

Ammonium *N*-(6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidin-2-yl)glycinate monohydrate forms hydrogen-bonded bilayers

Paloma Arranz Mascarós,^a Rafael Cuesta Martos,^a
Christopher Glidewell^{b*} and John N. Low^{c†}

^aDepartamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, ^bSchool of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland, and ^cDepartment of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland
Correspondence e-mail: cg@st-andrews.ac.uk

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In the title compound, $\text{NH}_4^+ \cdot \text{C}_7\text{H}_8\text{N}_5\text{O}_4^- \cdot \text{H}_2\text{O}$, the independent components are linked into bilayers by an extensive series of two-centre $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds [$\text{H} \cdots \text{O} = 1.85\text{--}1.96 \text{ \AA}$, $\text{N} \cdots \text{O} = 2.776(2)\text{--}2.840(2) \text{ \AA}$ and $\text{N}-\text{H} \cdots \text{O} = 149\text{--}172^\circ$], and by asymmetric three-centre $\text{N}-\text{H} \cdots (\text{O})_2$, $\text{O}-\text{H} \cdots (\text{N}, \text{O})$ and $\text{O}-\text{H} \cdots (\text{O})_2$ hydrogen bonds.

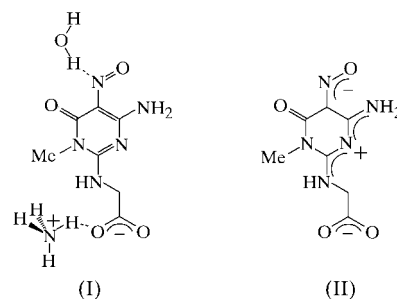
Comment

The structure of *N*-(6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidin-2-yl)glycine was determined, as the dihydrate, several years ago (Low *et al.*, 1997), and more recently we have reported the structures of a number of hydrated complexes formed by the *N*-(6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidin-2-yl)glycinate anion with monovalent cations, including Li^+ , Na^+ and K^+ (Low *et al.*, 2000). In addition, the structures of the simple salts of the $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ cations have recently been reported (Arranz Mascarós *et al.*, 1999, 2000). Continuing with this study, we now report the molecular and supramolecular structure of the hydrated ammonium salt $\text{NH}_4^+ \cdot \text{C}_7\text{H}_8\text{N}_5\text{O}_4^- \cdot \text{H}_2\text{O}$, (I).

The bond distances within the substituted pyrimidine ring and its immediate substituents (Table 1) show the usual evidence for a highly polarized molecular–electronic structure. In particular, the four C–N bonds in the sequence from N2 to N6 are all rather similar in length, the bond distances C4–C5 and C5–C6 being almost identical, and the C5–N5 and N5–O5 distances differing by only *ca* 0.055 Å; these observations all indicate the importance of the polarized form (II).

† Postal address: Department of Electrical Engineering and Physics, University of Dundee, Dundee DD1 4HN, Scotland.

There are two $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds (Table 2) within the anion, forming *S*(6) motifs (Bernstein *et al.*, 1995), and these may have some influence in controlling the overall molecular conformation of the anion, where the non-H atoms are almost coplanar (Table 1 and Fig. 1). Two further hydrogen bonds link the three independent components within the selected asymmetric unit, where N11 acts as a hydrogen-bond donor, *via* H11*D*, to O22, and O1 acts as donor, *via* H1A, primarily to nitroso atom N5 (Fig. 1). However, this H atom makes a second short contact, to O4, which may be adventitious; however, since the sum of the angles at H1A is 360° , these two interactions may alternatively be considered as forming an asymmetric three-centre $\text{O}-\text{H} \cdots (\text{N}, \text{O})$ system (Table 1).



There are two other asymmetric three-centre hydrogen bonds in the crystal structure of (I) formed by H1B in an $\text{O}-\text{H} \cdots (\text{O})_2$ system and by H6B in an $\text{N}-\text{H} \cdots (\text{O})_2$ system. In all, there are five hydrogen bonds, three of the two-centre type and two of the three-centre type, linking together the three-component aggregates (Fig. 1) into a bilayer structure, whose formation is readily analysed using the substructure approach (Gresgon *et al.*, 2000).

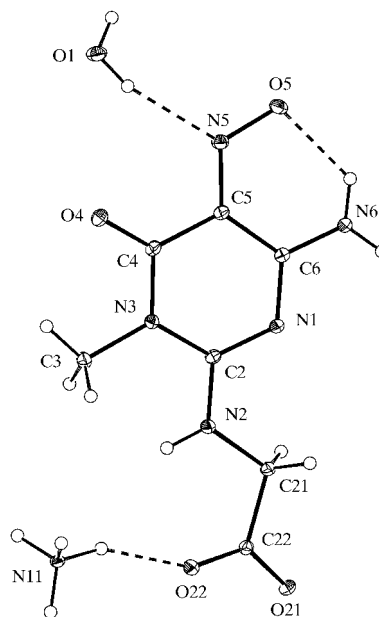


Figure 1

The independent components of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

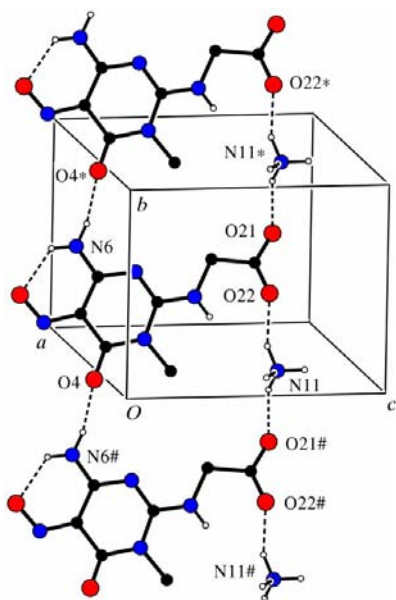


Figure 2

Part of the crystal structure of (I), showing the formation of a molecular ladder by the ionic components only. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(x, 1 + y, z)$ and $(x, -1 + y, z)$, respectively.

The anions alone form hydrogen-bonded chains running parallel to the $[010]$ direction; atom N6 in the anion at (x, y, z) acts as a donor, *via* H6A, to O4 in the anion at $(x, 1 + y, z)$, so forming a $C(6)$ chain by translation (Fig. 2). This chain is reinforced by the ammonium ions; atom N11 at (x, y, z) acts as a hydrogen-bond donor, *via* H11A, to carboxylate atom O21 in the anion at $(x, -1 + y, z)$; in combination with the N11—H11D...O22 hydrogen bond, a $C_2^2(6)$ chain is generated by translation. The $C(6)$ and $C_2^2(6)$ chains thus act as the uprights of a $[010]$ molecular ladder in which the body of the anion provides the rungs, while between the rungs there are $R_3^2(20)$ rings (Fig. 2).

Adjacent ladders, related by translation along $[10\bar{1}]$, are linked into sheets by the water molecules and by the ammo-

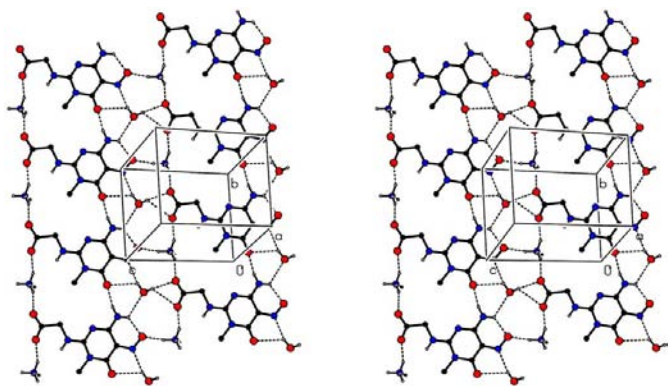


Figure 3

Stereoview of part of the crystal structure of (I), showing the formation of a (101) sheet. For the sake of clarity, H atoms bonded to C atoms have been omitted.

niun ions. Water atom O1 at (x, y, z) acts as a hydrogen-bond donor, *via* H1B, to both O21 and O22 in the anion at $(1 + x, -1 + y, -1 + z)$, while ammonium atom N11 at (x, y, z) acts as a donor, *via* H11C, to nitroso atom O5 in the anion at $(-1 + x, y, 1 + z)$. The combination of the resulting $[1\bar{1}\bar{1}]$ and $[10\bar{1}]$ motifs with the $[010]$ ladders generates a (101) sheet (Fig. 3). The (101) sheet is generated solely by translation and two such sheets, related to one another by inversion, pass through each unit cell; pairs of inversion-related sheets linked by one further hydrogen bond form bilayers. Ammonium atom N11 at (x, y, z) acts as a donor, *via* H11B, to water atom O1 at $(-x, -y, -z)$, so generating a centrosymmetric $R_6^6(26)$ ring (Fig. 4) which links the sheets in pairs.

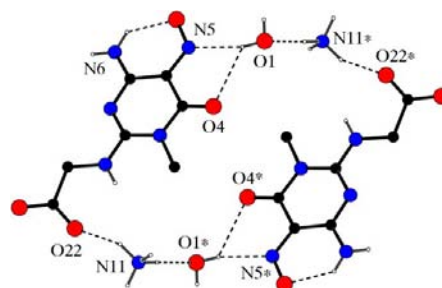


Figure 4

Part of the crystal structure of (I), showing the formation of the $R_6^6(26)$ ring motif which links pairs of (101) sheets. For the sake of clarity, the unit-cell box and H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(-x, -y, -z)$.

The only direction-specific interaction between adjacent bilayers is provided by an antiparallel carbonyl motif (Allen *et al.*, 1998). The carboxyl bonds C22—O22 in the anions at (x, y, z) and $(-x, 1 - y, 1 - z)$, which lie in different bilayers, form an almost exactly rectangular motif, with an $O22 \cdots C22^i$ distance of 2.898 (2) Å and a $C22-O22 \cdots C22^i$ angle of 89.9 (2)° [symmetry code: (i) $-x, 1 - y, 1 - z$].

Experimental

Compound (I) was an adventitious by-product from an attempt to prepare the corresponding rubidium salt. Rubidium chloride (0.5 mmol in 20 ml water) was added to a mixture of equimolar quantities (0.5 mmol) of *N*-(6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidin-2-yl)glycine and ammonium hydroxide in water (10 ml). After 3 d at ambient temperature, pink crystals of (I) had formed. These were collected by filtration and washed with ethanol. Analysis found: C 32.1, H 5.5, N 32.1%; $C_7H_{14}N_6O_4$ requires: C 32.1, H 5.4, N 32.1%.

Crystal data

$NH_4^+ \cdot C_7H_8N_5O_4^- \cdot H_2O$
 $M_r = 262.24$
 Triclinic, $P\bar{1}$
 $a = 7.2451$ (1) Å
 $b = 7.3772$ (2) Å
 $c = 11.1339$ (3) Å
 $\alpha = 88.416$ (1)°
 $\beta = 78.695$ (1)°
 $\gamma = 70.527$ (1)°
 $V = 549.71$ (2) Å³

$Z = 2$
 $D_x = 1.584$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2508 reflections
 $\theta = 2.9-27.4$ °
 $\mu = 0.13$ mm⁻¹
 $T = 120$ (2) K
 Block, pink
 0.20 × 0.20 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
 φ scans, and ω scans with κ offsets
 Absorption correction: multi-scan
 (DENZO-SMN; Otwinowski & Minor, 1997)
 $T_{\min} = 0.967$, $T_{\max} = 0.987$
 9766 measured reflections

2508 independent reflections
 2328 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.043$
 $\theta_{\text{max}} = 27.4^\circ$
 $h = -9 \rightarrow 8$
 $k = -9 \rightarrow 9$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.118$
 $S = 1.00$
 2508 reflections
 164 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0683P)^2 + 0.3320P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.39 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.42 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

N1—C2	1.329 (2)	C2—N2	1.329 (2)
C2—N3	1.385 (2)	C4—O4	1.224 (2)
N3—C4	1.398 (2)	C5—N5	1.342 (2)
C4—C5	1.456 (2)	N5—O5	1.287 (2)
C5—C6	1.447 (2)	C6—N6	1.315 (2)
C6—N1	1.344 (2)		
N1—C2—N2—C21	−4.47 (19)	N2—C21—C22—O22	−14.22 (16)
C2—N2—C21—C22	176.50 (11)	O4—C4—C5—N5	−2.0 (2)

Table 2

Hydrogen-bonding 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>
N2—H2...O22	0.88	2.28	2.655 (2)	105
N6—H6B...O5	0.88	1.98	2.627 (2)	129
O1—H1A...N5	0.88	2.13	2.990 (2)	165
O1—H1A...O4	0.88	2.53	3.113 (2)	125
N11—H11D...O22	0.98	1.88	2.803 (2)	155
N6—H6A...O4 ⁱ	0.88	1.91	2.776 (2)	167
N6—H6B...O1 ⁱ	0.88	2.47	3.000 (2)	119
O1—H1B...O21 ⁱⁱ	0.80	2.12	2.917 (2)	175
O1—H1B...O22 ⁱⁱ	0.80	2.56	3.043 (2)	120
N11—H11A...O21 ⁱⁱⁱ	0.98	1.96	2.840 (2)	149
N11—H11B...O1 ^{iv}	0.96	1.88	2.840 (2)	172
N11—H11C...O5 ^v	0.96	1.85	2.782 (2)	162

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

Crystals of (I) are triclinic; space group $P\bar{1}$ was selected and confirmed by the successful structure analysis. H atoms bonded to C atoms were treated as riding atoms, with C—H distances of 0.98

(CH₃) or 0.99 Å (CH₂). All H atoms bonded to N or O atoms were located from difference maps and allowed to ride on their parent atoms at the distances deduced from the maps; the resulting distances were N—H = 0.88 (in the anion) and 0.96–0.98 Å (in the ammonium ion), and O—H = 0.80–0.88 Å.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1636). Services for accessing these data are described at the back of the journal.

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