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Crystal structure and Hirshfeld surface analysis of poly[[di- μ_3 -glycine-lithium] perchlorate]

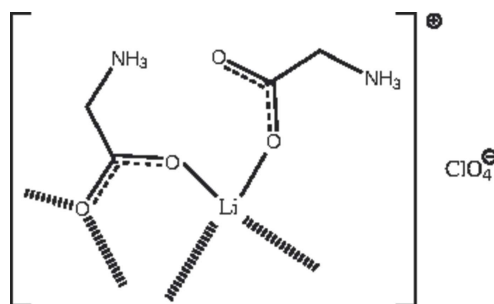
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In the title salt, $\{[\text{Li}(\text{C}_2\text{H}_5\text{NO}_2)_2]\text{ClO}_4\}_n$, the Li⁺ cation is coordinated by four carboxylate oxygen atoms of the glycine molecules with a distorted tetrahedral geometry. The glycine exists in a zwitterionic form with protonated amino and deprotonated carboxylate groups. In the crystalline state, the title salt is primarily stabilized by intermolecular N—H...O and C^α—H...O interactions which interconnect various units. Hirshfeld surface analysis indicates that the intermolecular H...O/O...H interactions are the most important contributors to the crystal packing.

1. Chemical context

As part of an ongoing effort aimed at the elucidation of the crystal and molecular structures of several metal complexes/co-crystals originating from simple amino acids (Balakrishnan *et al.*, 2013*a,b*; Revathi *et al.*, 2015; Sathiskumar *et al.*, 2015*a,b*), we report herein the crystal structure of (I), a bis-(glycinium)lithium perchlorate salt complex and discuss the hydrogen-bonding interactions it forms. The crystal packing and important molecular geometries of (I) are compared with a closely related structure bis(glycine)lithium nitrate salt complex (Baran *et al.*, 2009).



2. Structural commentary

An ORTEP view of the title salt is shown in Fig. 1. The asymmetric unit contains two glycinium units, one Li cation and a perchlorate anion. Both glycine molecules exhibit a zwitterionic structure, as evident from the bond lengths involving the carboxylate atoms (Table 1) and the protonation of the N atoms of the glycine molecules. In (I), the torsion angle N1A—C2A—C1A—O1A in the one of the glycinium is $-0.18(19)^\circ$, while the corresponding angle is $20.75(18)^\circ$ in the

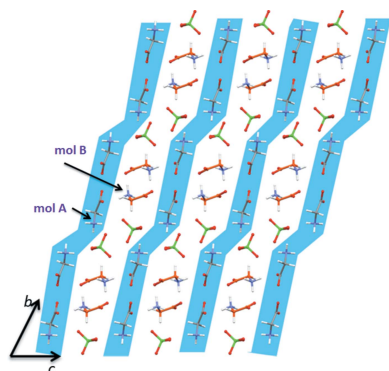


Table 1
Selected geometric parameters (Å, °).

O1A—Li1 ⁱ	1.991 (3)	O2A—Li1	2.015 (3)
O2A—Li1 ⁱⁱ	1.966 (3)	O1B—Li1	1.906 (3)
O1B—Li1—O1A ⁱⁱⁱ	108.95 (12)	O1B—Li1—O2A	102.15 (11)
O2A ^{iv} —Li1—O1A ⁱⁱⁱ	102.03 (11)	O2A ^{iv} —Li1—O2A	109.18 (12)

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

other glycine. The superposition of these two glycine molecules involving non-hydrogen atoms reveals high degree of similarity with an r.m.s.d. value of 0.13 Å, the maximum deviation (0.19 Å) being observed at the C^α (C2A and C2B) atom.

In the crystal, the Li cation is coordinated by four carboxylate oxygen atoms of the glycine molecules. One oxygen atom from each glycine molecule is incorporated in the Li coordination sphere with Li—O distances ranging from 1.906 (3) to 2.015 (3) Å. The geometry around the Li cation is distorted tetrahedral, as discernible from the angles around the Li cation (Table 1). The lithium coordination is extended as a layer that runs parallel to the *b* axis. The distance between two adjacent Li ions is 3.270 (13) Å.

In a closely related structure of the complex bis(glycine) lithium nitrate (Baran *et al.*, 2009), the Li cation is surrounded by four carboxylate oxygen atoms in a distorted tetrahedral geometry as in (I). The distance between two adjacent Li ions is 5.034 Å.

3. Supramolecular features

As shown in Table 2, the title salt is stabilized by a network of intermolecular N—H...O, N—H...Cl and C^α—H...O inter-

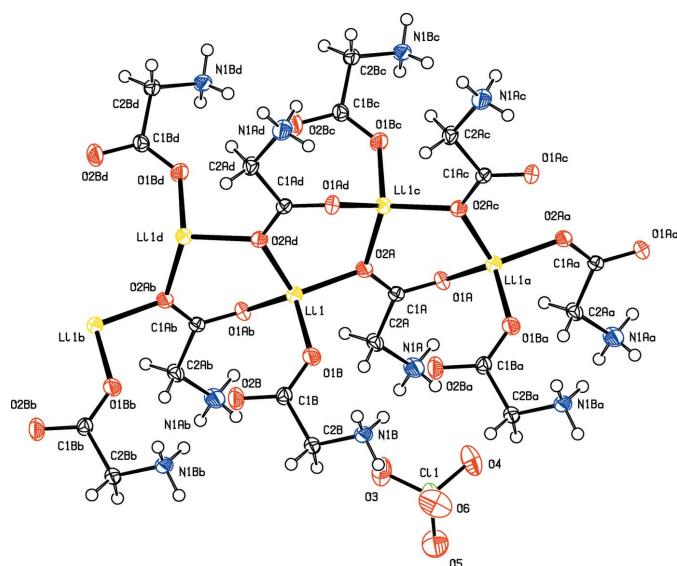


Figure 1
Part of the crystal structure of (I) showing the atomic labelling. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (a) $x, y - 1, z$; (b) $x, y + 1, z$; (c) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (d) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$].

Table 2
Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
N1A—H11...Cl1 ^v	0.88 (3)	2.97 (3)	3.7635 (17)	151 (2)
N1A—H11...O4 ^v	0.88 (3)	2.16 (3)	3.037 (2)	178 (2)
N1A—H12...O5 ^{vi}	0.90 (3)	2.23 (3)	2.965 (2)	139 (2)
N1A—H12...O6 ^{vii}	0.90 (3)	2.51 (3)	3.125 (2)	126 (2)
N1A—H13...O4	0.85 (3)	2.29 (3)	3.091 (2)	156 (2)
N1B—H14...O2B ⁱ	0.90 (2)	2.00 (2)	2.8653 (19)	160.5 (18)
N1B—H15...O1A ^{viii}	0.89 (2)	2.05 (2)	2.9308 (16)	169.8 (19)
N1B—H16...O1B ^{ix}	0.93 (2)	2.35 (3)	2.9249 (17)	119 (2)
N1B—H16...O2B ^x	0.93 (2)	2.28 (2)	3.119 (2)	150 (2)
C2A—H21...O1B	0.97	2.63	3.3747 (18)	134
C2A—H22...O5 ^v	0.97	2.44	3.185 (2)	133
C2B—H23...O2A ^{xi}	0.97	2.60	3.4867 (18)	152
C2B—H24...O4 ⁱⁱⁱ	0.97	2.55	3.360 (2)	141

Symmetry codes: (i) $x, y - 1, z$; (iii) $x, y + 1, z$; (v) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (vi) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (vii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (viii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (ix) $-x + 1, -y + 1, -z + 1$; (x) $-x + 1, -y + 2, -z + 1$; (xi) $x, -y + \frac{3}{2}, z + \frac{1}{2}$.

actions. Overall, the crystal structure of the title salt can be described as alternate layers of perchlorate anions and Li-glycine cations (Fig. 2); these layers extend along the *c*-axis direction. In the crystalline state, each of the zwitterionic glycine molecule is arranged in a different way. The first glycine, molecule *A* (shown in grey), forms double arrays that run parallel to the *b*- and *c*-axis directions. In the array parallel to the *b* axis, the molecules are oriented in opposite directions, as shown in Fig. 3. The first glycine molecule also forms arrays running parallel to the *b* axis. The second glycine molecules (shown in orange) and the perchlorate anions are sandwiched

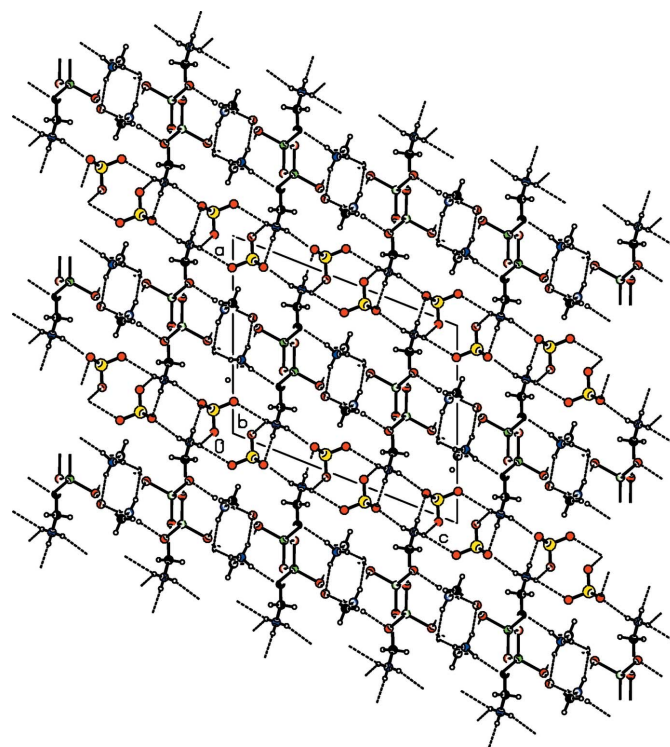


Figure 2
The crystal structure of (I), comprising alternate layers of Li-glycine units and perchlorate anions, viewed down the *b* axis. Hydrogen bonds are indicated by dashed lines.

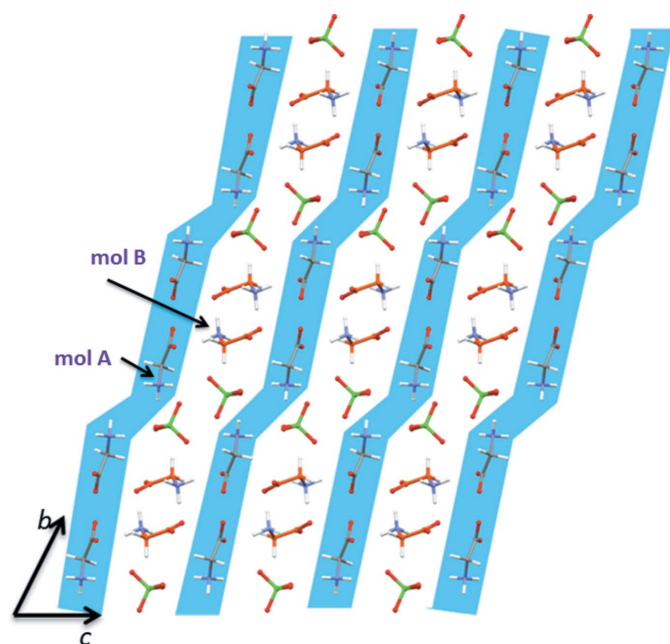


Figure 3
Second glycine molecules (orange) and perchlorate anions are sandwiched between arrays of the first glycine molecules (grey).

between adjacent arrays formed by the first glycine molecules (Fig. 3). Similar packing features are observed for bis(glycine)lithium nitrate (Baran *et al.*, 2009).

Furthermore, a careful examination of the crystal structure reveals that the first glycine molecule does not self-assemble in the solid state. It interacts with the perchlorate anion through intermolecular N—H···O and N—H···Cl interactions and with the second glycine via intermolecular C^α—H···O interactions. In contrast, the second glycine molecule is able to self-associate in the crystal through N—H···O interactions (involving H14···O2B and H16···O2B). The former linear hydrogen bond links the glycine molecules in a head-to-tail fashion in which amino acids are self-associated via their amino and carboxylate groups. This is one of the characteristic features observed in many amino acids and amino acid complexes (Sharma *et al.*, 2006; Selvaraj *et al.*, 2007; Balakrishnan *et al.*, 2013a,b; Revathi *et al.*, 2015). Moreover, this head-to-tail chain sequence extends along the *b*-axis direction and adjacent chains are oriented in an anti-

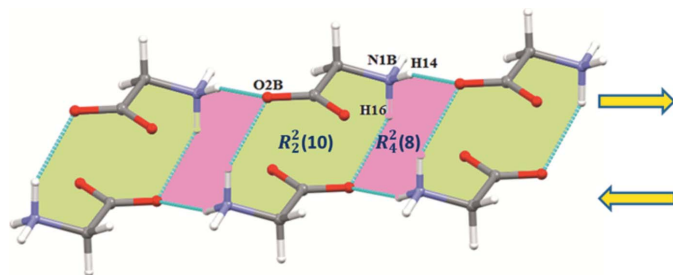


Figure 4
Anti-parallel glycine arrays showing the formation of alternate $R_2^2(10)$ and $R_4^2(8)$ motifs.

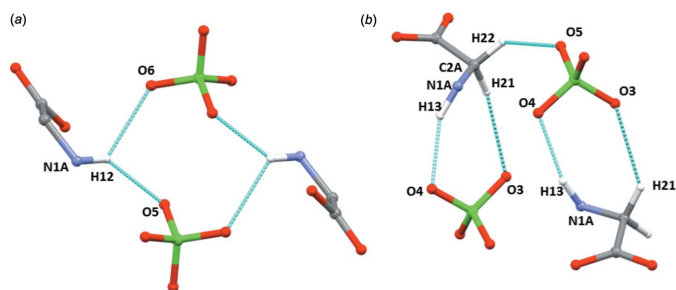


Figure 5
(a) The glycine molecules and perchlorate anions form a closed $R_2^4(8)$ loop through intermolecular N—H···O hydrogen bonds. (b) The glycine molecules and perchlorate anions are interconnected by N—H···O and C^α—H···O interactions, forming a ring motif, with adjacent rings connected by C^α—H···O interactions.

parallel fashion. Centrosymmetrically related dimers [$R_2^2(10)$ motif] of the second glycine molecules are generated through H16···O2B interactions. Together, the H14···O2B and H16···O2B interactions lead to alternating $R_2^2(10)$ and $R_4^2(8)$ motifs (Fig. 4).

The protonated amino group of the first glycine (mol A) is involved in five hydrogen-bonding (N—H···O and N—H···Cl) interactions (see Table 2). One of the bifurcated hydrogen-bonding interactions is formed between H12 and atoms O5 and O6 of the perchlorate anions. This interactions generate an $R_2^4(8)$ loop motif in which two glycine and two perchlorate ions are involved [Fig. 5(a)]. Intermolecular N1A—H13···O4 and C2A—H21···O3 interactions connect the glycine molecules and perchlorate anions into a loop with adjacent loops being interconnected by C2A—H22···O5 interactions [Fig. 5(b)]. As mentioned earlier, the second glycine interacts with carboxylate groups through its protonated amino group (N1B) (Fig. 4). It also interacts with the perchlorate anion through C2B—H24···O4 interaction.

4. Hirshfeld surface analysis and 2D fingerprint plots

The Hirshfeld surface (HS) analysis was carried out in order to understand the nature of the intermolecular interactions present in the crystal structure. The shorter and longer contacts are indicated as red and blue spots on the HS and contacts with distances equal to the sum of the van der Waals radii are represented as white. The Hirshfeld surfaces for the cation (consisting of two glycine molecules and a lithium ion) and anion of the title salt complex were generated and analysed separately using the program *CrystalExplorer* (Wolff *et al.*, 2012). The HS of the cation mapped over the normalized distance, d_{norm} , and the 2D fingerprint plots (Spackman & McKinnon, 2002) are illustrated in Fig. 6. In the cation, intermolecular O···H/H···O interactions are predominant making a 66.9% contribution to the total HS. In the two-dimensional fingerprint plots, these contacts are depicted as a pair of sharp spikes with $d_e + d_i \sim 1.9$ Å. There is a remarkable difference observed in the relative contribution of the H···O (donor region where $d_e > d_i$) and O···H (acceptor region where $d_e < d_i$) contacts. The former contact contributes 47.3%,

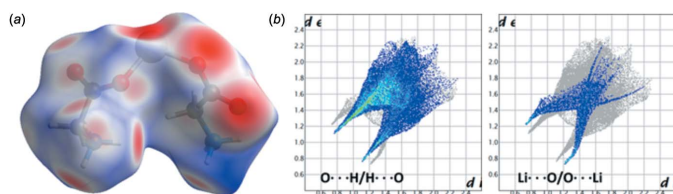


Figure 6
(a) Hirshfeld surface of the bis(glycinium)lithium unit and (b) two-dimensional fingerprint plots for the intermolecular O...H/H...O and Li...O/O...Li contacts.

while the contribution of the latter reciprocal contact is 19.6%. Similarly, the relative contribution of the Li...O/O...Li contacts is calculated to be 12.7% and these contacts appear as sharp spikes at a distance of around 1.9 Å. The proportions of Li...O and O...Li contacts are comparable (5.9 and 6.8%, respectively). The H...H contacts contribute 11.3% to the total HS of the cation part. The H...Li/Li...H (2.5%), O...C/C...O (2.4%) and O...O (2.0%) contacts play a minor role in the stabilization of the crystal structure.

In the perchlorate anion, the relative contributions of the O...H/H...O and O...O contacts are 81.4 and 18.2%, respectively (Fig. 7). The O...H/H...O contacts visible on the HS are due to the N—H...O and C—H...O hydrogen bonds. The O...O contacts are also visible on the HS and this contact of around 2.8 Å has the shortest distances of d_e and d_i of around 1.4 Å (Fig. 8). This O...O short contact [2.879 (2) Å] links the anionic molecules into a chain running parallel to the *b*-axis direction.

5. Database survey

A search of the Cambridge Structural Database (CSD, version 5.39, last update August 2018; Groom *et al.*, 2016) using the keywords 'lithium (name)' and 'amino-acids, peptides and complexes (class)' yielded 50 hits of which 18 are glycine amino acids. In most of the complexes, carboxylate oxygen atoms are involved in the Li coordination as described in the following examples. In the *catena*-[μ^3 -glycinato-*O,O'*-(nitrate-*O*)]lithium complex, one of oxygen atoms of the nitro group is involved in the Li coordination along with the glycine carboxylate O atoms (ALUNEA, Baran *et al.*, 2003). In three complexes (HEFWUK, Müller *et al.*, 1994; NEPWUC, Balakrishnan *et al.*, 2013*b*; UCIYOV, Fleck *et al.*, 2006), the water O atom and three glycine carboxylate O atoms

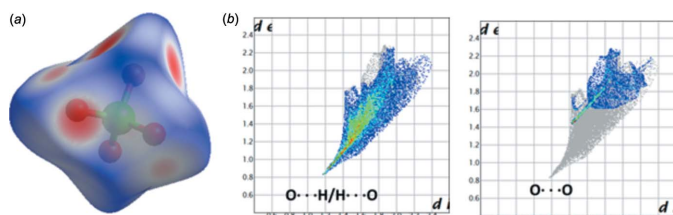


Figure 7
(a) Hirshfeld surface of the perchlorate unit and (b) two-dimensional fingerprint plots for the intermolecular O...H/H...O and O...O contacts.

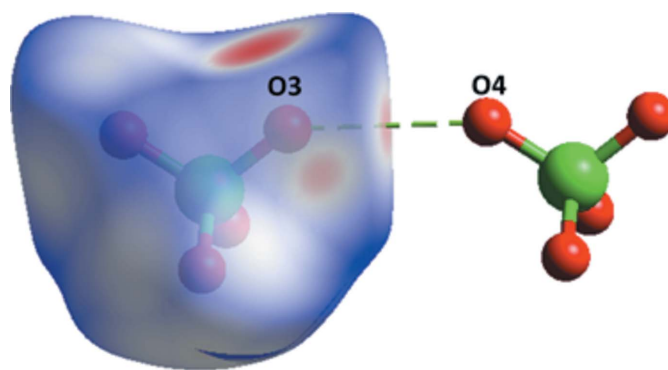


Figure 8
An intermolecular O...O contact interconnects adjacent perchlorate anions.

participate in the Li coordination. In the *catena*-[[μ^4 -glycyl-*N,O,O,O'*]]lithium complex (HEFXAR, Müller *et al.*, 1994), the deprotonated amino group N atom is involved in the Li coordination sphere and in cyclo[tris(glycyl-prolyl-*O*)]isothiocyanatolithium trihydrate (YUWXUJ, Thomas *et al.*, 1994), the N atom of the isothiocyanate, which acts as a fourth ligand, participates in the Li coordination sphere.

A detailed survey was also been conducted in the protein data bank (www.rcsb.org) to understand the Li⁺ coordination with protein molecules. The keyword 'lithium' was used in the search, which resulted in 74 hits (up to 3.0 Å resolution). There are 30 structures found with better than 1.5 Å resolution and these structures were examined further. In this dataset, we found that Li is three- to six-coordinate with a water molecule belonging to the Li complex cation. Moreover, the residues aspartate and glutamate are included in the Li coordination in several structures.

6. Synthesis and crystallization

The title salt was synthesized by dissolving AR-grade glycine and lithium perchlorate in a 2:1 stoichiometric ratio in double distilled water and stirred continuously for 2 h. Slow evaporation of this aqueous solution at room temperature yielded transparent colourless single crystals of the title salt.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The positions of N-bound H atoms were located from a difference-Fourier map and refined freely along with their isotropic displacement parameters. The remaining H atoms were placed in calculated positions (C—H = 0.97 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Reflections 1 0 0 and 0 0 2 were obscured by the beam stop and were omitted during final refinement cycle.

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Table 3
Experimental details.

Crystal data	
Chemical formula	[Li(C ₂ H ₅ NO ₂) ₂]ClO ₄
<i>M_r</i>	256.53
Crystal system, space group	Monoclinic, <i>P</i> ₂ /c
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.7792 (14), 5.2144 (4), 15.6368 (18)
β (°)	111.808 (4)
<i>V</i> (Å ³)	967.40 (17)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.43
Crystal size (mm)	0.35 × 0.30 × 0.30
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2004)
<i>T_{min}</i> , <i>T_{max}</i>	0.865, 0.883
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	7318, 2304, 2047
<i>R_{int}</i>	0.023
(sin θ/λ) _{max} (Å ⁻¹)	0.662
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.033, 0.092, 1.07
No. of reflections	2304
No. of parameters	170
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.52, -0.42

Computer programs: *APEX2*, *SAIN*T and *XPREP* (Bruker, 2004), *SIR92* (Altomare *et al.*, 1994), *SHELXL2014/7* (Sheldrick, 2015), *PLATON* (Spek, 2009), *Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip, 2010).

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supporting information

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Crystal structure and Hirshfeld surface analysis of poly[[di- μ_3 -glycine-lithium] perchlorate]

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Computing details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT* (Bruker, 2004); data reduction: *SAINT* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

Poly[[di- μ_3 -glycine-lithium] perchlorate]

Crystal data

[Li(C₂H₅NO₂)₂]ClO₄

$M_r = 256.53$

Monoclinic, $P2_1/c$

$a = 12.7792$ (14) Å

$b = 5.2144$ (4) Å

$c = 15.6368$ (18) Å

$\beta = 111.808$ (4)°

$V = 967.40$ (17) Å³

$Z = 4$

$F(000) = 528$

$D_x = 1.761$ Mg m⁻³

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

Cell parameters from 4824 reflections

$\theta = 5.4$ – 56.2°

$\mu = 0.43$ mm⁻¹

$T = 296$ K

Block, colourless

$0.35 \times 0.30 \times 0.30$ mm

Data collection

Bruker Kappa APEXII CCD
diffractometer

ω and ϕ scan

Absorption correction: multi-scan
(SADABS; Bruker, 2004)

$T_{\min} = 0.865$, $T_{\max} = 0.883$

7318 measured reflections

2304 independent reflections

2047 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 28.1^\circ$, $\theta_{\min} = 3.4^\circ$

$h = -16 \rightarrow 16$

$k = -6 \rightarrow 4$

$l = -20 \rightarrow 20$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.092$

$S = 1.07$

2304 reflections

170 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0468P)^2 + 0.4555P]$

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

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

$\Delta\rho_{\max} = 0.52$ e Å⁻³

$\Delta\rho_{\min} = -0.42$ e Å⁻³

Extinction correction: SHELXL2014/7
 (Sheldrick 2015),
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.051 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1A	0.32780 (8)	0.05574 (18)	0.19473 (6)	0.0197 (2)
O2A	0.41860 (8)	0.43353 (19)	0.22629 (7)	0.0215 (2)
O1B	0.41750 (10)	0.7653 (2)	0.38667 (7)	0.0268 (3)
O2B	0.37499 (12)	1.1669 (2)	0.41178 (8)	0.0356 (3)
N1A	0.13201 (12)	0.2513 (3)	0.19284 (12)	0.0312 (3)
H11	0.068 (2)	0.335 (5)	0.1779 (16)	0.049 (6)*
H12	0.128 (2)	0.138 (6)	0.1487 (19)	0.062 (7)*
H13	0.135 (2)	0.163 (5)	0.2393 (19)	0.056 (7)*
N1B	0.38884 (12)	0.5778 (3)	0.53719 (9)	0.0255 (3)
H14	0.3687 (17)	0.465 (4)	0.4903 (16)	0.037 (5)*
H15	0.3625 (17)	0.529 (4)	0.5801 (15)	0.037 (5)*
H16	0.466 (2)	0.599 (5)	0.5661 (16)	0.051 (7)*
C1A	0.33341 (11)	0.2912 (3)	0.21201 (8)	0.0157 (3)
C1B	0.38168 (11)	0.9307 (3)	0.42732 (9)	0.0198 (3)
C2A	0.22888 (11)	0.4280 (3)	0.21347 (10)	0.0224 (3)
H21	0.2455	0.5039	0.2737	0.027*
H22	0.2090	0.5653	0.1684	0.027*
C2B	0.34142 (13)	0.8330 (3)	0.50229 (10)	0.0229 (3)
H23	0.3636	0.9542	0.5530	0.027*
H24	0.2598	0.8225	0.4775	0.027*
Li1	0.4371 (2)	0.7982 (5)	0.27213 (16)	0.0196 (5)
Cl1	0.07919 (3)	0.27547 (7)	0.41247 (3)	0.02800 (14)
O3	0.09668 (13)	0.4960 (3)	0.36429 (11)	0.0504 (4)
O4	0.08777 (12)	0.0478 (2)	0.36201 (10)	0.0453 (4)
O5	-0.03202 (11)	0.2865 (3)	0.41610 (11)	0.0483 (4)
O6	0.16270 (12)	0.2672 (3)	0.50378 (9)	0.0506 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1A	0.0213 (5)	0.0155 (5)	0.0206 (5)	0.0022 (4)	0.0060 (4)	-0.0015 (4)
O2A	0.0183 (5)	0.0196 (5)	0.0296 (5)	-0.0016 (4)	0.0123 (4)	-0.0026 (4)
O1B	0.0422 (7)	0.0217 (5)	0.0228 (5)	0.0042 (4)	0.0192 (5)	0.0016 (4)
O2B	0.0639 (8)	0.0171 (5)	0.0338 (6)	0.0026 (5)	0.0275 (6)	0.0039 (4)
N1A	0.0194 (6)	0.0278 (7)	0.0493 (9)	-0.0026 (5)	0.0160 (6)	-0.0073 (7)

N1B	0.0357 (7)	0.0230 (7)	0.0248 (6)	0.0074 (5)	0.0192 (6)	0.0075 (5)
C1A	0.0161 (6)	0.0176 (6)	0.0129 (5)	0.0019 (5)	0.0050 (4)	0.0005 (4)
C1B	0.0256 (7)	0.0175 (7)	0.0167 (6)	-0.0007 (5)	0.0081 (5)	0.0006 (5)
C2A	0.0169 (6)	0.0182 (7)	0.0324 (7)	0.0002 (5)	0.0096 (5)	-0.0038 (5)
C2B	0.0312 (7)	0.0180 (7)	0.0246 (7)	0.0043 (5)	0.0163 (6)	0.0029 (5)
Li1	0.0217 (11)	0.0180 (11)	0.0206 (10)	0.0008 (9)	0.0096 (9)	0.0017 (9)
Cl1	0.0232 (2)	0.0203 (2)	0.0330 (2)	0.00037 (12)	0.00177 (15)	-0.00111 (13)
O3	0.0580 (9)	0.0278 (7)	0.0699 (10)	0.0008 (6)	0.0290 (8)	0.0097 (6)
O4	0.0509 (8)	0.0263 (7)	0.0500 (8)	0.0016 (5)	0.0085 (6)	-0.0107 (6)
O5	0.0259 (7)	0.0473 (8)	0.0679 (10)	-0.0025 (5)	0.0131 (6)	-0.0002 (7)
O6	0.0341 (7)	0.0704 (11)	0.0346 (7)	0.0116 (6)	-0.0019 (6)	-0.0082 (6)

Geometric parameters (Å, °)

O1A—C1A	1.2535 (16)	N1B—H16	0.93 (2)
O1A—Li1 ⁱ	1.991 (3)	C1A—C2A	1.5219 (18)
O2A—C1A	1.2670 (16)	C1B—C2B	1.5318 (19)
O2A—Li1 ⁱⁱ	1.966 (3)	C2A—H21	0.9700
O2A—Li1	2.015 (3)	C2A—H22	0.9700
O1B—C1B	1.2543 (17)	C2B—H23	0.9700
O1B—Li1	1.906 (3)	C2B—H24	0.9700
O2B—C1B	1.2525 (18)	Li1—O2A ⁱⁱⁱ	1.966 (3)
N1A—C2A	1.4793 (19)	Li1—O1A ^{iv}	1.991 (3)
N1A—H11	0.88 (3)	Li1—Li1 ⁱⁱⁱ	3.270 (3)
N1A—H12	0.90 (3)	Li1—Li1 ⁱⁱ	3.270 (3)
N1A—H13	0.85 (3)	Cl1—O6	1.4308 (13)
N1B—C2B	1.4796 (19)	Cl1—O3	1.4371 (14)
N1B—H14	0.90 (2)	Cl1—O5	1.4443 (14)
N1B—H15	0.89 (2)	Cl1—O4	1.4521 (13)
C1A—O1A—Li1 ⁱ	123.96 (11)	H21—C2A—H22	107.9
C1A—O2A—Li1 ⁱⁱ	122.18 (11)	N1B—C2B—C1B	111.92 (12)
C1A—O2A—Li1	126.51 (11)	N1B—C2B—H23	109.2
Li1 ⁱⁱ —O2A—Li1	110.42 (9)	C1B—C2B—H23	109.2
C1B—O1B—Li1	127.90 (12)	N1B—C2B—H24	109.2
C2A—N1A—H11	111.7 (17)	C1B—C2B—H24	109.2
C2A—N1A—H12	112.5 (17)	H23—C2B—H24	107.9
H11—N1A—H12	110 (2)	O1B—Li1—O2A ⁱⁱⁱ	118.06 (13)
C2A—N1A—H13	112.8 (17)	O1B—Li1—O1A ^{iv}	108.95 (12)
H11—N1A—H13	104 (2)	O2A ⁱⁱⁱ —Li1—O1A ^{iv}	102.03 (11)
H12—N1A—H13	106 (2)	O1B—Li1—O2A	102.15 (11)
C2B—N1B—H14	109.4 (13)	O2A ⁱⁱⁱ —Li1—O2A	109.18 (12)
C2B—N1B—H15	108.6 (13)	O1A ^{iv} —Li1—O2A	117.22 (12)
H14—N1B—H15	110.6 (19)	O1B—Li1—Li1 ⁱⁱⁱ	121.15 (12)
C2B—N1B—H16	106.7 (16)	O2A ⁱⁱⁱ —Li1—Li1 ⁱⁱⁱ	35.28 (8)
H14—N1B—H16	114 (2)	O1A ^{iv} —Li1—Li1 ⁱⁱⁱ	67.82 (6)
H15—N1B—H16	107.5 (19)	O2A—Li1—Li1 ⁱⁱⁱ	132.77 (14)
O1A—C1A—O2A	126.04 (12)	O1B—Li1—Li1 ⁱⁱ	111.95 (11)

O1A—C1A—C2A	118.81 (12)	O2A ⁱⁱⁱ —Li1—Li1 ⁱⁱ	75.88 (12)
O2A—C1A—C2A	115.11 (12)	O1A ^{iv} —Li1—Li1 ⁱⁱ	134.29 (14)
O2B—C1B—O1B	126.11 (13)	O2A—Li1—Li1 ⁱⁱ	34.30 (3)
O2B—C1B—C2B	117.23 (13)	Li1 ⁱⁱⁱ —Li1—Li1 ⁱⁱ	105.77 (13)
O1B—C1B—C2B	116.66 (12)	O6—C11—O3	110.10 (10)
N1A—C2A—C1A	111.90 (12)	O6—C11—O5	110.00 (9)
N1A—C2A—H21	109.2	O3—C11—O5	109.62 (9)
C1A—C2A—H21	109.2	O6—C11—O4	109.79 (8)
N1A—C2A—H22	109.2	O3—C11—O4	108.16 (9)
C1A—C2A—H22	109.2	O5—C11—O4	109.15 (8)
Li1 ⁱ —O1A—C1A—O2A	53.01 (19)	Li1—O1B—C1B—O2B	-17.0 (2)
Li1 ⁱ —O1A—C1A—C2A	-129.18 (14)	Li1—O1B—C1B—C2B	162.37 (14)
Li1 ⁱⁱ —O2A—C1A—O1A	-2.3 (2)	O1A—C1A—C2A—N1A	-0.18 (19)
Li1—O2A—C1A—O1A	-170.40 (12)	O2A—C1A—C2A—N1A	177.86 (13)
Li1 ⁱⁱ —O2A—C1A—C2A	179.83 (12)	O2B—C1B—C2B—N1B	-159.82 (14)
Li1—O2A—C1A—C2A	11.73 (18)	O1B—C1B—C2B—N1B	20.75 (18)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1A—H11 \cdots C11 ^v	0.88 (3)	2.97 (3)	3.7635 (17)	151 (2)
N1A—H11 \cdots O4 ^v	0.88 (3)	2.16 (3)	3.037 (2)	178 (2)
N1A—H12 \cdots O5 ^{vi}	0.90 (3)	2.23 (3)	2.965 (2)	139 (2)
N1A—H12 \cdots O6 ^{vii}	0.90 (3)	2.51 (3)	3.125 (2)	126 (2)
N1A—H13 \cdots O4	0.85 (3)	2.29 (3)	3.091 (2)	156 (2)
N1B—H14 \cdots O2B ⁱ	0.90 (2)	2.00 (2)	2.8653 (19)	160.5 (18)
N1B—H15 \cdots O1A ^{viii}	0.89 (2)	2.05 (2)	2.9308 (16)	169.8 (19)
N1B—H16 \cdots O1B ^{ix}	0.93 (2)	2.35 (3)	2.9249 (17)	119 (2)
N1B—H16 \cdots O2B ^x	0.93 (2)	2.28 (2)	3.119 (2)	150 (2)
C2A—H21 \cdots O1B	0.97	2.63	3.3747 (18)	134
C2A—H22 \cdots O5 ^v	0.97	2.44	3.185 (2)	133
C2B—H23 \cdots O2A ^{xi}	0.97	2.60	3.4867 (18)	152
C2B—H24 \cdots O4 ^{iv}	0.97	2.55	3.360 (2)	141

Symmetry codes: (i) $x, y-1, z$; (iv) $x, y+1, z$; (v) $-x, y+1/2, -z+1/2$; (vi) $-x, y-1/2, -z+1/2$; (vii) $x, -y+1/2, z-1/2$; (viii) $x, -y+1/2, z+1/2$; (ix) $-x+1, -y+1, -z+1$; (x) $-x+1, -y+2, -z+1$; (xi) $x, -y+3/2, z+1/2$.