

Two new non-centrosymmetric lithium salts of glycine: bis(glycine) lithium chromate monohydrate and bis(glycine) lithium molybdate

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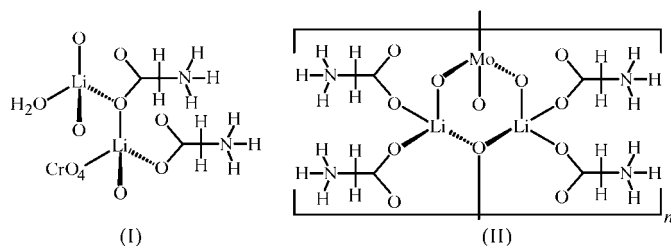
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In bis(glycine) lithium chromate monohydrate {systematic name: poly[aquadi- μ -glycinato- μ -tetraoxochromato(VI)-dilithium(I)]}, $[\text{CrLi}_2(\text{C}_2\text{H}_5\text{NO}_2)_2\text{O}_4(\text{H}_2\text{O})]_n$, (I) (space group $P2_12_12_1$), and bis(glycine) lithium molybdate {systematic name: poly[di- μ -glycinato- μ -tetraoxomolybdate(VI)-dilithium(I)]}, $[\text{Li}_2\text{Mo}(\text{C}_2\text{H}_5\text{NO}_2)_2\text{O}_4]_n$, (II) (space group $P2_1$), all atoms are located on general positions. The crystal structure of (I) is characterized by infinite chains of corner-sharing $[\text{LiO}_4]$ tetrahedra, which are connected by glycine molecules to form layers. $[\text{CrO}_4]$ tetrahedra are attached to the $[\text{LiO}_4]$ tetrahedra. Compound (II) contains dimers of $[\text{LiO}_4]$ tetrahedra which are connected by $[\text{MoO}_4]$ tetrahedra to form chains, which are in turn connected by glycine molecules to form double layers.

Comment

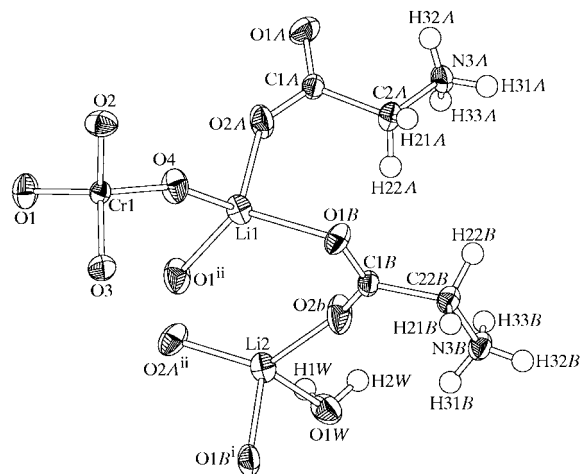
Compounds of glycine and inorganic lithium salts are rare; to date, only four such structures have been published (if lithium glycinate is included), namely glycine lithium nitrate (Baran *et al.*, 2003), glycine lithium sulfate (Fleck & Bohatý, 2004), glycine lithium chloride monohydrate and lithium glycinate (both Müller *et al.*, 1994). During our studies of compounds of glycine and inorganic salts, we have found two new examples,



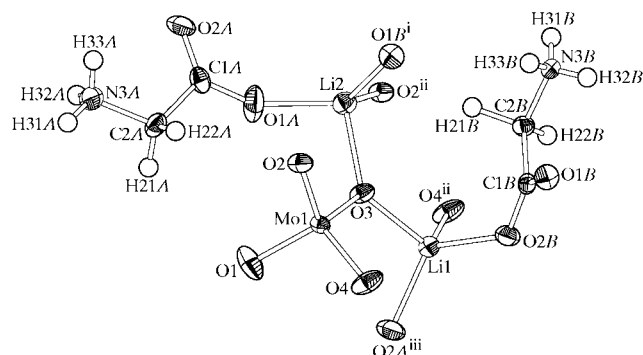
namely bis(glycine) dilithium chromate monohydrate, (I), and bis(glycine) dilithium molybdate, (II).

Although stoichiometrically similar, the title compounds differ greatly in terms of their crystal structures. Both can be considered as layer structures if only strong bonds are considered. (Weak hydrogen bonds connect all units into three-dimensional frameworks in both structures). However, the connectivities are rather different in the two structures.

In compound (I), both crystallographically different Li atoms are four-coordinate. The coordination polyhedra can be described as distorted tetrahedra [Li1–O distances range from 1.980 (3) to 2.080 (2) Å and Li2–O distances range from 1.936 (3) to 2.104 (3) Å]. However, there is an additional long contact between atoms Li2 and O1A [2.395 (3) Å]. Bond-valence calculations [using the bond-valence parameters from Brese & O’Keeffe (1991) and the ionic radii from Shannon (1976)] have shown that the contribution of this ‘bond’ can be neglected. The $[\text{LiO}_4]$ tetrahedra are connected by shared corners into infinite chains parallel to $[100]$, which are in turn connected to form layers parallel to (001) by the glycine molecules in the interstices between the chains. Tetrahedral chromate groups $[\text{Cr–O} = 1.6339 (10)\text{–}1.6666 (9) \text{ Å}]$ are connected to these chains, but are not otherwise attached to the chains. Each $[\text{CrO}_4]$ tetrahedron shares one common


Figure 1

The connectivity in compound (I), shown with displacement ellipsoids at the 50% probability level. [Symmetry codes: (i) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.]


Figure 2

The connectivity in compound (II), shown with displacement ellipsoids at the 50% probability level. [Symmetry codes: (i) $-x, -\frac{1}{2} + y, -z$; (ii) $1 + x, y, z$; (iii) $x, 1 + y, z$.]

corner with an $[\text{LiO}_4]$ tetrahedron (namely atom O4). The amino acids provide additional connections: glycine molecules *A* and *B* act as bridging ligands between adjacent tetrahedral chains (Fig. 3). (If the long $\text{Li2}-\text{O1A}$ contact is taken into account, molecule *A* can be further considered as a bidentate ligand to atom Li2 .) Hydrogen bonds connect these units to form a three-dimensional framework (Table 1).

In compound (II) also, there are two crystallographically different four-coordinate Li atoms. As in the structure of (I), the $[\text{LiO}_4]$ polyhedra are slightly distorted tetrahedra [$\text{Li1}-\text{O}$ distances range from 1.904 (6) to 1.959 (7) Å and $\text{Li2}-\text{O}$ distances range from 1.906 (6) to 1.967 (7) Å]. Two neighbouring tetrahedra form dimers through shared corners, which are actually O3 atoms from the molybdate tetrahedra [$\text{Mo}-\text{O} = 1.751$ (3)– 1.7657 (13) Å]. As a result, these three tetrahedra are connected to $[\text{Li}_2\text{MoO}_{10}]$ clusters, the central O3 atoms being more or less centres of nearly planar triangles of the three different cations, *viz.* Li1, Li2 and Mo. The molybdate groups are also attached to two symmetry-equivalent LiO_4 tetrahedra *via* atoms O2 and O4, thus forming infinite chains parallel to $[100]$. In Fig. 4, these $[\text{Li}_2\text{MoO}_{10}]$ clusters are seen side on, and in Fig. 5 from above (as part of the chains). The two crystallographically different glycine molecules play different roles in the connectivity of these chains, although both act as bridging ligands. Glycine moiety *A* connects two

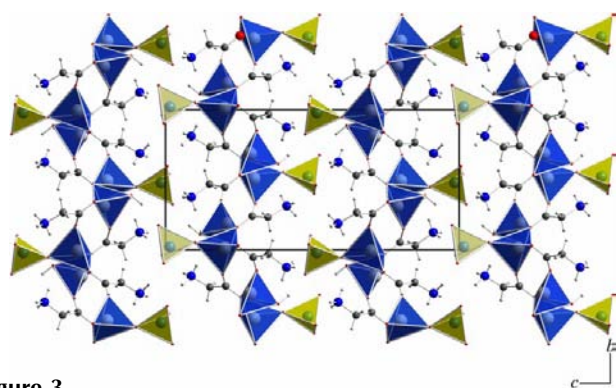


Figure 3
A packing diagram for compound (I), viewed perpendicular to the chains. The layers are oriented vertically.

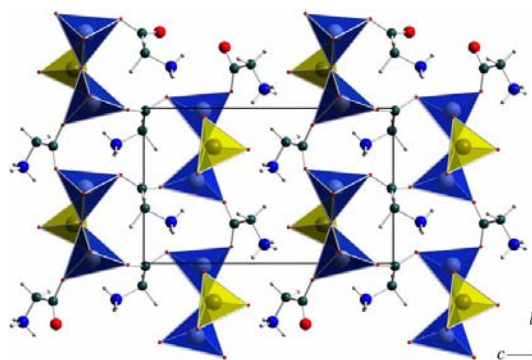


Figure 4
A packing diagram for compound (II). The double layers are oriented vertically. Note that two double layers are interlocked, but are not connected by any strong bonds (only by hydrogen bonds, which are not shown).

adjacent chains into layers parallel to (001), while glycine moiety *B* lies between two such layers and provides connection to form double layers (Fig. 4). Hydrogen bonds provide further interlayer connections, as well as linkage between the double layers, to form a three-dimensional structure (Table 2).

In both compounds, the glycine molecules exist as zwitterions, *viz.* $\text{NH}_3^+\text{CH}_2\text{COO}^-$, as is usually the case in compounds of amino acids with inorganic salts. The glycine molecules are more or less planar and their backbones have extended conformations. The $\text{O1}-\text{C1}-\text{C2}-\text{N}$ torsion angles are 168.9 (1) and -173.6 (1) $^\circ$ for the molecules in (I), and -173.2 (2) and -176.3 (2) $^\circ$ for the molecules in (II). Perfectly planar glycine molecules (torsion angle 180°) are very rare, the only example being glycine magnesium dichloride tetrahydrate (Fleck & Bohatý, 2005). All covalent bond lengths in the organic molecules of (I) and (II) are unremarkable and in good agreement with the values given by Allen *et al.* (1987).

All six known structures of compounds of glycine with lithium or inorganic lithium salts are rather different (Table 3). In most cases, however, building units of $[\text{LiO}_4]$ tetrahedra and linkage by the organic ligands occurs. Lithium glycinate (Müller *et al.*, 1994) is the only member of this group that contains $[\text{LiO}_3\text{N}]$ tetrahedra. The connectivity of the tetrahedra varies throughout this group: corner-sharing dimers [compound (II)], edge-sharing dimers (glycine lithium nitrate; Baran *et al.*, 2003), tetrahedral chains [compound (I), and lithium glycinate and glycine lithium chloride monohydrate (both Müller *et al.*, 1994)], and tetrahedral layers (glycine lithium sulfate; Fleck & Bohatý, 2004). The carboxylate groups always assume the role of bridging ligands. In one case, namely lithium glycinate (Müller *et al.*, 1994), the organic molecule acts as a triply bridging ligand, *i.e.* through both O atoms and

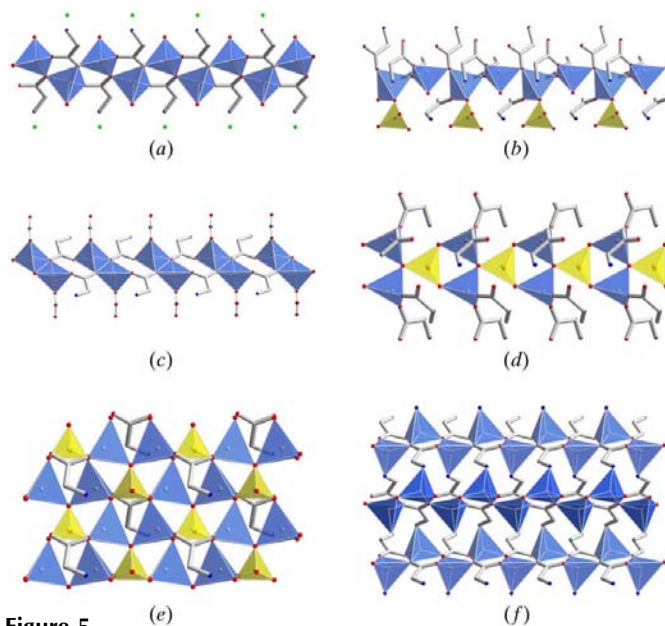


Figure 5
Connectivities and building units in compounds of glycine with lithium and inorganic lithium salts. (a) Glycine lithium chloride monohydrate (Müller *et al.*, 1994); (b) compound (I); (c) glycine lithium nitrate (Baran *et al.*, 2003); (d) compound (II); (e) glycine lithium sulfate (Fleck & Bohatý, 2004); (f) lithium glycinate (Müller *et al.*, 1994).

the N atoms of the molecule, are part of coordination tetrahedra. Fig. 5 shows the connectivities of these compounds.

It is striking that four out of these six compounds are non-centrosymmetric, including both title compounds. Although the atomic arrangement of compound (II) is close to being centrosymmetric [*i.e.* $P2_1/m$, for which the program *PLATON* (Spek, 2003) indicated an 82% probability], a refinement in this space group does not give any sensible results.

Experimental

Radiating aggregates of yellow transparent acicular to bladed crystals of (I) were grown by slow evaporation of an aqueous solution containing dissolved Li_2CO_3 , CrO_3 and glycine (molar ratio 1:1:1) at about 295 K and pH 7. Aggregates of colourless tabular crystals of (II) were grown by slow evaporation of an aqueous solution of Li_2MoO_4 and glycine (approximate molar ratio 1:2) at about 295 K and pH 8.

Compound (I)

Crystal data

$[\text{CrLi}_2(\text{C}_2\text{H}_5\text{NO}_2)_2\text{O}_4(\text{H}_2\text{O})]$
 $M_r = 298.04$
 Orthorhombic, $P2_12_12_1$
 $a = 6.2020$ (10) Å
 $b = 9.192$ (2) Å
 $c = 19.294$ (4) Å
 $V = 1099.9$ (4) Å³
 $Z = 4$
 $D_x = 1.800$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 1654 reflections
 $\theta = 3.9\text{--}28.7^\circ$
 $\mu = 1.08$ mm⁻¹
 $T = 293$ (2) K
 Plate, yellow
 $0.20 \times 0.20 \times 0.05$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (Otwinowski *et al.*, 2003)
 $T_{\min} = 0.813$, $T_{\max} = 0.948$
 4010 measured reflections

4010 independent reflections
 3872 reflections with $I > 2\sigma(I)$
 $\theta_{\max} = 32.6^\circ$
 $h = -9 \rightarrow 9$
 $k = -13 \rightarrow 13$
 $l = -28 \rightarrow 29$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.061$
 $S = 1.10$
 4010 reflections
 210 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0363P)^2 + 0.171P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.32$ e Å⁻³
 $\Delta\rho_{\min} = -0.38$ e Å⁻³
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.0168 (14)
 Absolute structure: Flack (1983), with 1908 Friedel pairs
 Flack parameter: 0.003 (11)

Table 1

Hydrogen-bond geometry (Å, °) for (I).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
$\text{N3A--H31A}\cdots\text{O3}^i$	0.89 (2)	1.90 (2)	2.7592 (15)	161 (2)
$\text{N3A--H32A}\cdots\text{O1W}^{ii}$	0.80 (3)	2.16 (3)	2.8377 (17)	142 (2)
$\text{N3A--H33A}\cdots\text{O3}^{iii}$	0.99 (2)	1.83 (2)	2.7877 (16)	162 (2)
$\text{N3B--H31B}\cdots\text{O4}^{iv}$	0.88 (2)	2.15 (2)	2.9801 (17)	157.5 (19)
$\text{N3B--H32B}\cdots\text{O2}^v$	0.85 (2)	2.02 (2)	2.8349 (15)	160 (2)
$\text{N3B--H33B}\cdots\text{O1}^{iii}$	0.79 (2)	2.05 (2)	2.8166 (17)	164 (2)
$\text{O1W--H1W}\cdots\text{O2A}^{vi}$	0.68 (2)	2.65 (2)	3.0887 (17)	125 (2)
$\text{O1W--H2W}\cdots\text{O2}^{iii}$	0.90 (2)	1.84 (2)	2.7273 (15)	167.5 (18)

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

Compound (II)

Crystal data

$[\text{Li}_2\text{Mo}(\text{C}_2\text{H}_5\text{NO}_2)_2\text{O}_4]$
 $M_r = 323.96$
 Monoclinic, $P2_1$
 $a = 5.1924$ (10) Å
 $b = 7.7339$ (15) Å
 $c = 12.492$ (3) Å
 $\beta = 94.28$ (3)°
 $V = 500.27$ (17) Å³
 $Z = 2$
 $D_x = 2.151$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 1222 reflections
 $\theta = 4.1\text{--}27.5^\circ$
 $\mu = 1.34$ mm⁻¹
 $T = 293$ (2) K
 Block, colourless
 $0.10 \times 0.06 \times 0.06$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (Otwinowski *et al.*, 2003)
 $T_{\min} = 0.878$, $T_{\max} = 0.924$
 2257 measured reflections

2257 independent reflections
 2233 reflections with $I > 2\sigma(I)$
 $\theta_{\max} = 27.5^\circ$
 $h = -6 \rightarrow 6$
 $k = -10 \rightarrow 9$
 $l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.016$
 $wR(F^2) = 0.040$
 $S = 1.11$
 2257 reflections
 195 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0187P)^2 + 0.143P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.47$ e Å⁻³
 $\Delta\rho_{\min} = -0.38$ e Å⁻³
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.0209 (14)
 Absolute structure: Flack (1983), with 1094 Friedel pairs
 Flack parameter: 0.01 (3)

Table 2

Hydrogen-bond geometry (Å, °) for (II).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
$\text{N3A--H31A}\cdots\text{O1}^i$	0.86 (4)	1.92 (4)	2.752 (3)	164 (4)
$\text{N3A--H32A}\cdots\text{O1A}^{ii}$	0.88 (4)	2.45 (4)	3.095 (4)	131 (4)
$\text{N3A--H32A}\cdots\text{O1}^{ii}$	0.88 (4)	2.52 (4)	3.225 (4)	138 (4)
$\text{N3A--H33A}\cdots\text{O1}^{iii}$	0.87 (6)	2.39 (6)	3.128 (5)	143 (4)
$\text{N3B--H31B}\cdots\text{O2B}^{iv}$	0.87 (5)	2.36 (5)	3.204 (4)	164 (4)
$\text{N3B--H32B}\cdots\text{O2}^v$	0.81 (4)	2.07 (4)	2.814 (4)	151 (3)
$\text{N3B--H33B}\cdots\text{O2B}^{vi}$	0.82 (3)	2.01 (4)	2.820 (3)	171 (3)

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

Table 3

An overview of stoichiometries, space groups and connectivities for compounds of glycine with lithium and inorganic lithium salts.

Where connectivities are described with two words, the first term refers to the connection of the tetrahedra *via* shared corners or edges and the second to the connection of the tetrahedral units *via* glycine molecules.

Compound	Space group	Connectivity	Reference
Lithium glycinate	$P2_12_12_1$	Chains/framework	(a)
Glycine $\text{LiCl}\cdot\text{H}_2\text{O}$	$P2_1/c$	Chains	(a)
Glycine Li_2SO_4	$Pna2_1$	Layer	(b)
Glycine LiNO_3	$P\bar{1}$	Dimers/chains	(c)
Glycine ₂ $\text{Li}_2\text{CrO}_4\cdot\text{H}_2\text{O}$	$P2_12_12_1$	Chains/layers	(d)
Glycine ₂ Li_2MoO_4	$P2_1$	Dimers/layers	(d)

References: (a) Müller *et al.* (1994); (b) Fleck & Bohatý (2004); (c) Baran *et al.* (2003); (d) this work.

For (I), the positions of the water H atoms were refined but their $U_{\text{iso}}(\text{H})$ values were constrained. All other H atoms of (I) and all those of (II) were refined freely.

For both compounds, data collection: *COLLECT* (Nonius, 2003); cell refinement: *SCALEPACK* (Otwinowski *et al.*, 2003); data reduction: *DENZO* (Otwinowski *et al.*, 2003) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Version 3.0; Bergerhoff *et al.*, 1996); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EM1005). Services for accessing these data are described at the back of the journal.

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