

Poly[μ -aqua-diaqua(μ_2 -pyrazine-2,3-dicarboxylato)dilithium(I)]

Mustafa Tombul^{a*} and Kutalmis Guven^b

^aDepartment of Chemistry, Faculty of Art and Science, University of Kirikkale, Campus, Yahsihan, Kirikkale, 71450 Kirikkale, Turkey, and ^bDepartment of Physics, Faculty of Art and Science, University of Kirikkale, Campus, Yahsihan, Kirikkale, 71450 Kirikkale, Turkey

Correspondence e-mail: mustafatombul38@gmail.com

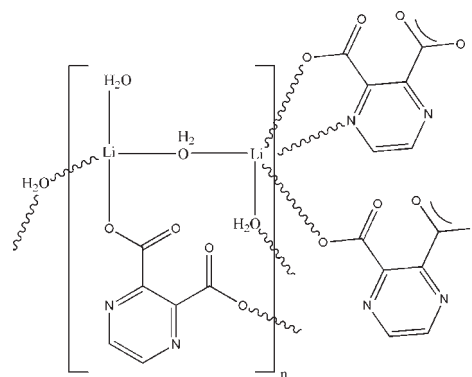
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.062; wR factor = 0.211; data-to-parameter ratio = 34.0.

The asymmetric unit of the title compound, $[\text{Li}_2(\text{C}_6\text{H}_2\text{N}_2\text{O}_4)(\text{H}_2\text{O})_3]_n$, consists of two independent Li^+ cations, one pyrazine-2,3-dicarboxylate dianion and three water molecules. One of the Li^+ cations has a distorted tetrahedral geometry, coordinated by one of the carboxylate O atoms of the pyrazine-2,3-dicarboxylate ligand and three O atoms from three water molecules, whereas the other Li^+ cation has a distorted trigonal-bipyramidal geometry, coordinated by a carboxylate O atom of a symmetry-related pyrazine-2,3-dicarboxylate ligand, two water molecules and a chelating pyrazine-2,3-dicarboxylate ligand (by utilizing both N and O atoms) of an adjacent molecule. The synthesis of a hydrated polymeric dinuclear lithium complex formed with two pyrazine-2,3-dicarboxylic acid ligands has been reported previously [Tombul *et al.* (2008a). *Acta Cryst. E* **64**, m491–m492]. By comparison to the complex reported here, the dinuclear complex formed with two pyrazine-2,3-dicarboxylic acid ligands differs in the coordination geometry of both Li atoms. The crystal structure further features $\text{O}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{N}$ hydrogen-bonding interactions involving the water molecules and carboxylate O atoms.

Related literature

For a general background to multidendate carboxylic acids, see: Erxleben (2003); Ye *et al.* (2005); Fei *et al.* (2006). For further information on pyrazine-2,3-dicarboxylic acid, see: Takusagawa & Shimada (1973); Richard *et al.* (1973); Nepveu *et al.* (1993). For further information on the synthesis of metal complexes with pyrazine-2,3-dicarboxylic acid ligand, see: Tombul & Guven (2009); Tombul *et al.* (2006, 2007, 2008b). For a related structure of lithium with pyrazine-2,3-dicarboxylic acid ligand, see: Tombul *et al.* (2008a). For Li–O bond distances, see: Chen *et al.* (2007); Kim *et al.* (2007). For Li–N bond lengths, see: Grossie *et al.* (2006); Boyd *et al.* (2002).



Experimental

Crystal data

$[\text{Li}_2(\text{C}_6\text{H}_2\text{N}_2\text{O}_4)(\text{H}_2\text{O})_3]$
 $M_r = 234.02$
 Monoclinic, $P2_1/c$
 $a = 7.487$ (3) Å
 $b = 16.409$ (8) Å
 $c = 7.958$ (2) Å
 $\beta = 92.92$ (3)°

$V = 976.4$ (7) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.14$ mm⁻¹
 $T = 298$ K
 0.40 × 0.20 × 0.06 mm

Data collection

Rigaku AFC-7S diffractometer
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\text{min}} = 0.948$, $T_{\text{max}} = 0.994$
 6366 measured reflections
 6045 independent reflections

2427 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.120$
 3 standard reflections
 frequency: 150 reflections
 intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.062$
 $wR(F^2) = 0.211$
 $S = 0.96$
 6045 reflections
 178 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.49$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.54$ e Å⁻³

Table 1

Selected bond lengths (Å).

O5–Li1	2.046 (4)	Li2–O1 ⁱⁱ	1.942 (3)
O5–Li2	2.069 (4)	Li2–O3 ⁱⁱⁱ	1.988 (3)
O6–Li2	2.129 (4)	Li1–O7	1.918 (4)
O2–Li1	1.927 (3)	Li1–O6 ⁱⁱⁱ	1.973 (4)
N1–Li2 ⁱ	2.317 (4)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O5–H5A \cdots O2 ^{iv}	0.81 (3)	1.92 (3)	2.723 (3)	172.60 (3)
O5–H5B \cdots O4	0.87 (4)	2.28 (4)	3.068 (3)	152 (3)
O6–H6A \cdots N2 ^v	0.86 (3)	2.00 (3)	2.857 (3)	169.66 (4)
O6–H6B \cdots O3	0.88 (3)	1.86 (3)	2.719 (3)	163 (3)
O7–H7A \cdots O4 ^{iv}	0.88 (4)	2.02 (4)	2.841 (3)	154.89 (6)
O7–H7B \cdots O4 ^{vi}	0.88 (4)	1.86 (4)	2.730 (3)	169.51 (6)

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

Data collection: *MSC/AFD Diffractometer Control Software* (Molecular Structure Corporation, 1989); cell refinement: *MSC/AFD Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1993); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2293).

References

- Boyd, C. L., Tyrrell, B. R. & Mountford, P. (2002). *Acta Cryst.* **E58**, m597–m598.
- Chen, Z., Fei, Z., Zhao, D., Feng, Y. & Yu, K. (2007). *Inorg. Chem. Commun.* **10**, 77–79.
- Erxleben, A. (2003). *Coord. Chem. Rev.* **246**, 203–228.
- Fei, Z., Geldbach, T. J., Zhao, D. & Dyson, P. J. (2006). *Chem. Eur. J.* **12**, 2122–2130.
- Grossie, D. A., Feld, W. A., Scanlon, L., Sandi, G. & Wawrzak, Z. (2006). *Acta Cryst.* **E62**, m827–m829.
- Kim, E.-J., Kim, C.-H. & Yun, S.-S. (2007). *Acta Cryst.* **C63**, m427–m429.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Molecular Structure Corporation (1989). *MSC/AFD Diffractometer Control Software*. MSC, The Woodlands, Texas, USA.
- Molecular Structure Corporation (1993). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, The Woodlands, Texas, USA.
- Nepveu, F., Berkaoui, M. 'H. & Walz, L. (1993). *Acta Cryst.* **C49**, 1465–1466.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Richard, P., Tran Qui, D. & Bertaut, E. F. (1973). *Acta Cryst.* **B29**, 1111–1115.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Takusagawa, T. & Shimada, A. (1973). *Chem. Lett.* pp. 1121–1126.
- Tombul, M. & Güven, K. (2009). *Acta Cryst.* **E65**, m213–m214.
- Tombul, M., Güven, K. & Alkış, N. (2006). *Acta Cryst.* **E62**, m945–m947.
- Tombul, M., Güven, K. & Büyükgüngör, O. (2007). *Acta Cryst.* **E63**, m1783–m1784.
- Tombul, M., Güven, K. & Büyükgüngör, O. (2008a). *Acta Cryst.* **E64**, m491–m492.
- Tombul, M., Güven, K. & Svoboda, I. (2008b). *Acta Cryst.* **E64**, m246–m247.
- Westrip, S. P. (2009). *publCIF*. In preparation.
- Ye, B.-H., Tong, M.-L. & Chen, X.-M. (2005). *Coord. Chem. Rev.* **249**, 545–565.

supplementary materials

Acta Cryst. (2009). E65, m1704-m1705 [doi:10.1107/S1600536809050570]

Poly[μ -aqua-diaqua(μ_2 -pyrazine-2,3-dicarboxylato)dilithium(I)]

M. Tombul and K. Guven

Comment

Multidentate carboxylic acids are found to be excellent ligands for the synthesis of coordination polymers, giving structures with a diverse range of topologies and conformations, owing to the carboxylate groups being able to coordinate to a metal centre as a mono-, bi-, or multidentate ligand (Erxleben, 2003; Ye *et al.*, 2005; Fei *et al.*, 2006). Pyrazine-2,3-dicarboxylic acid (Takusagawa & Shimada, 1973) and its dianion (Richard *et al.*, 1973; Nepveu *et al.*, 1993) have been reported to be well suited for the construction of multidimensional frameworks (nD, n = 1–3), due to the presence of two adjacent carboxylate groups (O donor atoms) as substituents on the N-heterocyclic pyrazine ring (N donor atoms). In recent years, metal complexes with pyrazine-2,3-dicarboxylic acid ligand have been extensively studied because of their wide applications and growing interest in supramolecular chemistry. Examples include sodium (Tombul *et al.*, 2006), caesium (Tombul *et al.*, 2007), potassium (Tombul *et al.*, 2008b), lithium (Tombul *et al.*, 2008a) and rubidium (Tombul & Guven, 2009) complexes. As a continuation of our ongoing research on Group I dicarboxylates, we report here the synthesis and crystal structure of the hydrated polymeric dinuclear lithium complex formed with one molar equivalent of pyrazine-2,3-dicarboxylic acid.

As shown in Fig. 1, the title compound is a polymeric dinuclear complex with two kinds of Li atoms, one pyrazine-2,3-dicarboxylate ligand and three water molecules in the asymmetric unit. The geometries of the two independent Li atoms are different and the coordination modes of the pyrazine-2,3-dicarboxylate towards the cations are dissimilar. The Li1 ion has a distorted four-coordinate geometry and achieves the coordination number by bonding to one of the carboxylate O atom of pyrazine-2,3-dicarboxylate ligand, three O atoms from three water molecules, one of which is a symmetry-related bridging O atom. The Li2 ion has a distorted trigonal bipyramidal geometry, with one water molecule in bridging mode that connects the two distinct Li ions, one symmetry related carboxylate O atom of pyrazine-2,3-dicarboxylate ligand and a chelated pyrazine-2,3-dicarboxylate ligand (through the interactions of both N and O atoms) of the adjacent molecule. It should be emphasized that, depending on the starting material and stoichiometric ratio utilized, the synthesis of dinuclear lithium complexes formed with one or two pyrazine-2,3-dicarboxylic acid ligands can be accessible (Tombul *et al.*, 2008a). The Li–O distances are in the range 1.918 (4) Å to 2.046 (4) Å (for Li1) and 1.942 (3) Å to 2.129 (4) Å (for Li2), in good agreement with the corresponding values reported for other lithium complexes (Chen *et al.*, 2007; Kim *et al.*, 2007). It is interesting to note that Li–N bond lengths are in accord with the normal ranges reported for the dinuclear bis-structure (Tombul *et al.*, 2008a), however, the Li–N distances are notably longer than similar bond lengths reported in the literature (Grossie *et al.*, 2006; Boyd *et al.*, 2002). The dinuclear complex is linked in a three-dimensional manner by further intra- and intermolecular O—H—O and O—H—N hydrogen bonds (Figure 2 and Table 2).

Experimental

To an aqueous solution (30 ml) of pyrazine 2,3-dicarboxylic acid (1681 mg, 1 mmol), LiOH (479 mg, 2 mmol) was carefully added. The reaction mixture gave a colourless and clear solution which was stirred at 303 K for 4 h. After solvent removal in vacuo, the white solid product was then redissolved in water (5 ml) and allowed to stand for 15 d at ambient temperature, after which transparent fine crystals were harvested from the mother liquor.

Refinement

H atoms associated with water molecules were located in the difference map and freely refined during subsequent cycles of least squares. H atoms of carbons were repositioned geometrically. They were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H = 0.93 Å) and $U_{iso}(H)$ (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.

Figures

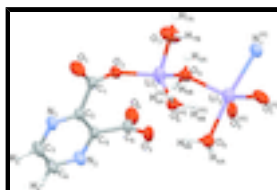


Fig. 1. Showing the atom-labelling scheme with symmetry codes: ii = $-x, y + 1/2, -z + 1/2$; iii = $-x, -y + 1, -z + 1$.] Atoms were drawn with 50% thermal ellipsoid probability contours.

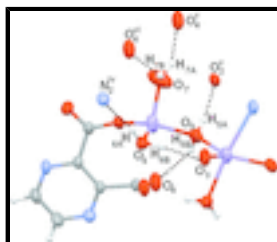


Fig. 2. A view of the hydrogen bonding interactions in the structure. Symmetry codes: iv = $-x + 1, -y + 1, -z + 1$; v = $-x, -y + 1, -z$; vi = $x - 1, y, z$. Atoms were drawn with 50% thermal ellipsoid probability contours.

Poly[μ -aqua-diaqua(μ_2 -pyrazine-2,3-dicarboxylato)dilithium(I)]

Crystal data

[Li₂(C₆H₂N₂O₄)(H₂O)₃]

$M_r = 234.02$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 7.487\ (3)\ \text{\AA}$

$b = 16.409\ (8)\ \text{\AA}$

$c = 7.958\ (2)\ \text{\AA}$

$\beta = 92.92\ (3)^\circ$

$V = 976.4\ (7)\ \text{\AA}^3$

$Z = 4$

$F(000) = 480$

$D_x = 1.592\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71069\ \text{\AA}$

Cell parameters from 25 reflections

$\theta = 3.0\text{--}7.9^\circ$

$\mu = 0.14\ \text{mm}^{-1}$

$T = 298\ \text{K}$

Prism, yellow

$0.4 \times 0.2 \times 0.06\ \text{mm}$

Data collection

Rigaku
diffractometer

Radiation source: fine-focus sealed tube

graphite

ω - 2θ scans

Absorption correction: ψ scan

2427 reflections with $I > 2\sigma(I)$

$R_{int} = 0.120$

$\theta_{max} = 40.0^\circ$, $\theta_{min} = 2.7^\circ$

$h = 0 \rightarrow 13$

$k = 0 \rightarrow 29$

(North *et al.*, 1968)

$T_{\min} = 0.948$, $T_{\max} = 0.994$

6366 measured reflections

6045 independent reflections

$l = -14 \rightarrow 14$

3 standard reflections every 150 reflections

intensity decay: none%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.062$

$wR(F^2) = 0.211$

$S = 0.96$

6045 reflections

178 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

$w = 1/[\sigma^2(F_o^2) + (0.0977P)^2]$

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

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

$\Delta\rho_{\max} = 0.49 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.54 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	-0.01123 (18)	0.24672 (8)	0.0505 (2)	0.0341 (3)
O2	0.06063 (17)	0.37715 (7)	0.09640 (16)	0.0236 (3)
O3	0.20616 (17)	0.43281 (7)	0.43623 (16)	0.0238 (3)
O4	0.39167 (18)	0.47554 (7)	0.24601 (18)	0.0277 (3)
O5	0.03262 (19)	0.56609 (8)	0.21735 (17)	0.0252 (3)
H5A	0.004 (4)	0.5875 (17)	0.129 (4)	0.043 (8)*
H5B	0.147 (5)	0.558 (2)	0.222 (4)	0.069 (10)*
O6	0.17467 (17)	0.58515 (8)	0.56590 (16)	0.0224 (2)
H6A	0.272 (4)	0.613 (2)	0.581 (4)	0.058 (9)*
H6B	0.206 (4)	0.5391 (19)	0.519 (3)	0.048 (8)*
O7	-0.2951 (2)	0.46974 (13)	0.0850 (2)	0.0479 (5)
H7A	-0.316 (5)	0.501 (2)	-0.004 (5)	0.082 (12)*
H7B	-0.394 (5)	0.465 (2)	0.139 (4)	0.064 (10)*

supplementary materials

N1	0.29092 (19)	0.19673 (8)	0.21499 (19)	0.0228 (3)
N2	0.52735 (19)	0.30911 (9)	0.3651 (2)	0.0246 (3)
C1	0.0838 (2)	0.30153 (9)	0.1146 (2)	0.0195 (3)
C2	0.2524 (2)	0.27631 (9)	0.2158 (2)	0.0172 (3)
C3	0.4472 (3)	0.17365 (11)	0.2881 (3)	0.0296 (4)
H3	0.4761	0.1185	0.2920	0.036*
C4	0.5669 (2)	0.22967 (11)	0.3582 (3)	0.0300 (4)
H4	0.6777	0.2118	0.4017	0.036*
C5	0.3672 (2)	0.33240 (9)	0.2984 (2)	0.0171 (3)
C6	0.31766 (19)	0.42055 (9)	0.3264 (2)	0.0168 (3)
Li1	-0.0795 (5)	0.4524 (2)	0.2209 (4)	0.0289 (7)
Li2	-0.0490 (4)	0.63229 (18)	0.4210 (4)	0.0252 (6)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0312 (7)	0.0205 (6)	0.0488 (9)	-0.0017 (5)	-0.0159 (6)	-0.0045 (6)
O2	0.0304 (6)	0.0161 (5)	0.0240 (6)	0.0064 (4)	-0.0028 (5)	-0.0005 (4)
O3	0.0310 (6)	0.0158 (5)	0.0257 (6)	0.0022 (4)	0.0123 (5)	0.0002 (4)
O4	0.0300 (6)	0.0176 (5)	0.0367 (7)	-0.0035 (4)	0.0129 (5)	0.0050 (5)
O5	0.0298 (6)	0.0255 (6)	0.0201 (6)	0.0068 (5)	0.0016 (5)	0.0034 (5)
O6	0.0224 (5)	0.0192 (5)	0.0253 (6)	-0.0002 (4)	-0.0005 (4)	-0.0020 (4)
O7	0.0300 (8)	0.0775 (14)	0.0371 (9)	0.0162 (8)	0.0109 (6)	0.0208 (9)
N1	0.0256 (7)	0.0129 (5)	0.0297 (7)	0.0026 (5)	-0.0004 (5)	-0.0022 (5)
N2	0.0191 (6)	0.0208 (6)	0.0334 (8)	0.0025 (5)	-0.0024 (5)	-0.0025 (5)
C1	0.0225 (7)	0.0161 (6)	0.0197 (7)	0.0025 (5)	-0.0008 (5)	-0.0017 (5)
C2	0.0178 (6)	0.0133 (5)	0.0209 (7)	0.0012 (5)	0.0024 (5)	-0.0005 (5)
C3	0.0296 (8)	0.0169 (7)	0.0417 (11)	0.0074 (6)	-0.0043 (7)	-0.0015 (7)
C4	0.0229 (7)	0.0224 (7)	0.0438 (11)	0.0083 (6)	-0.0060 (7)	-0.0020 (7)
C5	0.0180 (6)	0.0132 (5)	0.0201 (7)	0.0007 (5)	0.0022 (5)	0.0000 (5)
C6	0.0174 (6)	0.0120 (5)	0.0212 (7)	-0.0002 (4)	0.0016 (5)	0.0002 (5)
Li1	0.0367 (17)	0.0197 (13)	0.0312 (17)	0.0031 (12)	0.0100 (13)	0.0010 (12)
Li2	0.0300 (15)	0.0163 (12)	0.0294 (16)	0.0004 (11)	0.0045 (12)	0.0027 (11)

Geometric parameters (\AA , $^\circ$)

O5—Li1	2.046 (4)	N2—C4	1.338 (2)
O5—Li2	2.069 (4)	N2—C5	1.342 (2)
O5—H5B	0.87 (4)	C2—C5	1.400 (2)
O5—H5A	0.80 (3)	C2—C1	1.519 (2)
O4—C6	1.2517 (19)	C5—C6	1.513 (2)
O6—Li2	2.129 (4)	C4—C3	1.382 (3)
O6—H6A	0.87 (3)	C4—H4	0.9300
O6—H6B	0.88 (3)	C3—H3	0.9300
O1—C1	1.241 (2)	Li2—O1 ⁱⁱ	1.942 (3)
O2—C1	1.260 (2)	Li2—O3 ⁱⁱⁱ	1.988 (3)
O2—Li1	1.927 (3)	Li2—N1 ⁱⁱ	2.317 (4)
O3—C6	1.2552 (19)	Li1—O7	1.918 (4)

N1—C3	1.335 (2)	Li1—O6 ⁱⁱⁱ	1.973 (4)
N1—C2	1.337 (2)	O7—H7A	0.88 (4)
N1—Li2 ⁱ	2.317 (4)	O7—H7B	0.88 (4)
Li1—O5—Li2	109.27 (14)	N1—C3—C4	121.58 (16)
Li1—O5—H5B	105 (2)	N1—C3—H3	119.2
Li2—O5—H5B	112 (2)	C4—C3—H3	119.2
Li1—O5—H5A	109 (2)	O1—C1—O2	126.41 (15)
Li2—O5—H5A	112 (2)	O1—C1—C2	117.66 (14)
H5B—O5—H5A	109 (3)	O2—C1—C2	115.79 (14)
Li1 ⁱⁱⁱ —O6—Li2	105.71 (15)	O4—C6—O3	124.60 (14)
Li1 ⁱⁱⁱ —O6—H6A	112 (2)	O4—C6—C5	119.72 (14)
Li2—O6—H6A	121 (2)	O3—C6—C5	115.64 (13)
Li1 ⁱⁱⁱ —O6—H6B	102.5 (18)	O1 ⁱⁱ —Li2—O3 ⁱⁱⁱ	126.42 (18)
Li2—O6—H6B	107.5 (18)	O1 ⁱⁱ —Li2—O5	121.53 (17)
H6A—O6—H6B	106 (3)	O3 ⁱⁱⁱ —Li2—O5	111.87 (15)
C1—O1—Li2 ⁱ	121.88 (15)	O1 ⁱⁱ —Li2—O6	96.70 (15)
C1—O2—Li1	130.35 (15)	O3 ⁱⁱⁱ —Li2—O6	88.14 (13)
C6—O3—Li2 ⁱⁱⁱ	138.22 (14)	O5—Li2—O6	88.74 (13)
C3—N1—C2	117.34 (14)	O1 ⁱⁱ —Li2—N1 ⁱⁱ	77.56 (12)
C3—N1—Li2 ⁱ	136.14 (14)	O3 ⁱⁱⁱ —Li2—N1 ⁱⁱ	92.34 (14)
C2—N1—Li2 ⁱ	106.51 (13)	O5—Li2—N1 ⁱⁱ	97.38 (14)
C4—N2—C5	117.17 (15)	O6—Li2—N1 ⁱⁱ	173.18 (17)
N1—C2—C5	121.12 (14)	O7—Li1—O2	105.65 (18)
N1—C2—C1	115.90 (13)	O7—Li1—O6 ⁱⁱⁱ	101.58 (17)
C5—C2—C1	122.89 (13)	O2—Li1—O6 ⁱⁱⁱ	118.14 (18)
N2—C5—C2	120.88 (14)	O7—Li1—O5	101.05 (17)
N2—C5—C6	115.78 (13)	O2—Li1—O5	110.05 (17)
C2—C5—C6	123.27 (13)	O6 ⁱⁱⁱ —Li1—O5	117.60 (17)
N2—C4—C3	121.58 (16)	Li1—O7—H7A	130 (3)
N2—C4—H4	119.2	Li1—O7—H7B	115 (2)
C3—C4—H4	119.2	H7A—O7—H7B	109 (3)
C3—N1—C2—C5	-3.5 (2)	C5—C2—C1—O2	6.1 (2)
Li2 ⁱ —N1—C2—C5	176.03 (15)	Li2 ⁱⁱⁱ —O3—C6—O4	174.97 (19)
C3—N1—C2—C1	173.33 (16)	Li2 ⁱⁱⁱ —O3—C6—C5	-7.5 (3)
Li2 ⁱ —N1—C2—C1	-7.18 (18)	N2—C5—C6—O4	73.8 (2)
C4—N2—C5—C2	-4.0 (3)	C2—C5—C6—O4	-109.25 (19)
C4—N2—C5—C6	172.98 (16)	N2—C5—C6—O3	-103.86 (18)
N1—C2—C5—N2	6.5 (3)	C2—C5—C6—O3	73.1 (2)
C1—C2—C5—N2	-170.03 (15)	Li1—O5—Li2—O1 ⁱⁱ	-174.09 (18)
N1—C2—C5—C6	-170.25 (15)	Li1—O5—Li2—O3 ⁱⁱⁱ	1.3 (2)
C1—C2—C5—C6	13.2 (2)	Li1—O5—Li2—O6	88.83 (16)
C5—N2—C4—C3	-1.1 (3)	Li1—O5—Li2—N1 ⁱⁱ	-94.19 (16)
C2—N1—C3—C4	-1.6 (3)	Li1 ⁱⁱⁱ —O6—Li2—O1 ⁱⁱ	105.93 (16)

supplementary materials

Li2 ⁱ —N1—C3—C4	179.05 (19)	Li1 ⁱⁱⁱ —O6—Li2—O3 ⁱⁱⁱ	-20.53 (16)
N2—C4—C3—N1	4.1 (3)	Li1 ⁱⁱⁱ —O6—Li2—O5	-132.46 (14)
Li2 ⁱ —O1—C1—O2	176.24 (17)	C1—O2—Li1—O7	-101.2 (2)
Li2 ⁱ —O1—C1—C2	0.7 (2)	C1—O2—Li1—O6 ⁱⁱⁱ	11.5 (3)
Li1—O2—C1—O1	87.8 (3)	C1—O2—Li1—O5	150.45 (16)
Li1—O2—C1—C2	-96.7 (2)	Li2—O5—Li1—O7	91.67 (18)
N1—C2—C1—O1	5.3 (2)	Li2—O5—Li1—O2	-156.99 (16)
C5—C2—C1—O1	-177.97 (16)	Li2—O5—Li1—O6 ⁱⁱⁱ	-17.8 (2)
N1—C2—C1—O2	-170.67 (15)		

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

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>
O5—H5A \cdots O2 ^{iv}	0.81 (3)	1.92 (3)	2.723 (3)	172.60 (3)
O5—H5B \cdots O4	0.87 (4)	2.28 (4)	3.068 (3)	152 (3)
O6—H6A \cdots N2 ^v	0.86 (3)	2.00 (3)	2.857 (3)	169.66 (4)
O6—H6B \cdots O3	0.88 (3)	1.86 (3)	2.719 (3)	163 (3)
O7—H7A \cdots O4 ^{iv}	0.88 (4)	2.02 (4)	2.841 (3)	154.89 (6)
O7—H7B \cdots O4 ^{vi}	0.88 (4)	1.86 (4)	2.730 (3)	169.51 (6)

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

Fig. 1

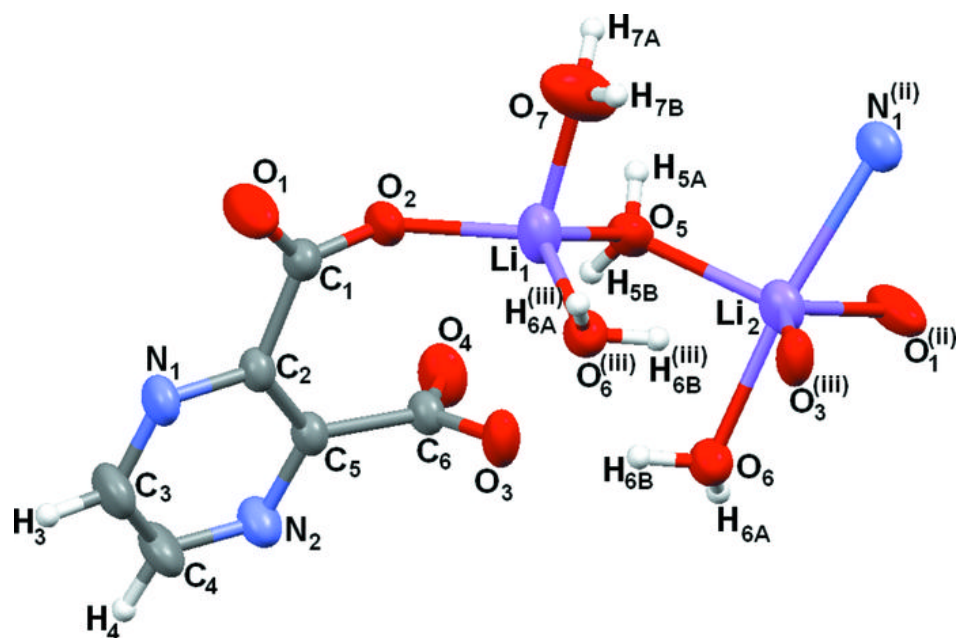


Fig. 2

