

[6-Amino-3-methyl-5-nitroso-pyrimidine-2,4(1*H*,3*H*)-dionato]-sodium dihydrate at 150 K: coordination-polymer ladders linked by hydrogen bonds

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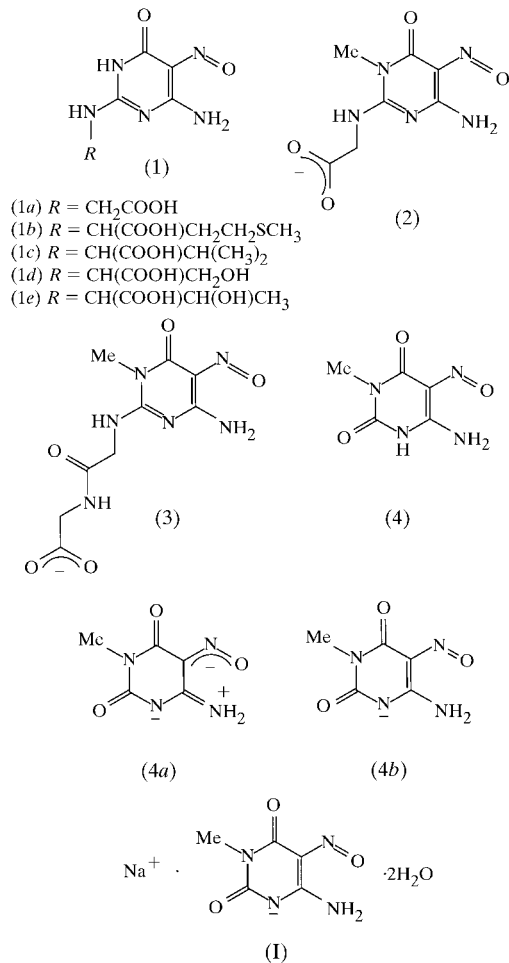
In the title compound, $[\text{Na}(\text{C}_5\text{H}_5\text{N}_4\text{O}_3)] \cdot 2\text{H}_2\text{O}$, each Na cation is linked to three $\text{C}_5\text{H}_4\text{N}_4\text{O}_3^-$ anions and two water molecules, forming approximately octahedral NaNO_5 units; the cations and the anions form molecular ladders, and each ladder is linked to four neighbouring ladders by $\text{O}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{N}$ hydrogen bonds.

Comment

In neutral nitrosopyrimidines of type (1) and in metal salts of the related glycinate anions, (2) and (3), the close interplay of molecular, molecular–electronic and supramolecular structures leads to an extensive polarization of the electronic structure of the organic fragment, consistently manifested in highly unusual interatomic distances (Low *et al.*, 2000; Low, Arranz Mascarós, Cobo Domingo, Fontecha, Godino, López Garzon & Glidewell, 2001; Low, Arranz Mascarós, Cobo Domingo, Fontecha, Godino, López Garzon, Cannon *et al.*, 2001; Low, Cannon *et al.*, 2001; Low, Moreno *et al.*, 2001). Continuing this study, we now report the molecular and supramolecular structure of the sodium salt, (I), derived from the simpler derivative (4), from which the amino-acid unit is absent; compound (I) crystallizes as the dihydrate $[\text{Na}(\text{C}_5\text{H}_4\text{N}_4\text{O}_3)] \cdot 2\text{H}_2\text{O}$ (Fig. 1). A very brief report on the room-temperature structure of (I) (Schwabenländer *et al.*, 1998) contains neither a description nor a discussion of any of the key features of the overall structure, *e.g.* the pyrimidine geometry, the metal–ligand coordination geometry, the coordination-polymer formation or the hydrogen bonding. The present study, undertaken at 150 (2) K, reveals a linear coordination polymer in the form of a molecular ladder, and the

linking of the ladders into a continuous framework by extensive hydrogen bonding.

The structure of the anion (Table 1), where the usual conformation having the nitroso group *trans* to the amidic O4 atom is reinforced by the formation of an intramolecular $\text{N}-\text{H} \cdots \text{O}$ hydrogen bond (Table 2), shows a number of the



metrical features characteristic of 5-nitrosopyrimidine (Low *et al.*, 2000; Low, Arranz Mascarós, Cobo Domingo, Fontecha, Godino, López Garzon & Glidewell, 2001; Low, Arranz Mascarós, Cobo Domingo, Fontecha, Godino, López Garzon, Cannon *et al.*, 2001; Low, Cannon *et al.*, 2001; Low, Moreno *et al.*, 2001). In particular, the C4–C5 and C5–C6 distances are very similar: the difference between the C5–N5 and N5–O5 distances is less than 0.050 Å, and the C6–N6 bond is very short for a single C–N bond between three connected atoms (Allen *et al.*, 1987). While the very similar C2–O2 and C4–O4 distances are both typical of those in neutral amides (Allen *et al.*, 1987), the N1–C6 bond is somewhat shorter than the N1–C2 bond. These observations taken together indicate polarization of the electronic structure, so that (4a) is a significantly better representation than (4b).

The cations and anions together form a one-dimensional coordination polymer in the form of a molecular ladder, or chain of fused rings. The Na atom at (x, y, z) is bonded to both O2 at (x, y, z) and O4 at $(x, y, -1 + z)$, and propagation of

these interactions by translation generates a chain running parallel to the [001] direction (Fig. 2). At the same time, Na at (x, y, z) is also bonded to O2 at $(1 - x, 2 - y, -z)$, and thus an antiparallel pair of chains is linked into a ladder. There are centrosymmetric rings centred at $(\frac{1}{2}, 1, n)$ ($n = \text{zero or integer}$)

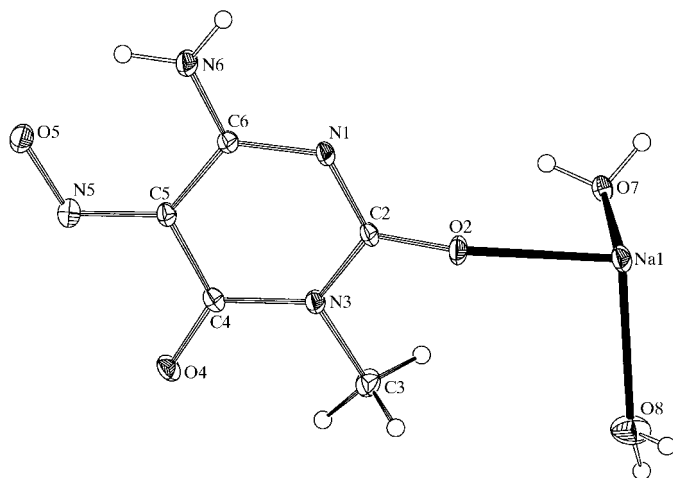


Figure 1
The asymmetric unit of compound (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

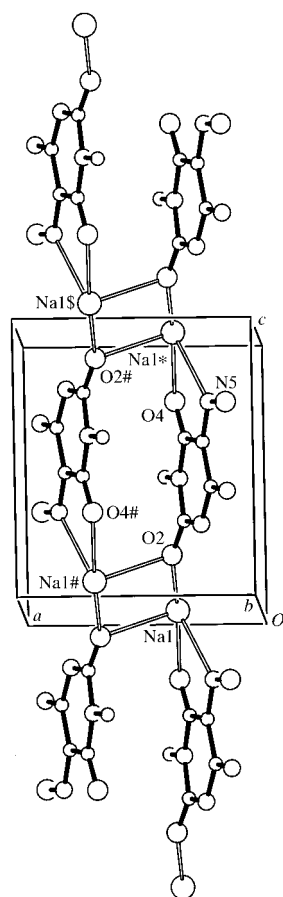


Figure 2
Part of the crystal structure of (I) showing the formation of the [001] chain containing the cations and anions only. For the sake of clarity, H atoms have been omitted. Atoms marked with an asterisk (*), hash (#) or dollar sign (\$) are at the symmetry positions $(x, y, 1 + z)$, $(1 - x, 2 - y, -z)$ and $(1 - x, 2 - y, 1 - z)$, respectively.

alternating with 12-membered rings centred at $(\frac{1}{2}, 1, n + \frac{1}{2})$ ($n = \text{zero or integer}$) (Fig. 2). There is one of these chains of fused rings per unit cell and the chains lie along the lines $(m + \frac{1}{2}, n, z)$ ($m, n = \text{zero or integer}$).

There are also two water molecules bound to each Na and the resulting NaO_5 unit has approximate square-pyramidal geometry (Table 1, Fig. 3). The mean value of the Na–O distances, 2.400 (2) Å, is biased by the outlier value, 2.6011 (16) Å, for the bond which links adjacent chains; this is probably due to steric repulsions between the organic ligands in the coupled chains. In addition, there is a (possibly adventitious) Na···N contact which completes an approximately octahedral geometry at Na (Fig. 3). The anion at (x, y, z) may thus be considered as monodentate to the Na centres at (x, y, z) and $(1 - x, 2 - y, -z)$, via O2, and bidentate to the Na at $(x, y, 1 + z)$ via O4 and N5, which make a bite angle at Na of 65.15 (5)°.

Both the metal coordination geometry and the metal–ligand coordination polymer in (I) may be contrasted with the corresponding Na salt of the anion (2) (Low, Moreno *et al.*, 2001), where the two independent Na centres both have trigonal-bipyramidal coordination and where centrosymmetric rings are linked into chains by isolated water molecules acting as single bridges between adjacent rings. In view of the polarized structure (4a), it is notable that the nitrosyl O5 atom is not coordinated to the metal in (I). By contrast, in the Na salt of (2), O5 is bonded to the metal, while in the K salts of (2) and (3), the nitrosyl group coordinates to the metal in η^2 and η^1 modes, respectively (Low, Arranz Mascarós, Cobo Domingo, Fontecha, Godino, López Garzon & Glidewell, 2001; Low, Moreno *et al.*, 2001). On the other hand, in (I), O5 is the acceptor in the shortest, and presumably strongest, of the O–H···O hydrogen bonds.

Both of the water molecules in (I) act as double donors of hydrogen bonds (Table 2). Although the formation of the chain motif (Fig. 2) is not dependent upon hydrogen bonding, nonetheless the hydrogen bonds serve to link each [001] chain to four neighbouring chains, and thereby to link all the chains into a three-dimensional continuum. Water O7 at (x, y, z) is a component of the chain along $(\frac{1}{2}, 1, z)$, and it acts as hydrogen-bond donor via H71 to N1 at $(-x, 2 - y, -z)$ and via H72 to O5 at $(-x, 2 - y, 1 - z)$, both of which are components of the chain along $(-\frac{1}{2}, 1, z)$. Atom O8 at (x, y, z) is also a component of the chain along $(\frac{1}{2}, 1, z)$ and it acts as hydrogen-bond donor

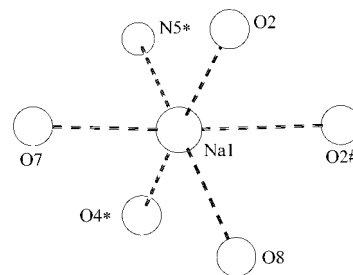


Figure 3
Part of the crystal structure of (I) showing the coordination around sodium. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(x, y, -1 + z)$ and $(1 - x, 2 - y, -z)$, respectively.

via H81 to O4 at $(1-x, 1-y, 1-z)$, which is a component of the chain along $(\frac{1}{2}, 0, z)$. Propagation by the space group of these hydrogen bonds links each [001] chain to its four immediate neighbours in the [100] and [010] directions, and hence all the [001] chains are linked into a single framework. The final, rather weak, hydrogen bond, from O8 at (x, y, z) to N1 at $(1-x, 2-y, -z)$, falls within the reference chain along $(\frac{1}{2}, 1, z)$. That N1 acts as a double acceptor of O—H...N hydrogen bonds (Table 2), with quasi-tetrahedral coordination (Fig. 4), is consistent with and supportive of the representation (4a).

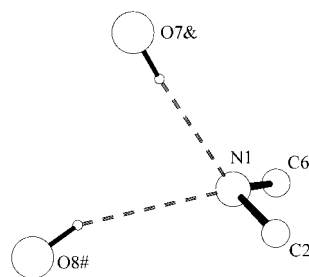


Figure 4
Part of the crystal structure of (I) showing the coordination at N1. Atoms marked with a hash (#) or ampersand (&) are at the symmetry positions $(1-x, 2-y, -z)$ and $(-x, 2-y, -z)$, respectively.

The cell dimensions and refined coordinates indicate that the structure reported here at 150 K is the same phase as that studied earlier at 293 K (Schwabländer *et al.*, 1998). The data set employed here is somewhat larger than that employed earlier, while in the earlier study all H parameters were refined. Consequently, the data/parameter ratio here, 14.6, is ca 50% higher than the value of 9.4 available previously.

Experimental

An aqueous solution of $\text{Na}_2[\text{CO}_3]$ (1.0 mmol in 10 ml) was added to a suspension of (1c) (0.135 g, 0.5 mmol) in methanol (40 ml). The mixture was heated under reflux for 1 h and then cooled to ambient temperature. After several days, pink crystals of (I) formed.

Crystal data

$[\text{Na}(\text{C}_5\text{H}_5\text{N}_4\text{O}_3)] \cdot 2\text{H}_2\text{O}$	$Z = 2$
$M_r = 228.15$	$D_x = 1.680 \text{ Mg m}^{-3}$
Triclinic, $P1$	Mo $K\alpha$ radiation
$a = 7.0529(2) \text{ \AA}$	Cell parameters from 1991 reflections
$b = 8.1852(2) \text{ \AA}$	$\theta = 3.9\text{--}27.5^\circ$
$c = 8.7450(6) \text{ \AA}$	$\mu = 0.19 \text{ mm}^{-1}$
$\alpha = 63.365(2)^\circ$	$T = 150(2) \text{ K}$
$\beta = 89.575(2)^\circ$	Plate, pink
$\gamma = 88.637(3)^\circ$	$0.20 \times 0.10 \times 0.02 \text{ mm}$
$V = 451.14(4) \text{ \AA}^3$	

Data collection

KappaCCD diffractometer	1991 independent reflections
φ and ω scans with κ offsets	1458 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (DENZO-SMN; Otwinowski & Minor, 1997)	$R_{\text{int}} = 0.067$
$T_{\text{min}} = 0.964$, $T_{\text{max}} = 0.996$	$\theta_{\text{max}} = 27.5^\circ$
4901 measured reflections	$h = -9 \rightarrow 8$
	$k = -10 \rightarrow 10$
	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.0779P)^2]$
$wR(F^2) = 0.136$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.98$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1991 reflections	$\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
136 parameters	$\Delta\rho_{\text{min}} = -0.47 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Na1—O2	2.3052 (15)	Na1—O4 ⁱ	2.4198 (15)
Na1—O7	2.3325 (15)	Na1—N5 ⁱ	2.5872 (18)
Na1—O8	2.3431 (16)	Na1—O2 ⁱⁱ	2.6011 (16)
N1—C2	1.352 (2)	C2—O2	1.234 (2)
C2—N3	1.408 (2)	N3—C3	1.472 (2)
N3—C4	1.378 (2)	C4—O4	1.240 (2)
C4—C5	1.454 (3)	C5—N5	1.336 (3)
C5—C6	1.452 (3)	N5—O5	1.287 (2)
C6—N1	1.339 (2)	C6—N6	1.318 (2)
O2—Na1—O7	96.20 (6)	N5 ⁱ —Na1—O2	105.25 (6)
O7—Na1—O4 ⁱ	91.45 (5)	N5 ⁱ —Na1—O7	89.58 (5)
O4 ⁱ —Na1—O2 ⁱⁱ	88.93 (5)	N5 ⁱ —Na1—O4 ⁱ	65.15 (5)
O2 ⁱⁱ —Na1—O2	82.90 (5)	N5 ⁱ —Na1—O2 ⁱⁱ	87.58 (5)
O8—Na1—O2	98.51 (6)	O2—Na1—O4 ⁱ	167.76 (6)
O8—Na1—O7	104.82 (6)	O7—Na1—O2 ⁱⁱ	176.67 (5)
O8—Na1—O4 ⁱ	88.71 (6)	O8—Na1—N5 ⁱ	150.70 (7)
O8—Na1—O2 ⁱⁱ	78.50 (5)	Na1—O2—Na1 ⁱⁱ	97.10 (5)
C4—C5—N5—O5	−177.88 (17)	N1—C2—O2—Na1	−106.8 (3)
C6—C5—N5—O5	2.9 (3)	N1—C2—O2—Na1 ⁱⁱ	76.4 (2)
C5—C4—O4—Na1 ⁱⁱⁱ	−10.0 (3)		

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

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{—H}\cdots A$	$D\text{—H}$	$\text{H}\cdots A$	$D\cdots A$	$D\text{—H}\cdots A$
N6—H6B...O5	0.88	1.96	2.621 (3)	130
O7—H71...N1 ⁱ	0.84	2.05	2.884 (2)	176
O7—H72...O5 ⁱⁱ	0.84	1.93	2.725 (2)	157
O8—H81...O4 ⁱⁱⁱ	0.84	2.16	2.972 (2)	164
O8—H82...N1 ^{iv}	0.84	2.34	3.135 (2)	158

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

Compound (I) crystallized in the triclinic system; space group $P\bar{1}$ was assumed and confirmed by the analysis. H atoms were treated as riding atoms with $\text{C—H} = 0.98$, $\text{N—H} = 0.88$ and $\text{O—H} = 0.84 \text{ \AA}$. The methyl group was modelled using six H-atom sites, with an occupancy of 0.50, offset from one another by a rotation of 60° .

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, 2001); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, using an Enraf-

Nonius KappaCCD diffractometer. The authors thank the staff for all their help and advice.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1058). Services for accessing these data are described at the back of the journal.

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