

catena-Poly[[*(*6-carboxypyrazine-2-carboxylato)lithium]- μ -aqua]

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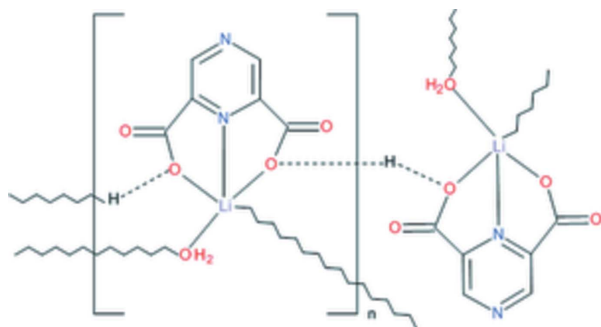
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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.054; wR factor = 0.171; data-to-parameter ratio = 14.7.

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 Li^{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 Li^{I} complex with a pyrazine-2,5-dicarboxylate ligand, see: Starosta & Leciejewicz (2011*a*) and for the structure of a Li^{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) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.15$ mm⁻¹
 $T = 293$ 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⁻³
 $\Delta\rho_{\text{min}} = -0.31$ e Å⁻³

Table 1

Selected bond lengths (Å).

N1—Li1	2.115 (7)	O3—Li1 ⁱ	2.085 (7)
O1—Li1	2.271 (2)	Li1—O1 ⁱⁱ	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 ⁱⁱⁱ ⋯O2 ⁱⁱⁱ	0.83 (2)	2.24 (2)	2.9987 (19)	152 (3)
O1—H1 ⁱⁱⁱ ⋯O1 ⁱⁱⁱ	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).

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supplementary materials

Acta Cryst. (2011). E67, m1708-m1709 [doi:10.1107/S1600536811046198]

***catena*-Poly[[*(6*-carboxypyrazine-2-carboxylato)lithium]-*n*-aqua]**

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Comment

The asymmetric unit of the title compound consists of a Li^I 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, O1ⁱ, hetero-ring N1, aqua O3 and O3ⁱⁱⁱ atoms. The coplanar Li1, N1, O3 and O3ⁱⁱⁱ form the base of a distorted trigonal bipyramid with O1 and O1ⁱ atoms at its apices. [Symmetry code: ⁱ*x*, -*y* + 3/2, *z*; ⁱⁱ*x* + 1, *y*, *z*, ⁱⁱⁱ*x* - 1, *y*, *z*, ^{iv}1 - *x*, 1 - *y*, -*z*]. The observed Li—O and Li—N bond distances (Table 1) are typical for Li^I 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 Liⁱⁱ 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^{iv}⋯O1^{iv} hydrogen bond of 2.455 (3) Å 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 C7ⁱ/O1ⁱ/O2ⁱ carboxylic groups make with it dihedral angles of 3.0 (1)°. 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^I 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^I 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.

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.

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.

Figures

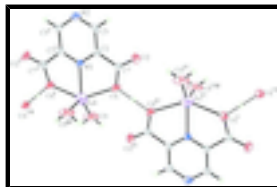


Fig. 1. The asymmetric unit of the title compound with atom labelling scheme and 50% probability displacement ellipsoids. Symmetry code: ⁱ $x, -y + 3/2, z$; ⁱⁱ $x + 1, y, z$; ⁱⁱⁱ $x - 1, y, z$; ^{iv} $1 - x, 1 - y, -z$; ^v $1 - x, -1/2 + y, -z$; ^{vi} $x, 1/2 - y, z$; ^{vii} $1 - x, 1/2 + y, -z$; ^{viii} $2 - x, 1 - y, -z$.

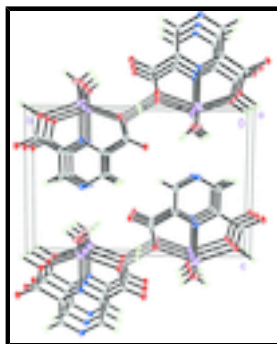


Fig. 2. The alignment of the ribbons viewed along the axis *a*.

catena-Poly[[[(6-carboxypyrazine-2-carboxylato)lithium]- μ -aqua]

Crystal data

[Li(C₆H₃N₂O₄)(H₂O)]

$M_r = 192.06$

Monoclinic, $P2_1/m$

Hall symbol: -P 2yb

$a = 3.5346 (7) \text{ \AA}$

$b = 12.519 (3) \text{ \AA}$

$c = 8.3583 (17) \text{ \AA}$

$\beta = 97.86 (3)^\circ$

$V = 366.37 (13) \text{ \AA}^3$

$Z = 2$

$F(000) = 196$

$D_x = 1.741 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 6\text{--}15^\circ$

$\mu = 0.15 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Plates, colourless

$0.31 \times 0.22 \times 0.08 \text{ mm}$

Data collection

Kuma KM-4 four-circle diffractometer

Radiation source: fine-focus sealed tube

graphite

Profile data from $\omega/2\theta$ scans

Absorption correction: analytical (*Crys.Alis 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	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.054$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.171$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.09$	$w = 1/[\sigma^2(F_o^2) + (0.1039P)^2 + 0.0995P]$
1106 reflections	where $P = (F_o^2 + 2F_c^2)/3$
75 parameters	$(\Delta/\sigma)_{\max} < 0.001$
2 restraints	$\Delta\rho_{\max} = 0.38 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
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 (\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

supplementary materials

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 (Å, °)

N1—C2 ⁱ	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 ⁱⁱ	2.085 (7)
O1—Li1	2.271 (2)	O3—H31	0.825 (17)
O1—H1	1.2275 (13)	Li1—O3 ⁱⁱⁱ	2.085 (7)
C2—C3	1.396 (2)	Li1—O1 ⁱ	2.271 (2)
C2—C7	1.506 (2)	Li1—Li1 ⁱⁱⁱ	3.5346 (7)
N2—C3 ⁱ	1.334 (2)	Li1—Li1 ⁱⁱ	3.5346 (7)
N2—C3	1.334 (2)		
C2 ⁱ —N1—C2	118.8 (2)	O3—Li1—N1	137.3 (3)
C2 ⁱ —N1—Li1	120.51 (10)	O3 ⁱⁱⁱ —Li1—N1	100.4 (3)
C2—N1—Li1	120.51 (10)	O3—Li1—O1 ⁱ	99.45 (16)
C7—O1—Li1	118.33 (19)	O3 ⁱⁱⁱ —Li1—O1 ⁱ	98.65 (16)
C7—O1—H1	115.31 (13)	N1—Li1—O1 ⁱ	71.83 (16)
Li1—O1—H1	126.08 (17)	O3—Li1—O1	99.45 (16)
N1—C2—C3	120.51 (16)	O3 ⁱⁱⁱ —Li1—O1	98.65 (16)
N1—C2—C7	115.98 (14)	N1—Li1—O1	71.84 (16)
C3—C2—C7	123.52 (15)	O1 ⁱ —Li1—O1	141.9 (3)
C3 ⁱ —N2—C3	117.5 (2)	O3—Li1—Li1 ⁱⁱⁱ	150.10 (19)
N2—C3—C2	121.34 (16)	O3 ⁱⁱⁱ —Li1—Li1 ⁱⁱⁱ	27.79 (19)
N2—C3—H3	119.3	N1—Li1—Li1 ⁱⁱⁱ	72.60 (17)
C2—C3—H3	119.3	O1 ⁱ —Li1—Li1 ⁱⁱⁱ	89.89 (15)
O2—C7—O1	126.77 (16)	O1—Li1—Li1 ⁱⁱⁱ	89.89 (15)
O2—C7—C2	121.16 (15)	O3—Li1—Li1 ⁱⁱ	29.90 (19)
O1—C7—C2	112.07 (15)	O3 ⁱⁱⁱ —Li1—Li1 ⁱⁱ	152.21 (18)
Li1—O3—Li1 ⁱⁱ	122.3 (3)	N1—Li1—Li1 ⁱⁱ	107.40 (17)
Li1—O3—H31	119 (3)	O1 ⁱ —Li1—Li1 ⁱⁱ	90.11 (15)
Li1 ⁱⁱ —O3—H31	93 (3)	O1—Li1—Li1 ⁱⁱ	90.11 (15)
O3—Li1—O3 ⁱⁱⁱ	122.3 (3)	Li1 ⁱⁱⁱ —Li1—Li1 ⁱⁱ	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··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O3—H31···O2 ^{iv}	0.83 (2)	2.24 (2)	2.9987 (19)	152 (3)
O1—H1···O1 ^{iv}	1.23 (1)	1.23 (1)	2.455 (3)	180.(1)

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

Fig. 1

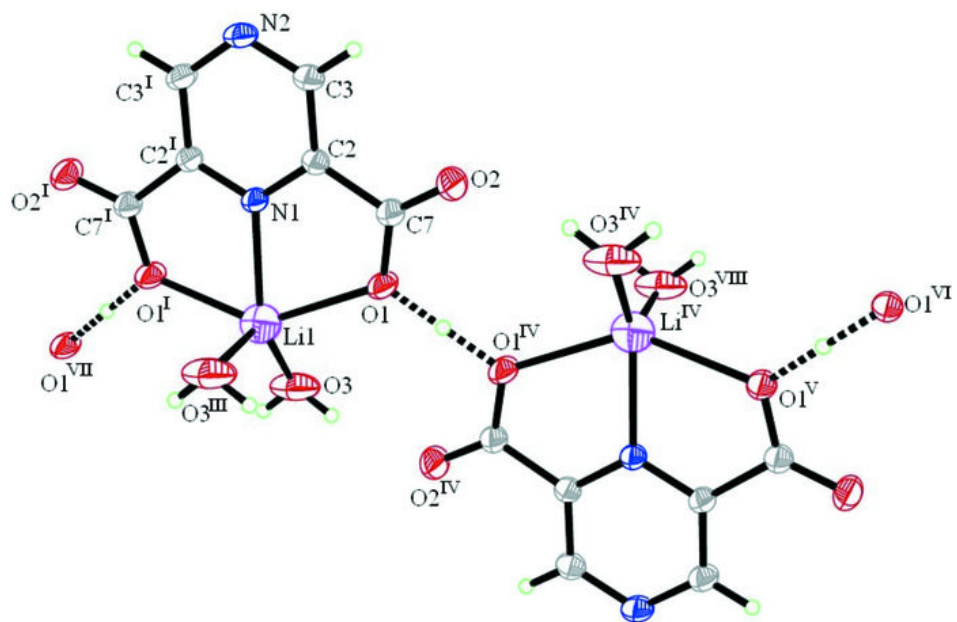


Fig. 2

