

Cytosinium nitrate

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$

R factor = 0.040

w R factor = 0.112

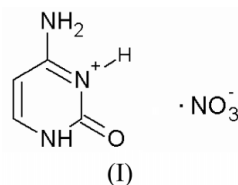
Data-to-parameter ratio = 11.1

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $\text{C}_4\text{H}_6\text{N}_3\text{O}^+\cdot\text{NO}_3^-$, a two-dimensional network of $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds between the anions and cations generates cytosinium–nitrate parallel layers, linked by enclosed van der Waals interactions. Cytosinium stacking is present, but cytosinium–cytosinium hydrogen bonds are prevented by the presence of planar nitrate anions.

Comment

Analogs of natural purine and pyrimidine nucleosides have proved to be quite effective as antibacterial, antiviral and antitumor agents, due to their roles as enzyme inhibitors and antagonists. Cytosine (6-aminopyrimidin-2-one) is one of the pyrimidines found in deoxyribonucleic acids. It has been the subject of several investigations aiming to study the electrostatic properties of its monohydrate form (Weber & Craven, 1990), the relative stabilities of tautomeric forms (Kobayashi, 1998) and hydration effects and hydrogen bonding (Sivanesan *et al.*, 2000). In several crystal structures of purines and pyrimidines with inorganic anions, the structural cohesion is assured by strong hydrogen bonds, as was observed in guaninium sulfate monohydrate (Cherouana *et al.*, 2003) and adeninium perchlorate (Bendjeddou, Cherouana, Berrah & Benali-Cherif, 2003). The potential importance of hydrogen bonding in the structure and function of biomolecules has been well established (Jeffrey & Saenger, 1991); in particular, $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds are most predominant in determining the formation of secondary structure elements in proteins, base-pairing in nucleic acids and their biomolecular interactions. This structure analysis of cytosinium nitrate (I) was undertaken as part of a more general investigation into the nature of hydrogen bonding between organic bases or amino acids and inorganic acids in their crystalline forms (Benali-Cherif, Abouimrane *et al.*, 2002; Benali-Cherif, Benguedouar *et al.*, 2002; Benali-Cherif, Bendheif *et al.*, 2002; Benali-Cherif, Cherouana *et al.*, 2002, Cherouana *et al.*, 2002; Bendjeddou, Cherouana, Dahaoui *et al.*, 2003).



The structure of (I) consists of nitrate ions and protonated cytosine rings (Fig. 1) forming a two-dimensional network of hydrogen bonds (Fig. 2). As observed in $[\text{cytosine}\cdot\text{H}^+]_2[\text{PdCl}_4^{2-}]$ (Kindberg & Amma, 1975) and cytosine hydrochloride (Mandel, 1977), cytosine is mono-

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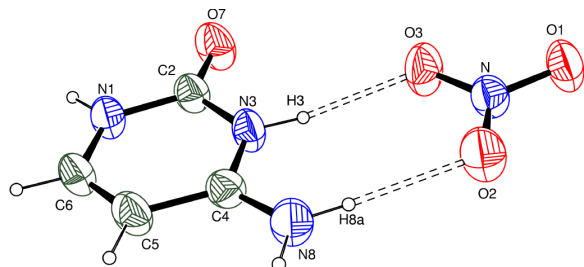


Figure 1
ORTEP-3 (Farrugia, 1997) view of the title compound, showing the hydrogen-bond interactions within the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level.

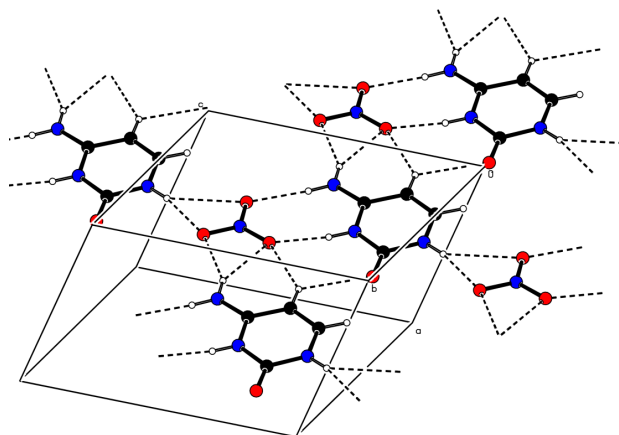


Figure 2
PLATON (Spek, 1990) view of the two-dimensional hydrogen-bond network in (I).

protonated at atom N3. Some base stacking is retained but hydrogen bonding between cytosine rings, as found in cytosine (Barker & Marsh, 1964), cytosine monohydrate (Jeffrey & Kinoshita, 1963) and cytosine hydrochloride, is completely prevented by the presence of the planar nitrate ions. The protonated cytosine rings are planar, with the greatest deviation from the least-squares plane being 0.0057 (17) Å for C4; the amino H atoms also lie in this plane. The pyrimidine ring bond distances are, in general, not significantly different from those found in cytosine or cytosine monohydrate. Each ring is linked to three nitrate anions by strong N—H···O hydrogen bonds *via* atoms N1, N3 and N8. The shortest hydrogen bond is observed between the protonated atom N3 of pyrimidine and atom O3 of nitrate. As observed in the crystal structure of guaninium dinitrate dihydrate (Bouchouit *et al.*, 2002), the hydrogen-bond system between cations and anions is two-dimensional and generates a succession of parallel layers of cytosinium and nitrate ions perpendicular to their stacking direction (*b* axis). The shortest interaction ensuring junction of parallel layers is a van der Waals interaction, between atoms C2 and O7 of the cytosinium cations [3.09 (2) Å; Fig. 3].

Experimental

Colorless single crystals of cytosinium nitrate were obtained after one week by slow evaporation, at room temperature, of an equimolar aqueous solution of cytosine and nitric acid.

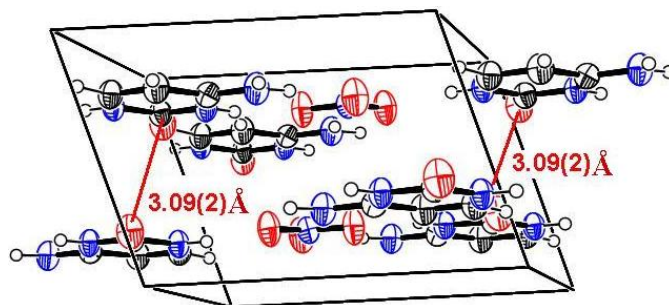


Figure 3
The layered structure in (I), viewed down the *c* axis.

Crystal data

$C_4H_6N_3O^+ \cdot NO_3^-$	$Z = 2$
$M_r = 174.13$	$D_x = 1.609 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.5300(2) \text{ \AA}$	Cell parameters from 3964 reflections
$b = 6.7240(2) \text{ \AA}$	$\theta = 2.4\text{--}25.5^\circ$
$c = 9.2110(3) \text{ \AA}$	$\mu = 0.14 \text{ mm}^{-1}$
$\alpha = 71.96(2)^\circ$	$T = 293(2) \text{ K}$
$\beta = 72.84(3)^\circ$	Prism, colorless
$\gamma = 73.75(3)^\circ$	$0.60 \times 0.25 \times 0.15 \text{ mm}$
$V = 359.44(7) \text{ \AA}^3$	

Data collection

Nonius KappaCCD diffractometer	$R_{\text{int}} = 0.033$
φ scans	$\theta_{\text{max}} = 25.5^\circ$
Absorption correction: none	$h = -7 \rightarrow 7$
3964 measured reflections	$k = -8 \rightarrow 8$
1206 independent reflections	$l = -10 \rightarrow 11$
1065 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0625P)^2 + 0.0661P]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.113$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.14 \text{ e \AA}^{-3}$
1206 reflections	$\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$
109 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

O1—N	1.2483 (17)	N1—C6	1.355 (2)
O2—N	1.2352 (17)	N1—C2	1.3670 (18)
O3—N	1.2432 (17)	N8—C4	1.310 (2)
O7—C2	1.2084 (18)	C4—C5	1.415 (2)
N3—C4	1.3510 (19)	C6—C5	1.339 (2)
N3—C2	1.3799 (19)		
O2—N—O3	120.97 (12)	O3—N—O1	118.56 (13)
O2—N—O1	120.46 (12)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N3—H3···O3	0.86	1.99	2.8419 (18)	170
N1—H1···O1 ⁱ	0.86	2.01	2.8553 (18)	169
N1—H1···O2 ⁱ	0.86	2.56	3.2285 (18)	135
N8—H8A···O2	0.86	2.08	2.9392 (19)	176
N8—H8B···O1 ⁱⁱ	0.86	2.30	3.0846 (19)	152
N8—H8B···O3 ⁱⁱ	0.86	2.36	3.1513 (19)	153

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

All H atoms were located at idealized positions. Riding isotropic displacement parameters were used for all H atoms.

Data collection: *KappaCCD Software* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLUTON* (Spek, 1990); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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