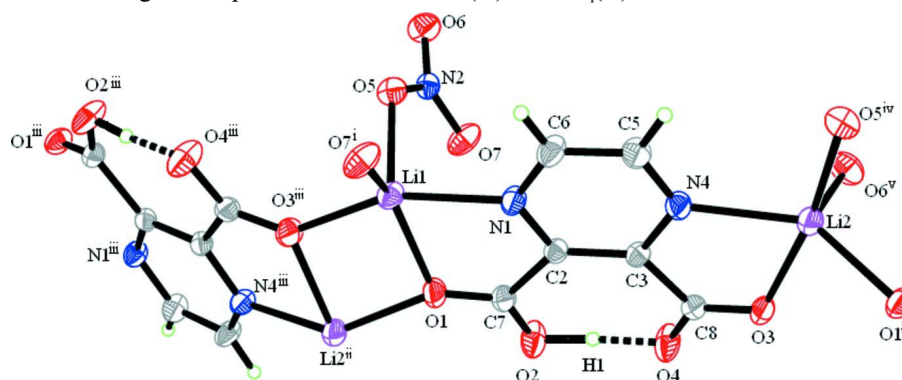
**S2. Experimental**

An aqueous solution containing 1 mmol of lithium(I) nitrate and 1 mmol of pyrazine-2,3-dicarboxylic acid dihydrate was boiled with stirring under reflux for 6 h. After cooling to room temperature three drops of 1 N nitric acid were added to maintain pH of 5. Then the solution was left to evaporate to dryness. Deposited single crystal plates were washed with cold ethanol and dried in the air.

**S3. Refinement**

The hydrogen atom of carboxylate group was located in a difference map and was refined independently with an isotropic displacement parameter. H atoms bonded to pyrazine ring C atoms were placed in calculated positions with C—H = 0.93

and 0.96 Å and treated as riding on the parent atoms with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .



**Figure 1**

A fragment of the structure of the title compound with atom labelling scheme and 50% probability displacement ellipsoids. Symmetry code: (i)  $x + 1, y, z$ ; (ii)  $-x + 1, y + 1/2, -z + 2$ ; (iii)  $-x + 1, y - 1/2, -z + 2$ ; (iv)  $-x + 1, y - 1/2, -z + 1$ ; (v)  $-x, y - 1/2, -z + 1$ .

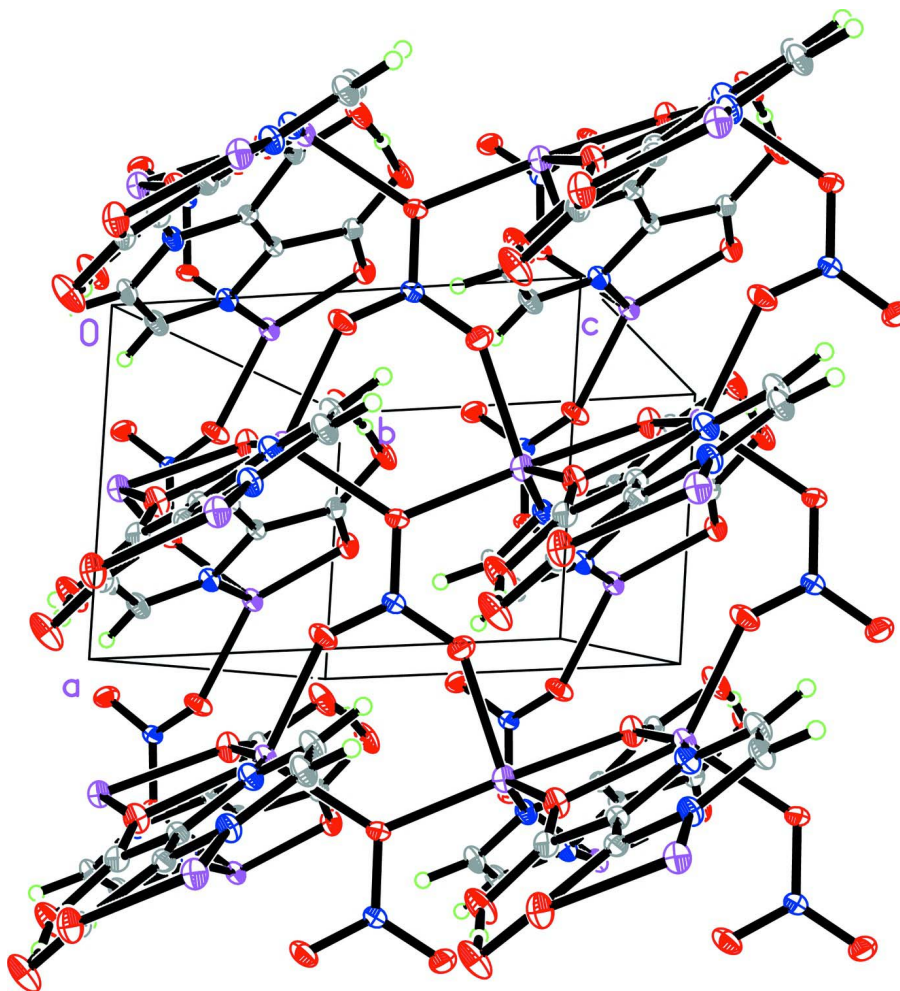


Figure 2

The packing of molecular ribbons in the structure of the title compound showing nitrate bridging mode.

**Poly[( $\mu_4$ -3-carboxypyrazine-2-carboxylato)( $\mu_4$ -nitrate)dilithium]**

*Crystal data*

[Li<sub>2</sub>(C<sub>6</sub>H<sub>3</sub>N<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>)]

$M_r = 241.99$

Monoclinic,  $P2_1$

Hall symbol: P 2yb

$a = 4.6273$  (1) Å

$b = 15.8565$  (3) Å

$c = 6.1719$  (2) Å

$\beta = 95.598$  (2)°

$V = 450.69$  (2) Å<sup>3</sup>

$Z = 2$

$F(000) = 242$

$D_x = 1.783$  Mg m<sup>-3</sup>

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

Cell parameters from 2509 reflections

$\theta = 3.3$ – $30.7^\circ$

$\mu = 0.16$  mm<sup>-1</sup>

$T = 293$  K

Block, colourless

$0.20 \times 0.14 \times 0.12$  mm

*Data collection*

Agilent SuperNova (Dual, Cu at zero, Eos) diffractometer

Radiation source: SuperNova (Mo) X-ray Source

Mirror monochromator

Detector resolution: 16.0131 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)

$T_{\min} = 0.936$ ,  $T_{\max} = 1.000$

4032 measured reflections

2572 independent reflections

2401 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.015$

$\theta_{\max} = 30.7^\circ$ ,  $\theta_{\min} = 3.3^\circ$

$h = -5 \rightarrow 6$

$k = -21 \rightarrow 22$

$l = -5 \rightarrow 8$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.084$

$S = 1.10$

2572 reflections

167 parameters

1 restraint

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

$w = 1/[\sigma^2(F_o^2) + (0.0337P)^2 + 0.0702P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.21$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.20$  e Å<sup>-3</sup>

*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>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.5316 (3)	0.40681 (8)	0.6101 (2)	0.0322 (3)
O5	0.4586 (3)	0.48672 (8)	0.0630 (2)	0.0297 (3)
C2	0.4874 (4)	0.27654 (10)	0.4273 (3)	0.0223 (3)
N4	0.5051 (4)	0.14644 (9)	0.2348 (2)	0.0279 (3)
N1	0.6499 (3)	0.31421 (9)	0.2871 (2)	0.0278 (3)
N2	0.1867 (3)	0.47658 (9)	0.0539 (2)	0.0243 (3)
O2	0.2330 (4)	0.31513 (9)	0.7378 (3)	0.0427 (4)
C8	0.2425 (4)	0.13507 (11)	0.5462 (3)	0.0261 (3)
C3	0.4152 (4)	0.19074 (10)	0.4027 (3)	0.0228 (3)
O7	0.0838 (3)	0.43786 (9)	0.2022 (3)	0.0393 (3)
O6	0.0354 (3)	0.50501 (10)	−0.1046 (2)	0.0388 (3)
C5	0.6615 (4)	0.18550 (12)	0.0970 (3)	0.0326 (4)
H5	0.7223	0.1559	−0.0205	0.039*
C7	0.4118 (4)	0.33782 (11)	0.6048 (3)	0.0267 (3)
C6	0.7368 (5)	0.27000 (11)	0.1245 (3)	0.0338 (4)
H6	0.8500	0.2957	0.0269	0.041*
Li1	0.7058 (7)	0.44849 (19)	0.3298 (5)	0.0289 (6)
Li2	0.3903 (7)	0.0133 (2)	0.2244 (5)	0.0300 (6)
O3	0.2524 (3)	0.05895 (8)	0.5143 (2)	0.0329 (3)
O4	0.1008 (4)	0.16985 (8)	0.6880 (3)	0.0444 (4)
H1	0.153 (8)	0.252 (2)	0.713 (6)	0.093 (11)*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0444 (8)	0.0222 (6)	0.0311 (7)	−0.0058 (6)	0.0086 (6)	−0.0054 (5)
O5	0.0184 (5)	0.0402 (7)	0.0307 (6)	−0.0033 (5)	0.0045 (4)	0.0052 (5)
C2	0.0242 (7)	0.0194 (7)	0.0236 (7)	0.0013 (6)	0.0044 (6)	0.0004 (6)
N4	0.0352 (8)	0.0224 (7)	0.0275 (8)	−0.0012 (6)	0.0092 (6)	−0.0022 (6)
N1	0.0337 (8)	0.0208 (6)	0.0303 (8)	−0.0019 (6)	0.0103 (6)	0.0006 (6)
N2	0.0223 (6)	0.0230 (6)	0.0285 (7)	−0.0014 (5)	0.0073 (5)	−0.0009 (5)
O2	0.0596 (9)	0.0274 (6)	0.0463 (9)	−0.0092 (7)	0.0320 (7)	−0.0110 (6)
C8	0.0308 (9)	0.0230 (8)	0.0249 (9)	−0.0012 (7)	0.0039 (7)	0.0008 (6)
C3	0.0237 (8)	0.0214 (7)	0.0239 (8)	0.0003 (6)	0.0050 (6)	0.0017 (6)
O7	0.0332 (7)	0.0416 (8)	0.0461 (8)	0.0019 (6)	0.0197 (6)	0.0144 (6)
O6	0.0280 (7)	0.0479 (8)	0.0392 (7)	−0.0007 (6)	−0.0036 (6)	0.0101 (6)
C5	0.0433 (10)	0.0271 (9)	0.0301 (9)	0.0005 (8)	0.0173 (8)	−0.0051 (7)
C7	0.0322 (9)	0.0217 (7)	0.0265 (8)	0.0010 (6)	0.0045 (7)	−0.0022 (6)
C6	0.0426 (11)	0.0258 (8)	0.0356 (10)	−0.0016 (8)	0.0171 (8)	0.0032 (7)
Li1	0.0342 (16)	0.0249 (14)	0.0288 (15)	0.0009 (12)	0.0097 (12)	0.0000 (12)
Li2	0.0382 (16)	0.0234 (13)	0.0287 (15)	0.0015 (13)	0.0052 (13)	0.0008 (12)
O3	0.0495 (8)	0.0207 (6)	0.0293 (6)	−0.0037 (5)	0.0085 (6)	0.0027 (5)
O4	0.0629 (10)	0.0275 (7)	0.0488 (9)	−0.0113 (7)	0.0359 (8)	−0.0059 (6)

## Geometric parameters (Å, °)

O1—C7	1.225 (2)	O2—C7	1.273 (2)
O1—Li <sup>2i</sup>	1.989 (3)	O2—H1	1.07 (4)
Li1—O1	2.086 (3)	C8—O3	1.224 (2)
O5—N2	1.2643 (18)	C8—O4	1.269 (2)
Li1—O5	2.005 (3)	C8—C3	1.530 (2)
Li1—N1	2.158 (3)	O7—Li <sup>1iv</sup>	1.994 (3)
Li1—O7 <sup>ii</sup>	1.994 (3)	O6—Li <sup>2v</sup>	2.040 (4)
Li1—O3 <sup>i</sup>	1.999 (3)	C5—C6	1.391 (3)
O5—Li <sup>2iii</sup>	2.014 (3)	C5—H5	0.9300
C2—N1	1.341 (2)	C6—H6	0.9300
C2—C3	1.406 (2)	Li1—Li <sup>2i</sup>	3.011 (4)
C2—C7	1.530 (2)	Li2—O1 <sup>vi</sup>	1.989 (3)
N4—C5	1.324 (2)	Li2—O5 <sup>vii</sup>	2.014 (3)
N4—C3	1.351 (2)	Li2—O6 <sup>viii</sup>	2.040 (4)
Li2—N4	2.176 (3)	Li2—O3	2.086 (3)
N1—C6	1.319 (2)	Li2—Li <sup>1vi</sup>	3.011 (4)
N2—O6	1.231 (2)	O3—Li <sup>1vi</sup>	1.999 (3)
N2—O7	1.2359 (19)	O4—H1	1.34 (4)
C7—O1—Li <sup>2i</sup>	146.19 (15)	C5—C6—H6	119.5
C7—O1—Li1	118.12 (15)	O7 <sup>ii</sup> —Li1—O3 <sup>i</sup>	102.51 (15)
Li <sup>2i</sup> —O1—Li1	95.24 (14)	O7 <sup>ii</sup> —Li1—O5	98.83 (14)
N2—O5—Li1	118.93 (13)	O3 <sup>i</sup> —Li1—O5	98.69 (14)
N2—O5—Li <sup>2iii</sup>	114.63 (14)	O7 <sup>ii</sup> —Li1—O1	136.49 (18)
Li1—O5—Li <sup>2iii</sup>	124.59 (14)	O3 <sup>i</sup> —Li1—O1	84.57 (13)
N1—C2—C3	120.27 (14)	O5—Li1—O1	122.78 (17)
N1—C2—C7	111.15 (14)	O7 <sup>ii</sup> —Li1—N1	88.16 (13)
C3—C2—C7	128.55 (15)	O3 <sup>i</sup> —Li1—N1	158.15 (18)
C5—N4—C3	118.59 (14)	O5—Li1—N1	98.41 (14)
C5—N4—Li2	125.60 (15)	O1—Li1—N1	74.76 (11)
C3—N4—Li2	115.76 (14)	O7 <sup>ii</sup> —Li1—Li <sup>2i</sup>	127.08 (16)
C6—N1—C2	119.08 (15)	O3 <sup>i</sup> —Li1—Li <sup>2i</sup>	43.67 (9)
C6—N1—Li1	125.14 (14)	O5—Li1—Li <sup>2i</sup>	121.60 (15)
C2—N1—Li1	115.41 (13)	O1—Li1—Li <sup>2i</sup>	41.13 (9)
O6—N2—O7	122.70 (15)	N1—Li1—Li <sup>2i</sup>	114.95 (13)
O6—N2—O5	118.37 (14)	O1 <sup>vi</sup> —Li2—O5 <sup>vii</sup>	102.31 (15)
O7—N2—O5	118.93 (15)	O1 <sup>vi</sup> —Li2—O6 <sup>viii</sup>	104.59 (16)
C7—O2—H1	114 (2)	O5 <sup>vii</sup> —Li2—O6 <sup>viii</sup>	94.18 (14)
O3—C8—O4	124.69 (17)	O1 <sup>vi</sup> —Li2—O3	84.81 (13)
O3—C8—C3	116.47 (15)	O5 <sup>vii</sup> —Li2—O3	171.64 (18)
O4—C8—C3	118.83 (14)	O6 <sup>viii</sup> —Li2—O3	88.17 (14)
N4—C3—C2	119.89 (14)	O1 <sup>vi</sup> —Li2—N4	141.01 (18)
N4—C3—C8	111.18 (14)	O5 <sup>vii</sup> —Li2—N4	97.16 (14)
C2—C3—C8	128.92 (14)	O6 <sup>viii</sup> —Li2—N4	107.32 (15)
N2—O7—Li <sup>1iv</sup>	131.81 (15)	O3—Li2—N4	74.49 (12)
N2—O6—Li <sup>2v</sup>	139.98 (15)	O1 <sup>vi</sup> —Li2—Li <sup>1vi</sup>	43.63 (9)

N4—C5—C6	121.23 (16)	O5 <sup>vii</sup> —Li2—Li1 <sup>vi</sup>	145.93 (15)
N4—C5—H5	119.4	O6 <sup>viii</sup> —Li2—Li1 <sup>vi</sup>	94.92 (13)
C6—C5—H5	119.4	O3—Li2—Li1 <sup>vi</sup>	41.41 (9)
O1—C7—O2	123.79 (16)	N4—Li2—Li1 <sup>vi</sup>	111.21 (14)
O1—C7—C2	116.83 (15)	C8—O3—Li1 <sup>vi</sup>	142.15 (15)
O2—C7—C2	119.38 (15)	C8—O3—Li2	119.94 (14)
N1—C6—C5	120.92 (17)	Li1 <sup>vi</sup> —O3—Li2	94.92 (14)
N1—C6—H6	119.5	C8—O4—H1	113.8 (17)
C3—C2—N1—C6	1.0 (3)	N2—O5—Li1—Li2 <sup>i</sup>	-57.2 (2)
C7—C2—N1—C6	179.39 (16)	Li2 <sup>iii</sup> —O5—Li1—Li2 <sup>i</sup>	139.21 (19)
C3—C2—N1—Li1	174.35 (15)	C7—O1—Li1—O7 <sup>ii</sup>	-88.5 (3)
C7—C2—N1—Li1	-7.3 (2)	Li2 <sup>i</sup> —O1—Li1—O7 <sup>ii</sup>	97.2 (3)
Li1—O5—N2—O6	175.52 (16)	C7—O1—Li1—O3 <sup>i</sup>	168.99 (15)
Li2 <sup>iii</sup> —O5—N2—O6	-19.3 (2)	Li2 <sup>i</sup> —O1—Li1—O3 <sup>i</sup>	-5.28 (15)
Li1—O5—N2—O7	-5.3 (2)	C7—O1—Li1—O5	72.1 (2)
Li2 <sup>iii</sup> —O5—N2—O7	159.91 (16)	Li2 <sup>i</sup> —O1—Li1—O5	-102.13 (19)
C5—N4—C3—C2	0.3 (3)	C7—O1—Li1—N1	-18.14 (18)
Li2—N4—C3—C2	177.86 (16)	Li2 <sup>i</sup> —O1—Li1—N1	167.59 (13)
C5—N4—C3—C8	-179.02 (17)	C7—O1—Li1—Li2 <sup>i</sup>	174.3 (2)
Li2—N4—C3—C8	-1.4 (2)	C6—N1—Li1—O7 <sup>ii</sup>	-34.8 (2)
N1—C2—C3—N4	-1.3 (3)	C2—N1—Li1—O7 <sup>ii</sup>	152.34 (15)
C7—C2—C3—N4	-179.31 (17)	C6—N1—Li1—O3 <sup>i</sup>	-155.0 (4)
N1—C2—C3—C8	177.86 (17)	C2—N1—Li1—O3 <sup>i</sup>	32.2 (6)
C7—C2—C3—C8	-0.2 (3)	C6—N1—Li1—O5	63.8 (2)
O3—C8—C3—N4	12.0 (2)	C2—N1—Li1—O5	-109.00 (16)
O4—C8—C3—N4	-167.97 (17)	C6—N1—Li1—O1	-174.35 (17)
O3—C8—C3—C2	-167.18 (17)	C2—N1—Li1—O1	12.80 (17)
O4—C8—C3—C2	12.8 (3)	C6—N1—Li1—Li2 <sup>i</sup>	-165.38 (18)
O6—N2—O7—Li1 <sup>iv</sup>	-32.3 (3)	C2—N1—Li1—Li2 <sup>i</sup>	21.8 (2)
O5—N2—O7—Li1 <sup>iv</sup>	148.58 (19)	C5—N4—Li2—O1 <sup>vi</sup>	112.0 (3)
O7—N2—O6—Li2 <sup>v</sup>	1.3 (3)	C3—N4—Li2—O1 <sup>vi</sup>	-65.4 (3)
O5—N2—O6—Li2 <sup>v</sup>	-179.55 (19)	C5—N4—Li2—O5 <sup>vii</sup>	-7.8 (2)
C3—N4—C5—C6	0.9 (3)	C3—N4—Li2—O5 <sup>vii</sup>	174.83 (14)
Li2—N4—C5—C6	-176.40 (18)	C5—N4—Li2—O6 <sup>viii</sup>	-104.4 (2)
Li2 <sup>i</sup> —O1—C7—O2	9.4 (4)	C3—N4—Li2—O6 <sup>viii</sup>	78.16 (19)
Li1—O1—C7—O2	-160.34 (19)	C5—N4—Li2—O3	172.54 (18)
Li2 <sup>i</sup> —O1—C7—C2	-170.2 (2)	C3—N4—Li2—O3	-4.88 (16)
Li1—O1—C7—C2	20.1 (2)	C5—N4—Li2—Li1 <sup>vi</sup>	153.02 (18)
N1—C2—C7—O1	-7.9 (2)	C3—N4—Li2—Li1 <sup>vi</sup>	-24.4 (2)
C3—C2—C7—O1	170.27 (18)	O4—C8—O3—Li1 <sup>vi</sup>	-43.1 (4)
N1—C2—C7—O2	172.51 (18)	C3—C8—O3—Li1 <sup>vi</sup>	136.9 (2)
C3—C2—C7—O2	-9.3 (3)	O4—C8—O3—Li2	162.41 (19)
C2—N1—C6—C5	0.2 (3)	C3—C8—O3—Li2	-17.6 (2)
Li1—N1—C6—C5	-172.44 (19)	O1 <sup>vi</sup> —Li2—O3—C8	159.34 (16)
N4—C5—C6—N1	-1.2 (3)	O5 <sup>vii</sup> —Li2—O3—C8	10.7 (14)
N2—O5—Li1—O7 <sup>ii</sup>	158.55 (14)	O6 <sup>viii</sup> —Li2—O3—C8	-95.84 (18)
Li2 <sup>iii</sup> —O5—Li1—O7 <sup>ii</sup>	-5.1 (2)	N4—Li2—O3—C8	12.71 (19)

N2—O5—Li1—O3 <sup>i</sup>	-97.24 (17)	Li1 <sup>vi</sup> —Li2—O3—C8	164.6 (2)
Li2 <sup>iii</sup> —O5—Li1—O3 <sup>i</sup>	99.13 (17)	O1 <sup>vi</sup> —Li2—O3—Li1 <sup>vi</sup>	-5.27 (15)
N2—O5—Li1—O1	-8.1 (2)	O5 <sup>vii</sup> —Li2—O3—Li1 <sup>vi</sup>	-153.9 (13)
Li2 <sup>iii</sup> —O5—Li1—O1	-171.75 (15)	O6 <sup>viii</sup> —Li2—O3—Li1 <sup>vi</sup>	99.55 (14)
N2—O5—Li1—N1	69.12 (17)	N4—Li2—O3—Li1 <sup>vi</sup>	-151.90 (13)
Li2 <sup>iii</sup> —O5—Li1—N1	-94.52 (18)		

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

*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>
O2—H1 $\cdots$ O4	1.07 (4)	1.34 (4)	2.3955 (19)	170 (4)