metal-organic compounds

[N-(6-Amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidin-2-yl)-glycylglycinato]aquapotassium, a three-dimensional coordination polymer

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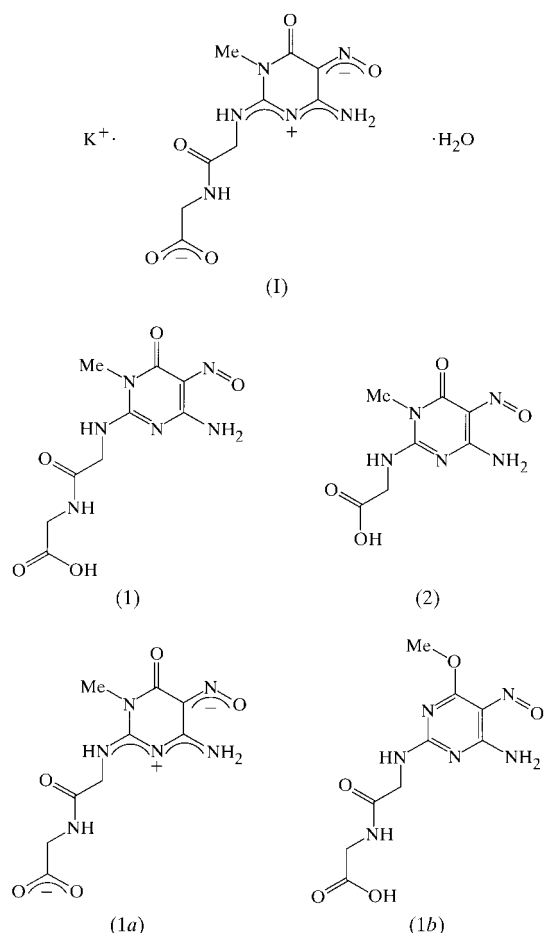
In the title compound, polymeric potassium N-(6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidin-2-yl)glycylglycinate hydrate, $(K^+ \cdot C_9H_{11}N_6O_5{}^- \cdot H_2O)_n$, the hexacoordinate K^+ cation is linked to five different anions as well as to the water molecule, with K—O distances in the range 2.617 (2)–2.850 (2) Å. Four of the O atoms in each anion coordinate to K centres, one of them acting as a bridging ligand, leading to the formation of nearly square centrosymmetric K_2O_2 rings. The structure is analysed in terms of (010) metal–ligand sheets linked by [010] chains of fused rings.

Comment

In this paper, we report the structure of a hydrated potassium salt, (I), of the pyrimidylglycylglycinate ligand L^- [where $LH =$ (1)]; we have recently reported the structure of the analogous hydrated K salt derived from the simpler pyrimidylglycine (2), in which the cations and anions form organic–inorganic hybrid sheets which are linked by hydrogen bonds into a three-dimensional framework (Low et al., 2001). The L^- anion contains further ligating sites in the form of the amidic O atom of the glycylglycinate fragment, and the resulting K salt takes the form of a three-dimensional coordination polymer.

The potassium in (I) is coordinated by six O atoms, one of which is the water O1 atom within the asymmetric unit, while the other five are components of five different anions. The K—O distances in (I) are typical of their type and the range of these distances is fairly small (Table 1). The coordination

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geometry at K is approximately octahedral, with the cis-O—K—O angles ranging from 74.09 (5) to 110.50 (5)° and having a mean of 90.08°. It is notable that although the nitroso O5 atom participates in the K coordination, there is no evidence for η^2-coordination of the nitroso group as was observed in the K salt of (2) (Low et al., 2001). In addition to O1 and O5, the three O atoms in the glycylglycinate unit all act as ligating atoms, and the amidic O21 atom acts as a bridging site between pairs of K centres. The structure which results from the octahedral coordination of K is the three-dimensional framework constructed from the K^+ cations and the anions; the water O1 atom occupies one coordination site but does not directly contribute to the formation of the framework. The framework is reinforced, although its character is not altered, by hydrogen bonds primarily involving the coordinated water molecules.

(I)

(1)

(2)

(1a)

(1b)

Adopting the sub-structure approach (Gregson et al., 2000), the framework structure can most readily be analysed in terms of two-dimensional sheets generated by translations only, with each sheet formed from two one-dimensional motifs, again generated by translation only. These sheets are linked by means of the bridging action of the amidic O atoms.

Within the asymmetric unit, the O1–K1–O23 array is approximately linear (Fig. 1 and Table 1) and atoms O21 at $(1 + x, y, z)$ and O5 at $(1 + x, y, -1 + z)$ complete an approximately square-planar KO_4 subset of the KO_6 coordi-

nation polyhedron. This KO$_4$ unit forms the basis of a two-dimensional net. Atom O21 in the anion at (x, y, z) is coordinated to K1 at ($-1 + x$, y, z), so producing by translation a chain motif running parallel to the [100] direction; adopting for coordination polymers (Starbuck *et al.*, 1999) the graph-set approach developed for hydrogen-bonded supramolecular aggregation (Etter, 1990; Bernstein *et al.*, 1995; Motherwell *et al.*, 2000), this chain is of $C(7)$ type. In the same anion at (x, y, z), O5 is coordinated to K1 at ($-1 + x$, y, $1 + z$), so producing a $C(14)$ chain parallel to [10$\bar{1}$]. The combination of the [100] and [10$\bar{1}$] chains generates a continuous sheet parallel to (010) and built from a single type of $R_6^3(32)$ ring (Fig. 2); in this descriptor, the number of donors defines the number of O atoms coordinated to K within the ring and the number of acceptors defines the number of K centres within the ring. There are two such sheets running through each unit cell, related to one another by the action of the centres of inversion; the linking of these sheets into a continuous framework is most readily analysed in terms of a chain of fused rings running parallel to [010].

Two of the O atoms coordinated to K1 at (x, y, z) are the amidic O21 atoms of the two anions at ($1 + x$, y, z) and ($2 - x$, $-y$, $-z$); this pair of O atoms also coordinates to K1 at ($3 - x$, $-y$, $-z$), so generating a centrosymmetric K$_2$O$_2$ parallelogram centred at ($\frac{3}{2}$,0,0). In such a K$_2$O$_2$ ring, the K atoms are components of different (010) nets. A stack of K$_2$O$_2$ rings centred at ($\frac{3}{2}$,n,0) (n = zero or integer) are linked by the anions acting as bidentate ligands. The reference K$_2$O$_2$ ring centred at ($\frac{3}{2}$,0,0) contains O atoms which are components of the anions at ($1 + x$, y, z) and ($2 - x$, $-y$, $-z$); the carboxylate O22 atom in the anion at ($1 + x$, y, z) is coordinated to K1 at ($3 - x$, $1 - y$, $-z$), which is a component of the K$_2$O$_2$ ring centred at ($\frac{3}{2}$,1,0), while O22 in the anion at ($2 - x$, $-y$, $-z$) is coordinated to K1 at (x, $-1 + y$, z), a component of the K$_2$O$_2$ unit centred at ($\frac{3}{2}$,$\bar{1}$,0). In this manner, adjacent K$_2$O$_2$ units along the [010] direction, centred at ($\frac{3}{2}$,n,0) (n = zero or integer), are linked by pairs of anions forming 14-membered rings centred at ($\frac{3}{2}$,$n + \frac{1}{2}$,0) (n = zero or integer), producing a chain of fused rings (Fig. 3). The combination of the (010) sheets and the [010] chains then generates the overall framework, built solely from K—O interactions.
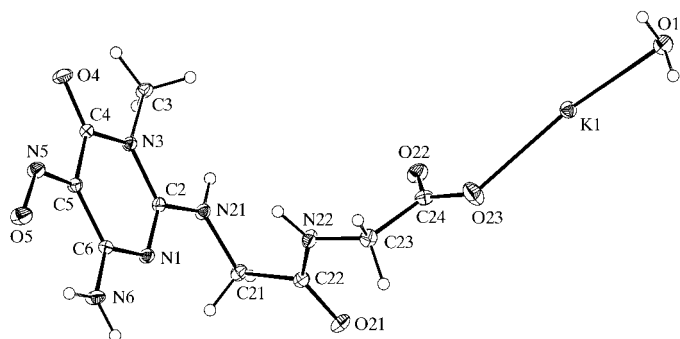
The K$_2$O$_2$ ring motif is also a characteristic feature of the hydrated K salt derived from the simpler pyrimidylglycine derivative (2) (Low *et al.*, 2001). However, in this latter compound, the structure is based upon continuous ribbons of K$_2$O$_2$ rings, fused in a spiro fashion at the K sites; the metal–oxygen ribbons are linked into sheets by the anions, so that the sheets are thus organic–inorganic hybrids consisting of alternating strips of inorganic metal–oxygen ribbons and organic heterocyclic linkers.

Although the water molecules play no direct role in the construction of the three-dimensional coordination polymer framework, the hydrogen bonds formed by the water molecules serve to reinforce this framework (Table 2). Thus, water O1 at (x, y, z) acts as a hydrogen-bond donor, *via* H1A, to carboxylate O22 at ($1 + x$, y, z), so reinforcing the (010) sheet (*cf.* Fig. 2), and the same water acts as donor, *via* H1B, to carboxylate O23 at ($3 - x$, $-y$, $-z$), so reinforcing the [010] chain (*cf.* Fig. 3).

The dimensions of the pyrimidyl ring (Table 1) show the marked polarization noted in previous studies of amino acid derivatives containing this heterocycle (Low *et al.*, 2000, 2001). In particular, the N1—C2 bond is similar in length to the C2—N21 and C6—N6 bonds, and it is not possible to assign the one as a double bond and the remainder as single bonds; secondly, the dimensions of the C-nitroso fragment provide evidence of significant electronic delocalization since in simple neutral compounds where there is no possibility of such delocalization these distances normally differ by at least 0.20 Å (Talberg, 1977; Schlemper *et al.*, 1986) and the N—O distance rarely exceeds 1.25 Å (Davis *et al.*, 1965; Bauer & Andreassen, 1972;
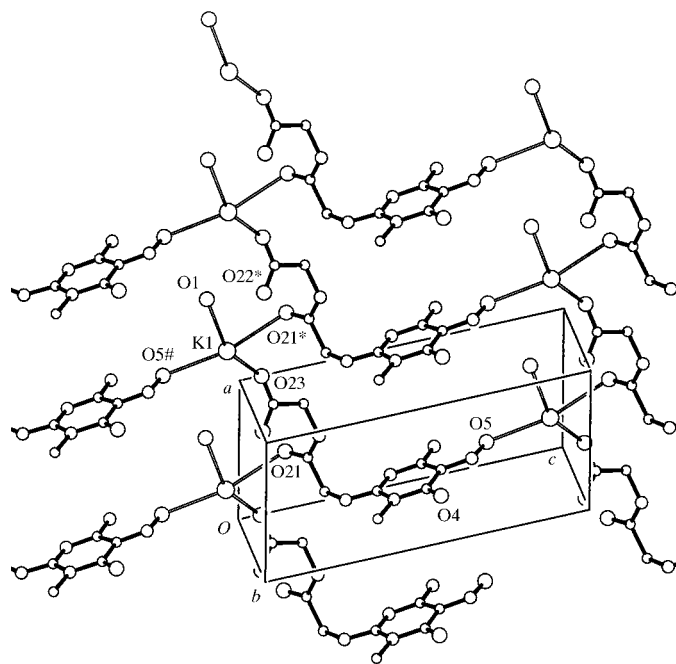

Figure 2
Part of the crystal structure of (I) showing the formation of a (010) sheet. For the sake of clarity, H atoms have been omitted. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions ($1 + x$, y, z) and ($1 + x$, y, $-1 + z$), respectively.

Figure 1
The asymmetric unit of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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Talberg, 1977; Schlemper *et al.*, 1986). Consequently, the charge-separated form (1*a*) is a more realistic representation of the electronic structure of the anion in (I). The conformation of the glycyl side chain shows some unexpected features: in addition to the usual *trans* planar –C(O)—N(H)– fragment, the torsion angles in the chain from C2 to C24 follow the sequence *sc, sp, ap, sc*. The synthesis of (1) involves a methylation step to introduce the methyl group at N3; in addition to (1), the X-ray analysis revealed the presence of 4.6 (4)% of the isomeric form (1*b*), in which methylation had occurred at O4 rather than at N3. This small quantity cannot readily be detected spectroscopically, nor readily removed. However, since O4 is not involved in the coordination to K, the presence of a small quantity of (1*b*) does not affect the resulting structure in any way.
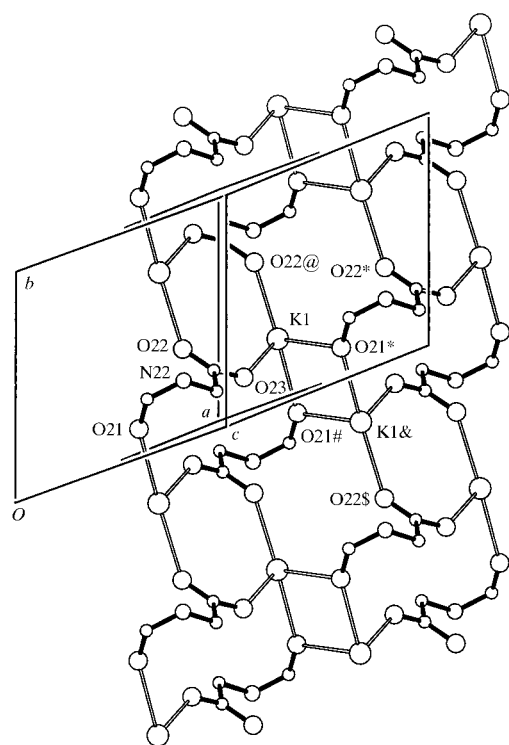

Figure 3
Part of the crystal structure of (I) showing the formation of a [010] chain of fused rings. For the sake of clarity, the pyrimidyl rings have been omitted, with only the O21 to O22 and O23 fragment shown. H atoms have also been omitted. Atoms marked with an asterisk (*), hash (#), dollar sign ($), ampersand (&) or at symbol (@) are at the symmetry positions $(1 + x, y, z)$, $(2 - x, -y, -z)$, $(1 + x, -1 + y, z)$, $(3 - x, -y, -z)$ and $(2 - x, 1 - y, -z)$, respectively.

Experimental

A solution of glycylglycine (16 mmol) in aqueous KOH (16 ml, 1 mol dm⁻³) was added to a suspension of 6-amino-3,4-dihydro-3-methyl-2-methoxy-5-nitroso-4-oxopyrimidine (16 mmol) in acetonitrile (50 ml). The mixture was heated under reflux for 1.5 h, producing a violet solid, which was filtered off and washed with ethanol and diethyl ether. Crystals suitable for single-crystal X-ray diffraction study were grown from water. Analysis, found: C 31.4, H 3.9, N 24.7%; C₉H₁₃KN₆O₆ requires: C 31.8, H 3.8, N 24.7%.

Table 1
Selected geometric parameters (Å, °).

K1—O23	2.617 (2)	C4—O4	1.224 (2)
K1—O22ⁱ	2.632 (2)	C5—N5	1.351 (2)
K1—O21ⁱⁱ	2.747 (2)	N5—O5	1.280 (2)
K1—O5ⁱⁱⁱ	2.769 (2)	C6—N6	1.317 (2)
K1—O1	2.772 (2)	N21—C21	1.458 (2)
K1—O21ⁱᵛ	2.850 (2)	C21—C22	1.527 (3)
N1—C2	1.327 (2)	C22—O21	1.232 (2)
C2—N3	1.381 (2)	C22—N22	1.329 (2)
N3—C4	1.403 (2)	N22—C23	1.453 (2)
C4—C5	1.444 (3)	C23—C24	1.531 (3)
C5—C6	1.439 (3)	C24—O22	1.250 (2)
C6—N1	1.344 (2)	C24—O23	1.247 (2)
C2—N21	1.333 (2)	O4—C41	1.41 (4)
N3—C3	1.471 (2)		

O23—K1—O5ⁱⁱⁱ	110.50 (5)	O5ⁱⁱⁱ—K1—O1	90.22 (4)
O23—K1—O21ⁱᵛ	74.09 (5)	O21ⁱᵛ—K1—O1	82.27 (4)
O23—K1—O21ⁱⁱ	90.62 (5)	O21ⁱⁱ—K1—O1	77.49 (4)
O23—K1—O22ⁱ	100.40 (5)	O22ⁱ—K1—O1	96.14 (5)
O21ⁱⁱ—K1—O5ⁱⁱⁱ	76.04 (4)	O23—K1—O1	153.06 (5)
O22ⁱ—K1—O5ⁱⁱⁱ	90.89 (4)	O5ⁱⁱⁱ—K1—O21ⁱᵛ	167.50 (4)
O21ⁱᵛ—K1—O21ⁱⁱ	92.51 (4)	O22ⁱ—K1—O21ⁱⁱ	165.30 (4)
O21ⁱᵛ—K1—O22ⁱ	99.81 (4)	K1ᵛ—O21—K1ⁱⁱ	87.49 (4)

C2—N21—C21—C22	−86.2 (2)	C22—N22—C23—C24	82.8 (2)
N21—C21—C22—N22	15.1 (2)	N22—C23—C24—O22	−5.3 (3)
C21—C22—N22—C23	−175.9 (2)	N22—C23—C24—O23	175.4 (2)

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

Compound (I) crystallized in the triclinic system; space group $P\bar{1}$ was assumed and confirmed by the analysis. It was apparent from an early stage that, in addition to C3 bonded to N3, there was a small population of a C atom, C41, bonded to O4; the site-occupation factors of C3 and C41 were subsequently constrained to sum to unity, and C41 was refined isotropically. H atoms were located from difference maps and those in the organic fragment were treated as

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$A\cdots$O22[i]	0.82	1.93	2.742 (2)	170
O1—H1$B\cdots$O23[ii]	0.82	1.89	2.687 (2)	164
N6—H6$A\cdots$O4[iii]	0.88	1.99	2.820 (2)	156
N6—H6$B\cdots$O5	0.88	1.96	2.614 (2)	130
N21—H21$\cdots$O1[iv]	0.88	1.92	2.715 (2)	150

Symmetry codes: (i) $1 + x, y, z$; (ii) $3 - x, -y, -z$; (iii) $x, y - 1, z$; (iv) $2 - x, 1 - y, -z$.

riding atoms with C—H distances of 0.98 (CH$_3$) or 0.99 Å (CH$_2$), and an N—H distance of 0.88 Å. H atoms in the water molecule were initially handled using a *DFIX* command with an O—H distance of 0.82 Å, and latterly using *AFIX*.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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