

Poly[triaquabis(μ_2 -3-carboxypyrazine-2-carboxylato)dilithium(I)]

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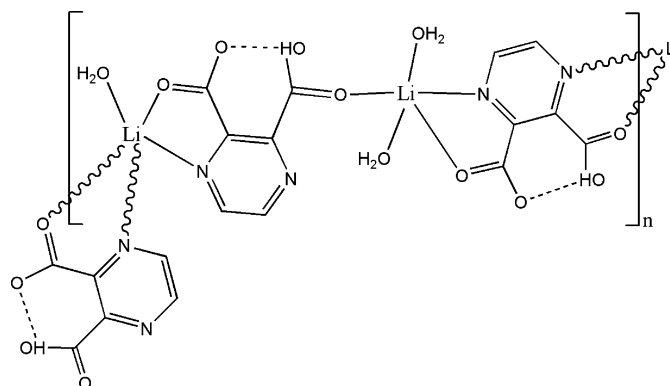
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Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.052; wR factor = 0.144; data-to-parameter ratio = 11.3.

In the title compound, $[\text{Li}_2(\text{C}_6\text{H}_3\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_3]_n$, the coordination number for both independent Li^+ cations is five. One of the Li^+ ions has a distorted trigonal-bipyramidal geometry, coordinated by one of the carboxyl O atoms of a 3-carboxypyrazine-2-carboxylate ligand, two O atoms from two water molecules, and an N and a carboxylate O atom of a second 3-carboxypyrazine-2-carboxylate ligand. The other Li^+ ion also has a distorted trigonal-bipyramidal geometry, coordinated by one water molecule and two 3-carboxypyrazine-2-carboxylate ligands through an N and a carboxylate O atom from each. One of the carboxyl groups of the two ligands takes part in an intramolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond. The stabilization of the crystal structure is further assisted by $\text{O}-\text{H}\cdots\text{O}$, $\text{O}-\text{H}\cdots\text{N}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions involving the water molecules and carboxylate O atoms.

Related literature

For related literature, see: Chen *et al.* (2007); Clark & Reid (1995); Erxleben (2003); Fei, Ang *et al.* (2006); Fei, Geldbach *et al.* (2006); Gao *et al.* (2005); López Garzón *et al.* (2003); Grossie *et al.* (2006); Haiduc & Edlmann (1999); Janiak (2003); Kim *et al.* (2007); Kitagawa *et al.* (2004); Lehn (1995); Mueller *et al.* (2006); Nepveu *et al.* (1993); Pancholi & Patel (1996); Ptasiewicz-Bak & Leciejewicz (1997*a,b*); Richard *et al.* (1973); Speakman (1972); Sreenivasulu & Vittal (2004); Starosta & Leciejewicz (2005); Takusagawa & Shimada (1973); Tombul *et al.* (2006, 2007, 2008); Ye *et al.* (2005).



Experimental

Crystal data

$[\text{Li}_2(\text{C}_6\text{H}_3\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_3]$
 $M_r = 402.14$
Monoclinic, $P2_1/c$
 $a = 15.3413$ (9) Å
 $b = 7.9415$ (4) Å
 $c = 14.9097$ (9) Å
 $\beta = 117.371$ (4)°

$V = 1613.13$ (16) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.14$ mm⁻¹
 $T = 295$ (2) K
 $0.43 \times 0.30 \times 0.11$ mm

Data collection

Stoe IPDSII diffractometer
Absorption correction: integration
(*X-RED32*; Stoe & Cie, 2002)
 $T_{\min} = 0.947$, $T_{\max} = 0.985$

13081 measured reflections
3337 independent reflections
2127 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.083$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.143$
 $S = 1.00$
3337 reflections
295 parameters
2 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.38$ e Å⁻³
 $\Delta\rho_{\min} = -0.34$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Li1—O2	1.980 (5)	Li2—O3	1.974 (5)
Li1—O8	2.029 (5)	Li2—O5	1.990 (5)
Li1—O1	2.037 (5)	Li2—N3 ⁱ	2.198 (5)
Li1—O9	2.074 (5)	Li2—N2	2.272 (5)
Li1—N1	2.326 (5)	N3—Li2 ⁱⁱ	2.198 (5)
Li2—O4	1.901 (5)		
O2—Li1—O8	109.5 (2)	O4—Li2—O3	101.8 (2)
O2—Li1—O1	102.2 (2)	O4—Li2—O5	104.1 (2)
O8—Li1—O1	146.8 (3)	O3—Li2—O5	154.0 (3)
O2—Li1—O9	99.7 (2)	O4—Li2—N3 ⁱ	101.6 (2)
O8—Li1—O9	87.89 (19)	O3—Li2—N3 ⁱ	76.07 (15)
O1—Li1—O9	96.5 (2)	O5—Li2—N3 ⁱ	97.47 (19)
O2—Li1—N1	102.5 (2)	O4—Li2—N2	99.97 (19)
O8—Li1—N1	71.58 (15)	O3—Li2—N2	101.89 (19)
O1—Li1—N1	92.45 (19)	O5—Li2—N2	74.75 (16)
O9—Li1—N1	153.7 (2)	N3 ⁱ —Li2—N2	158.3 (2)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H4A \cdots O3 ⁱⁱⁱ	0.926 (10)	1.830 (12)	2.743 (3)	168 (3)
O4—H4B \cdots O5 ^{iv}	0.93 (4)	1.89 (3)	2.816 (3)	171 (4)
O2—H2A \cdots N4 ^v	0.93 (4)	1.98 (4)	2.898 (3)	171 (4)
O2—H2B \cdots O8 ^v	0.93 (3)	1.84 (3)	2.772 (3)	175 (3)
O1—H1A \cdots O2 ^v	0.94 (5)	2.11 (4)	2.892 (3)	141 (6)
O1—H1B \cdots O7 ^{vi}	0.93 (5)	2.38 (5)	3.305 (3)	174 (6)
C7—H7 \cdots O11 ^{vii}	0.93	2.52	3.184 (3)	129
O10—H10 \cdots O11	0.86 (3)	1.55 (3)	2.404 (3)	174 (5)
O6—H7A \cdots O7	0.86 (3)	1.53 (4)	2.380 (3)	172 (9)

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

Data collection: *X-Area* (Stoe & Cie, 2002); cell refinement: *X-Area*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2542).

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Acta Cryst. (2008). E64, m491-m492 [doi:10.1107/S1600536808004467]

Poly[triaquabis(μ -2,3-carboxypyrazine-2-carboxylato)dilithium(I)]

M. Tombul, K. Güven and O. Büyükgüngör

Comment

The systematic design of metal-organic frameworks has become the most fascinating and challenging area of research particularly during the last decade (Lehn, 1995; Haiduc & Edelman, 1999). Hence, the synthesis of novel coordination polymers has advanced rapidly because of their applications in many areas such as, hydrogen storage (Kitagawa *et al.*, 2004; Mueller *et al.*, 2006), ion-exchange resins (Pancholi & Patel, 1996) and catalysis (Janiak, 2003). Multidentate carboxylic acids are found to be excellent ligands for the synthesis of coordination polymers giving the structures with a diverse range of topologies and conformations, due 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, Geldbach *et al.*, 2006). Although most of the studies conducted in this area is primarily focused on coordination polymers containing transition metals as connectors, such as Zn, Ni and Co (Sreenivasulu & Vittal, 2004; Fei, Ang *et al.*, 2006), there is little attention on the Group I metal (López Garzón *et al.*, 2003; Gao *et al.*, 2005; Chen *et al.*, 2007).

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), owing 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, a variety of metal-organic compound of pyrazine-2,3-dicarboxylic acid have been characterized crystallographically due to growing interest in supramolecular chemistry. Examples are including the calcium (Ptasiewicz-Bak & Leciejewicz, 1997*a*; Starosta & Leciejewicz, 2005), magnesium (Ptasiewicz-Bak & Leciejewicz, 1997*b*), sodium (Tombul *et al.* 2006), caesium (Tombul *et al.* 2007) and potassium (Tombul *et al.* 2008) complexes. Continuation our research on Group I dicarboxylates, we present here the synthesis and crystal structure of the hydrated polymeric dinuclear lithium complex, (I), formed with pyrazine-2,3-dicarboxylic acid.

As shown in Fig. 1, compound (I) is a polymeric dinuclear complex with two kinds of Li atoms, two kinds of pyrazine-2,3-dicarboxylate ligands and three water molecules in the asymmetric unit. The geometries of the two independent Li atoms are distorted trigonal-bipyramidal, while the coordination modes of the pyrazine-2,3-dicarboxylate ligands are chelation. The Li1 ion has a five-coordinate geometry and achieves the coordination number by bonding to one of the carboxylate O atom of pyrazine-2,3-dicarboxylate ligand, two O atoms from two water molecules and a chelation pyrazine-2,3-dicarboxylate ligand (through the interactions by utilizing both N and O atoms) of the adjacent molecule. The Li2 ion has also distorted trigonal-bipyramidal geometry, with one water molecule, one chelation ligand molecule (through the interactions by utilizing both N and O atoms of the same ligand) and symmetry related chelation pyrazine-2–3-dicarboxylate ligand. There is no metal to-metal interaction; the Li–Li distance is 7.221 (2) Å. The Li–O distances are in the range 1.980 (5) Å to 2.074 (4) Å (for Li1) and 1.901 (5) Å to 1.974 (4) Å (for Li2), in accordance with the corresponding values reported for other lithium complexes (Chen *et al.* 2007; Kim *et al.* 2007). Li–N bond lengths also lie within the normal ranges found for similar bonds in the literature (Grossie *et al.* 2006). The C–O distances are comparable with structurally similar compounds (Chen *et al.* 2007). There are appreciable differences between the two carboxyl groups of the each ligand molecule. The C–O distances at C6 and C12 are (1.228 (3) Å, 1.275 and 1.216 (3) Å, 1.283 (3) Å respectively), and these are fairly typical for

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a carboxylic acid group (Speakman, 1972). On the other hand, those at C5 and C11 are (1.236 (3) Å, 1.268 (3) Å and 1.247 (3) Å, 1.258 (3) Å respectively), giving a strong indication of a carboxylate ion. As is typically the case, the mean value of the four C—O distances in the different carboxyl/carboxylate groups is almost the same, at 1.254 (3) Å, 1.251 (3) Å and 1.252 (3) Å, 1.251 (3) Å, respectively.

In (I), one of the carboxyl groups of each ligand molecule holds its H atom, which takes part in an O—H \cdots O [O \cdots O = 2.380 (3) 2.402 (3) Å respectively] intramolecular hydrogen bonds. Atoms H6A and H10A involved in these bonds and maintain the charge balance within the structure. The dinuclear complexes are linked in a three-dimensional manner by further numerous intermolecular O—H \cdots O \cdots O—H \cdots N and C—H \cdots O hydrogen bonds (Table 2).

Experimental

Li₂CO₃ (220 mg, 3 mmol) was carefully added to an aqueous solution (20 ml) of pyrazine 2,3-dicarboxylic acid (1008 mg, 6 mmol), until no further bubbles formed. The reaction mixture gave a colourless and clear solution which was stirred at 323 K for 10 h, until it solidified. The solid product was then redissolved in water (5 ml) and allowed to stand for a day at ambient temperature, after which transparent fine crystals were harvested.

Refinement

All H atoms 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, O—H in the range 0.86 – 0.94 Å) and $U_{\text{iso}}(\text{H})$ (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.

Figures

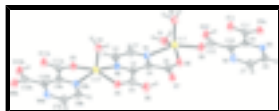


Fig. 1. Showing the atom-labelling scheme of (I). Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (a) $-1 + x, y, -1 + z$; (b) $1 + x, y, 1 + z$].

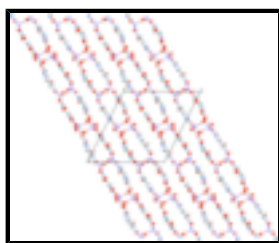


Fig. 2. View of the stacking structure of (I) within the unit cell, down the b axis.

Poly[triaquabis(μ -2,3-carboxypyrazine-2-carboxylato)dilithium(I)]

Crystal data

[Li₂(C₆H₃N₂O₄)₂(H₂O)₃]

$M_r = 402.14$

Monoclinic, $P2_1/c$

Hall symbol: $-P 2_1bc$

$F_{000} = 824$

$D_x = 1.656 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 15847 reflections

$a = 15.3413 (9) \text{ \AA}$
 $b = 7.9415 (4) \text{ \AA}$
 $c = 14.9097 (9) \text{ \AA}$
 $\beta = 117.371 (4)^\circ$
 $V = 1613.13 (16) \text{ \AA}^3$
 $Z = 4$

$\theta = 1.5\text{--}27.2^\circ$
 $\mu = 0.15 \text{ mm}^{-1}$
 $T = 295 (2) \text{ K}$
 Prism, colourless
 $0.43 \times 0.30 \times 0.11 \text{ mm}$

Data collection

Stoe IPDSII diffractometer
 Monochromator: plane graphite
 Detector resolution: $6.67 \text{ pixels mm}^{-1}$
 $T = 295(2) \text{ K}$
 rotation method scans
 Absorption correction: integration (X-RED32; Stoe & Cie, 2002)
 $T_{\min} = 0.947, T_{\max} = 0.985$
 13081 measured reflections

3337 independent reflections
 2127 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.083$
 $\theta_{\max} = 26.5^\circ$
 $\theta_{\min} = 1.5^\circ$
 $h = -19 \rightarrow 19$
 $k = -9 \rightarrow 9$
 $l = -18 \rightarrow 18$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.143$
 $S = 1.00$
 3337 reflections
 295 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
 $w = 1/[\sigma^2(F_o^2) + (0.0627P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.011$
 $\Delta\rho_{\max} = 0.38 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.34 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97 (Sheldrick, 2008),
 $F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: $0.019 (3)$

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 $F^2 > 2\sigma(F^2)$ 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.

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Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	-0.3129 (2)	0.1510 (3)	0.0633 (2)	0.0544 (7)
H1	-0.3343	0.2598	0.0409	0.065*
C2	-0.2287 (2)	0.1293 (3)	0.15271 (19)	0.0483 (6)
H2	-0.1936	0.2230	0.1886	0.058*
C3	-0.24908 (16)	-0.1569 (3)	0.13584 (16)	0.0365 (5)
C4	-0.33418 (17)	-0.1336 (3)	0.04375 (17)	0.0380 (5)
C5	-0.20414 (17)	-0.3209 (3)	0.18826 (18)	0.0430 (6)
C6	-0.40262 (17)	-0.2658 (3)	-0.02839 (17)	0.0430 (6)
C7	-0.8269 (2)	-0.3841 (3)	-0.4244 (2)	0.0553 (7)
H7	-0.8155	-0.4940	-0.4002	0.066*
C8	-0.9085 (2)	-0.3489 (3)	-0.51354 (19)	0.0509 (7)
H8	-0.9488	-0.4367	-0.5512	0.061*
C9	-0.87144 (16)	-0.0679 (3)	-0.49270 (16)	0.0371 (5)
C10	-0.78391 (15)	-0.1039 (3)	-0.40504 (15)	0.0389 (5)
C11	-0.91273 (18)	0.1024 (3)	-0.53842 (17)	0.0412 (6)
C12	-0.70304 (15)	0.0156 (3)	-0.33600 (16)	0.0430 (6)
Li1	-0.4924 (3)	0.0277 (6)	-0.1557 (3)	0.0524 (10)
Li2	-0.0456 (3)	-0.1053 (5)	0.3065 (3)	0.0504 (10)
N1	-0.36462 (15)	0.0222 (3)	0.00823 (15)	0.0479 (5)
N2	-0.19698 (14)	-0.0232 (2)	0.18818 (14)	0.0418 (5)
N3	-0.93097 (15)	-0.1938 (3)	-0.54689 (14)	0.0440 (5)
N4	-0.76397 (16)	-0.2636 (3)	-0.37213 (16)	0.0501 (6)
O1	-0.53187 (16)	0.2659 (3)	-0.13886 (16)	0.0611 (5)
O2	-0.42243 (14)	0.0653 (2)	-0.23731 (14)	0.0512 (5)
O3	0.00554 (13)	0.1034 (2)	0.38530 (12)	0.0490 (5)
O4	0.02158 (14)	-0.1093 (2)	0.22662 (14)	0.0557 (5)
O5	-0.12608 (12)	-0.3144 (2)	0.26734 (13)	0.0504 (5)
O6	-0.24547 (15)	-0.4600 (2)	0.15083 (16)	0.0669 (6)
O7	-0.38628 (14)	-0.4221 (2)	-0.00814 (14)	0.0538 (5)
O8	-0.47216 (13)	-0.2138 (2)	-0.10579 (13)	0.0566 (5)
O9	-0.62851 (13)	-0.0447 (2)	-0.26899 (14)	0.0584 (5)
O10	-0.71593 (14)	0.1755 (2)	-0.34880 (15)	0.0559 (5)
O11	-0.86572 (14)	0.2348 (2)	-0.49878 (15)	0.0614 (5)
H4A	0.017 (2)	-0.198 (3)	0.1844 (19)	0.063 (9)*
H2A	-0.3649 (19)	0.128 (5)	-0.208 (3)	0.116 (15)*
H10	-0.767 (2)	0.195 (7)	-0.405 (2)	0.15 (2)*
H2B	-0.455 (2)	0.141 (4)	-0.290 (2)	0.095 (12)*
H4B	0.054 (3)	-0.014 (3)	0.221 (3)	0.115 (15)*
H7A	-0.294 (4)	-0.453 (11)	0.091 (2)	0.23 (4)*
H1A	-0.565 (4)	0.324 (8)	-0.200 (3)	0.19 (3)*
H1B	-0.494 (4)	0.359 (5)	-0.106 (4)	0.18 (3)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0642 (18)	0.0299 (13)	0.0526 (15)	0.0022 (11)	0.0128 (14)	0.0020 (11)
C2	0.0555 (15)	0.0325 (12)	0.0466 (14)	-0.0043 (11)	0.0145 (12)	-0.0015 (11)
C3	0.0414 (12)	0.0318 (12)	0.0338 (11)	-0.0007 (9)	0.0152 (10)	-0.0009 (9)
C4	0.0425 (12)	0.0333 (12)	0.0334 (11)	0.0004 (10)	0.0134 (10)	0.0031 (9)
C5	0.0444 (14)	0.0357 (12)	0.0418 (13)	0.0017 (10)	0.0139 (11)	0.0016 (11)
C6	0.0443 (13)	0.0390 (13)	0.0363 (12)	0.0013 (10)	0.0105 (11)	0.0009 (10)
C7	0.0664 (17)	0.0307 (13)	0.0525 (15)	-0.0025 (12)	0.0134 (14)	0.0038 (12)
C8	0.0583 (16)	0.0382 (14)	0.0426 (13)	-0.0091 (12)	0.0116 (12)	-0.0024 (11)
C9	0.0403 (12)	0.0348 (12)	0.0324 (11)	0.0008 (9)	0.0134 (10)	0.0006 (9)
C10	0.0435 (13)	0.0352 (12)	0.0340 (11)	0.0012 (10)	0.0145 (10)	0.0007 (10)
C11	0.0451 (13)	0.0382 (13)	0.0368 (12)	0.0007 (10)	0.0158 (11)	-0.0003 (10)
C12	0.0422 (13)	0.0400 (13)	0.0418 (12)	0.0001 (11)	0.0150 (11)	-0.0011 (11)
Li1	0.052 (2)	0.047 (2)	0.047 (2)	0.000 (2)	0.0136 (19)	0.003 (2)
Li2	0.051 (2)	0.047 (2)	0.042 (2)	0.0013 (19)	0.0126 (19)	0.0006 (19)
N1	0.0539 (12)	0.0336 (11)	0.0427 (11)	0.0021 (9)	0.0107 (10)	0.0024 (9)
N2	0.0445 (11)	0.0344 (10)	0.0399 (10)	-0.0040 (9)	0.0137 (9)	-0.0036 (9)
N3	0.0496 (12)	0.0379 (11)	0.0371 (10)	-0.0050 (9)	0.0136 (9)	-0.0009 (9)
N4	0.0543 (13)	0.0352 (11)	0.0466 (12)	0.0027 (9)	0.0112 (10)	0.0017 (9)
O1	0.0730 (14)	0.0499 (12)	0.0585 (12)	0.0091 (10)	0.0288 (11)	0.0100 (10)
O2	0.0530 (11)	0.0438 (10)	0.0471 (10)	-0.0026 (9)	0.0147 (9)	0.0027 (8)
O3	0.0503 (10)	0.0431 (10)	0.0405 (9)	0.0047 (8)	0.0096 (8)	0.0015 (8)
O4	0.0657 (12)	0.0475 (11)	0.0541 (11)	-0.0138 (9)	0.0277 (10)	-0.0132 (9)
O5	0.0468 (10)	0.0426 (10)	0.0457 (10)	0.0017 (8)	0.0076 (8)	0.0052 (8)
O6	0.0637 (12)	0.0315 (10)	0.0664 (13)	-0.0012 (8)	-0.0037 (10)	0.0030 (9)
O7	0.0620 (11)	0.0341 (9)	0.0468 (10)	-0.0019 (8)	0.0092 (9)	-0.0023 (8)
O8	0.0573 (11)	0.0441 (10)	0.0432 (10)	-0.0007 (8)	0.0015 (9)	-0.0002 (8)
O9	0.0437 (10)	0.0516 (11)	0.0562 (11)	-0.0001 (8)	0.0026 (9)	0.0031 (9)
O10	0.0527 (11)	0.0381 (10)	0.0572 (11)	-0.0038 (8)	0.0083 (9)	-0.0052 (9)
O11	0.0662 (12)	0.0322 (9)	0.0585 (11)	-0.0028 (8)	0.0053 (9)	-0.0004 (8)

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

C1—N1	1.323 (3)	C11—O3 ⁱ	1.247 (3)
C1—C2	1.376 (4)	C11—O11	1.258 (3)
C1—H1	0.9300	C12—O9	1.216 (3)
C2—N2	1.321 (3)	C12—O10	1.283 (3)
C2—H2	0.9300	Li1—O2	1.980 (5)
C3—N2	1.342 (3)	Li1—O8	2.029 (5)
C3—C4	1.406 (3)	Li1—O1	2.037 (5)
C3—C5	1.512 (3)	Li1—O9	2.074 (5)
C4—N1	1.342 (3)	Li1—N1	2.326 (5)
C4—C6	1.524 (3)	Li2—O4	1.901 (5)
C5—O5	1.236 (3)	Li2—O3	1.974 (5)
C5—O6	1.268 (3)	Li2—O5	1.990 (5)

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C6—O8	1.228 (3)	Li2—N3 ⁱⁱ	2.198 (5)
C6—O7	1.275 (3)	Li2—N2	2.272 (5)
C7—N4	1.328 (3)	N3—Li2 ⁱ	2.198 (5)
C7—C8	1.372 (4)	O1—H1A	0.94 (5)
C7—H7	0.9300	O1—H1B	0.93 (5)
C8—N3	1.313 (3)	O2—H2A	0.93 (4)
C8—H8	0.9300	O2—H2B	0.93 (3)
C9—N3	1.345 (3)	O3—C11 ⁱⁱ	1.247 (3)
C9—C10	1.404 (3)	O4—H4A	0.926 (10)
C9—C11	1.516 (3)	O4—H4B	0.93 (4)
C10—N4	1.341 (3)	O6—H7A	0.86 (3)
C10—C12	1.525 (3)	O10—H10	0.86 (3)
N1—C1—C2	122.2 (2)	O1—Li1—O9	96.5 (2)
N1—C1—H1	118.9	O2—Li1—N1	102.5 (2)
C2—C1—H1	118.9	O8—Li1—N1	71.58 (15)
N2—C2—C1	120.8 (2)	O1—Li1—N1	92.45 (19)
N2—C2—H2	119.6	O9—Li1—N1	153.7 (2)
C1—C2—H2	119.6	O4—Li2—O3	101.8 (2)
N2—C3—C4	120.1 (2)	O4—Li2—O5	104.1 (2)
N2—C3—C5	111.87 (19)	O3—Li2—O5	154.0 (3)
C4—C3—C5	128.1 (2)	O4—Li2—N3 ⁱⁱ	101.6 (2)
N1—C4—C3	120.4 (2)	O3—Li2—N3 ⁱⁱ	76.07 (15)
N1—C4—C6	110.76 (19)	O5—Li2—N3 ⁱⁱ	97.47 (19)
C3—C4—C6	128.9 (2)	O4—Li2—N2	99.97 (19)
O5—C5—O6	121.7 (2)	O3—Li2—N2	101.89 (19)
O5—C5—C3	117.9 (2)	O5—Li2—N2	74.75 (16)
O6—C5—C3	120.4 (2)	N3 ⁱⁱ —Li2—N2	158.3 (2)
O8—C6—O7	122.7 (2)	C1—N1—C4	117.9 (2)
O8—C6—C4	116.8 (2)	C1—N1—Li1	127.8 (2)
O7—C6—C4	120.5 (2)	C4—N1—Li1	113.84 (18)
N4—C7—C8	121.0 (2)	C2—N2—C3	118.8 (2)
N4—C7—H7	119.5	C2—N2—Li2	129.1 (2)
C8—C7—H7	119.5	C3—N2—Li2	110.33 (19)
N3—C8—C7	121.5 (2)	C8—N3—C9	118.8 (2)
N3—C8—H8	119.3	C8—N3—Li2 ⁱ	128.8 (2)
C7—C8—H8	119.3	C9—N3—Li2 ⁱ	111.81 (19)
N3—C9—C10	119.9 (2)	C7—N4—C10	118.8 (2)
N3—C9—C11	111.43 (19)	Li1—O1—H1A	114 (4)
C10—C9—C11	128.6 (2)	Li1—O1—H1B	131 (4)
N4—C10—C9	119.4 (2)	H1A—O1—H1B	93 (5)
N4—C10—C12	111.14 (19)	Li1—O2—H2A	117 (3)
C9—C10—C12	129.1 (2)	Li1—O2—H2B	113 (2)
O3 ⁱ —C11—O11	122.8 (2)	H2A—O2—H2B	94 (3)
O3 ⁱ —C11—C9	116.9 (2)	C11 ⁱⁱ —O3—Li2	119.70 (19)
O11—C11—C9	120.2 (2)	Li2—O4—H4A	122.7 (18)
O9—C12—O10	122.2 (2)	Li2—O4—H4B	120 (3)

O9—C12—C10	118.1 (2)	H4A—O4—H4B	116 (3)
O10—C12—C10	119.4 (2)	C5—O5—Li2	120.9 (2)
O2—Li1—O8	109.5 (2)	C5—O6—H7A	115 (6)
O2—Li1—O1	102.2 (2)	C6—O8—Li1	125.6 (2)
O8—Li1—O1	146.8 (3)	C12—O9—Li1	140.4 (2)
O2—Li1—O9	99.7 (2)	C12—O10—H10	110 (4)
O8—Li1—O9	87.89 (19)		
N1—C1—C2—N2	-1.3 (4)	C5—C3—N2—C2	-178.5 (2)
N2—C3—C4—N1	-0.9 (4)	C4—C3—N2—Li2	-164.2 (2)
C5—C3—C4—N1	179.3 (2)	C5—C3—N2—Li2	15.6 (3)
N2—C3—C4—C6	178.7 (2)	O4—Li2—N2—C2	-79.5 (3)
C5—C3—C4—C6	-1.1 (4)	O3—Li2—N2—C2	24.9 (3)
N2—C3—C5—O5	-2.9 (3)	O5—Li2—N2—C2	178.4 (2)
C4—C3—C5—O5	176.9 (2)	N3 ⁱⁱ —Li2—N2—C2	107.1 (6)
N2—C3—C5—O6	177.9 (2)	O4—Li2—N2—C3	84.5 (2)
C4—C3—C5—O6	-2.3 (4)	O3—Li2—N2—C3	-171.01 (19)
N1—C4—C6—O8	0.7 (3)	O5—Li2—N2—C3	-17.5 (2)
C3—C4—C6—O8	-178.9 (2)	N3 ⁱⁱ —Li2—N2—C3	-88.8 (6)
N1—C4—C6—O7	-180.0 (2)	C7—C8—N3—C9	1.0 (4)
C3—C4—C6—O7	0.4 (4)	C7—C8—N3—Li2 ⁱ	172.1 (3)
N4—C7—C8—N3	-4.7 (5)	C10—C9—N3—C8	3.6 (3)
N3—C9—C10—N4	-4.7 (3)	C11—C9—N3—C8	-175.8 (2)
C11—C9—C10—N4	174.5 (2)	C10—C9—N3—Li2 ⁱ	-168.9 (2)
N3—C9—C10—C12	175.9 (2)	C11—C9—N3—Li2 ⁱ	11.7 (3)
C11—C9—C10—C12	-4.8 (4)	C8—C7—N4—C10	3.5 (4)
N3—C9—C11—O3 ⁱ	2.4 (3)	C9—C10—N4—C7	1.1 (4)
C10—C9—C11—O3 ⁱ	-176.9 (2)	C12—C10—N4—C7	-179.5 (2)
N3—C9—C11—O11	-178.5 (2)	O4—Li2—O3—C11 ⁱⁱ	-80.7 (3)
C10—C9—C11—O11	2.1 (4)	O5—Li2—O3—C11 ⁱⁱ	96.8 (6)
N4—C10—C12—O9	7.6 (3)	N3 ⁱⁱ —Li2—O3—C11 ⁱⁱ	18.5 (2)
C9—C10—C12—O9	-173.1 (2)	N2—Li2—O3—C11 ⁱⁱ	176.33 (19)
N4—C10—C12—O10	-171.2 (2)	O6—C5—O5—Li2	164.5 (3)
C9—C10—C12—O10	8.2 (4)	C3—C5—O5—Li2	-14.7 (3)
C2—C1—N1—C4	2.1 (4)	O4—Li2—O5—C5	-79.1 (3)
C2—C1—N1—Li1	-168.8 (3)	O3—Li2—O5—C5	103.4 (5)
C3—C4—N1—C1	-1.0 (4)	N3 ⁱⁱ —Li2—O5—C5	176.8 (2)
C6—C4—N1—C1	179.3 (2)	N2—Li2—O5—C5	17.6 (2)
C3—C4—N1—Li1	171.2 (2)	O7—C6—O8—Li1	-169.6 (3)
C6—C4—N1—Li1	-8.5 (3)	C4—C6—O8—Li1	9.6 (4)
O2—Li1—N1—C1	74.5 (3)	O2—Li1—O8—C6	86.4 (3)
O8—Li1—N1—C1	-178.9 (3)	O1—Li1—O8—C6	-75.4 (5)
O1—Li1—N1—C1	-28.6 (3)	O9—Li1—O8—C6	-174.0 (2)
O9—Li1—N1—C1	-138.6 (5)	N1—Li1—O8—C6	-10.7 (3)
O2—Li1—N1—C4	-96.8 (2)	O10—C12—O9—Li1	-4.5 (5)
O8—Li1—N1—C4	9.8 (2)	C10—C12—O9—Li1	176.8 (3)
O1—Li1—N1—C4	160.1 (2)	O2—Li1—O9—C12	-78.6 (4)

supplementary materials

O9—Li1—N1—C4	50.1 (6)	O8—Li1—O9—C12	172.0 (3)
C1—C2—N2—C3	-0.6 (4)	O1—Li1—O9—C12	25.1 (4)
C1—C2—N2—Li2	162.3 (3)	N1—Li1—O9—C12	134.1 (5)
C4—C3—N2—C2	1.7 (3)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H4A \cdots O3 ⁱⁱⁱ	0.926 (10)	1.830 (12)	2.743 (3)	168 (3)
O4—H4B \cdots O5 ^{iv}	0.93 (4)	1.89 (3)	2.816 (3)	171 (4)
O2—H2A \cdots N4 ^v	0.93 (4)	1.98 (4)	2.898 (3)	171 (4)
O2—H2B \cdots O8 ^v	0.93 (3)	1.84 (3)	2.772 (3)	175 (3)
O1—H1A \cdots O2 ^v	0.94 (5)	2.11 (4)	2.892 (3)	141 (6)
O1—H1B \cdots O7 ^{vi}	0.93 (5)	2.38 (5)	3.305 (3)	174 (6)
C7—H7 \cdots O11 ^{vii}	0.93	2.52	3.184 (3)	129
O10—H10 \cdots O11	0.86 (3)	1.55 (3)	2.404 (3)	174 (5)
O6—H7A \cdots O7	0.86 (3)	1.53 (4)	2.380 (3)	172 (9)

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

Fig. 1

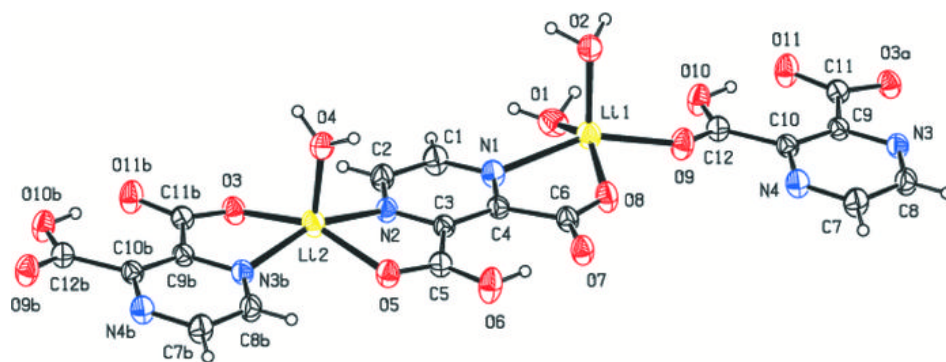


Fig. 2

