# Guaninium dinitrate dihydrate

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In the asymmetric unit of the title compound, $C_5H_7N_5O^{2+} \cdot 2NO_3^- \cdot 2H_2O$, the guanine base is diprotonated and cocrystallizes with two nitrate anions and two water molecules. The structure is a layered one, and in each layer all H atoms bonded to O and N atoms are involved in a two-dimensional hydrogen-bonding network. Short contacts are observed between parallel layers and ensure the cohesion of the crystals.

## Comment

Guanine, a purine base, is a constituent of nucleotides and, as such, pairs with cytosine in the helical structure of DNA. A number of purine and pyrimidine analogs are effective metabolic inhibitors with useful chemotherapeutic activity (Roy-Burman, 1970; Balis, 1968; Hitchings & Elion, 1963). This kind of hydrogen bonding in hybrid compounds is present in the active sites of several biological systems; for example N—H···O hydrogen bonds between guanine rings and phosphate ions are involved in the active-site inhibitor-binding mechanism in the ternary complex of calf spleen purine nucleoside phosphorylase. It also provides a new starting point for the design of inhibitors of PNP for therapeutic and other applications (Luić *et al.*, 2001). The crystal structures of guanine picrate monohydrate and thioguanine picrate monohydrate (Bugg & Thewalt, 1975), and guaninium dichloride (Matković-Čalogović & Sanković, 1999) have been reported previously. The present work is part of a series of structural studies on hybrid compounds of organic bases and inorganic acids; other examples are *m*-carboxyphenylammonium nitrate (Benali-Cherif, Cherouana *et al.*, 2002), *p*-carboxyphenylammonium dihydrogenmonophosphate monohydrate (Benali-Cherif, Abouimrane *et al.*, 2002) and L-histidinium dinitrate (Benali-Cherif, Benguedouar *et al.*, 2002). We report here the structure of guaninium dinitrate dihydrate, (I).
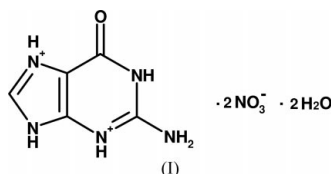


The main purpose of the present study is to examine the hydrogen bonding engineered in the crystals obtained from the reaction of guanine and nitric acid in water. The imino groups of the pyrimidine and imidazolyl portions ( N3 and N7, respectively) in guanine are protonated, and each resulting $C_5H_7N_5O^{2+}$ dication is surrounded by three nitrate anions and a water molecule (Fig. 2). The protonated N atoms are
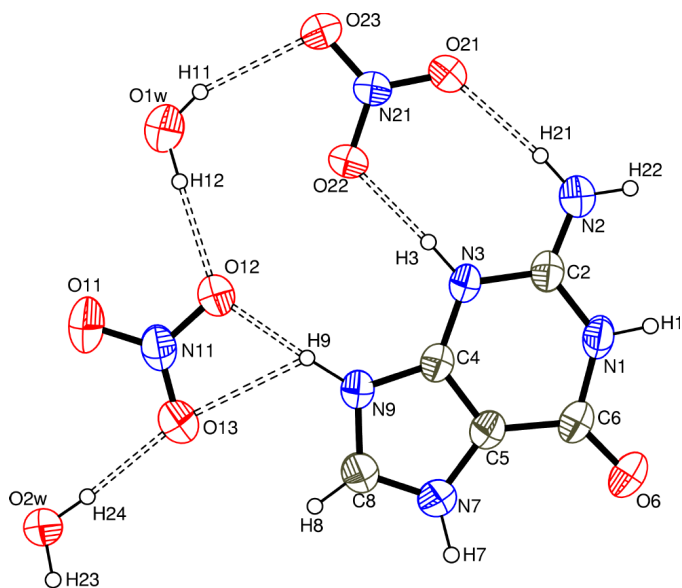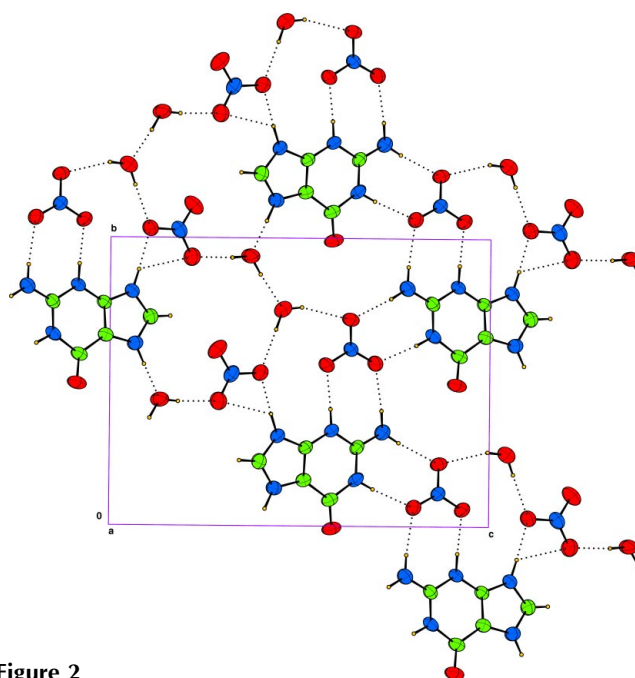
**Figure 1**
An *ORTEP*-3 (Farrugia, 1997) view of the asymmetric unit of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.



**Figure 2**
Packing diagram of the title compound, viewed down the *a* axis, showing a two-dimensional network of hydrogen bonds.

involved in the strongest hydrogen bonds; atoms N3 and N7 are hydrogen bonded *via* intermolecular interactions to nitrate [N3—H3···O22 = 2.737 (2) Å] and water O atoms [N7—H7···O2W = 2.566 (2) Å]. The guanine base is doubly linked to a single nitrate anion *via* intermolecular hydrogen bonds [N1—H1···O21 = 2.8417 (19) Å and N2—H22···O23 = 2.884 (2) Å], while N9 atom of the imidazolyl ring is hydrogen bonded to a nitrate anion by an intermolecular interaction [N9—H9···O12 = 2.741 (2) Å]. We also observe close contacts between atoms C8 and O11 [C8—H8···O11 = 3.267 (2) Å]. Atom O1W of a water molecule plays an important role in the three-dimensional network of hydrogen bonding. In a single layer, atom O1W is bound to two nitrate anions [O1W—H12···O12 = 2.853 (2) Å and O1W—H11···O23 = 2.989 (2) Å] and to the second molecule of water [O2W—H23···O1W = 2.643 (2) Å]. In each layer, anions, cations and water molecules constitute a two-dimensional network of hydrogen bonding (Fig. 2). The crystal packing (Fig. 3) is established by the arrangement of parallel layers along the *b* axis. This packing is stabilized by short contacts, the strongest being observed between atoms C2 and O1W [C2···O1W = 3.070 (2) Å]. The torsion angles N9—C4—N3—C2 = 178.79 (15)° and N1—C6—C5—N7 = −176.71 (16)° show clearly that the purine base geometry is not affected by protonation of atoms N3 and N7, *i.e.* the imidazolyl and pyrimidine rings are coplanar.
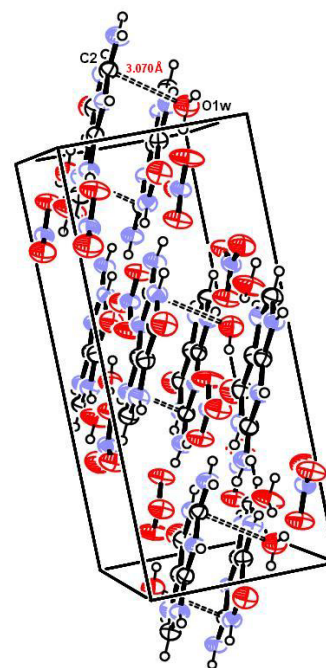
## Experimental

Guaninium dinitrate dihydrate was prepared from a solution of 1 mmol guanine and 2 mmol nitric acid in 10 ml water. Colorless crystals were formed upon slow evaporation of the solution over a period of two weeks.



**Figure 3**
An *ORTEP*-3 (Farrugia, 1997) diagram of the layered packing in (I), viewed approximately down the *b* axis.

*Crystal data*

| | |
|---|---|
| $C_5H_7N_5O^{2+} \cdot 2NO_3^{-} \cdot 2H_2O$ | $D_x = 1.657$ Mg m$^{-3}$ |
| $M_r = 313.21$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/c$ | Cell parameters from 8447 |
| $a = 6.6340$ (4) Å | reflections |
| $b = 11.9800$ (5) Å | $\theta = 3.1$–26.4° |
| $c = 15.8040$ (3) Å | $\mu = 0.16$ mm$^{-1}$ |
| $\beta = 91.01$ (2)° | $T = 293$ (2) K |
| $V = 1255.83$ (10) Å$^3$ | Prism, colorless |
| $Z = 4$ | $0.60 \times 0.45 \times 0.40$ mm |

## Data collection

| | |
|---|---|
| Nonius KappaCCD diffractometer | $R_{int} = 0.049$ |
| $\varphi$ scans | $\theta_{max} = 26.4°$ |
| Absorption correction: none | $h = -7 \rightarrow 8$ |
| 8447 measured reflections | $k = -14 \rightarrow 14$ |
| 2447 independent reflections | $l = -19 \rightarrow 19$ |
| 2103 reflections with $I > 2\sigma(I)$ | |

## Refinement

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.049P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.045$ | $+ 0.3341P]$ |
| $wR(F^2) = 0.124$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.07$ | $(\Delta/\sigma)_{max} = 0.020$ |
| 2447 reflections | $\Delta\rho_{max} = 0.19$ e $\text{Å}^{-3}$ |
| 234 parameters | $\Delta\rho_{min} = -0.22$ e $\text{Å}^{-3}$ |
| All H-atom parameters refined | |

**Table 1**
Hydrogen-bonding geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|---|---|---|---|
| N1—H1⋯O21[i] | 0.87 (3) | 1.98 (3) | 2.8417 (19) | 174 (2) |
| N3—H3⋯O22 | 0.90 (2) | 1.84 (2) | 2.737 (2) | 176 (2) |
| N7—H7⋯O2W[ii] | 1.02 (2) | 1.55 (2) | 2.566 (2) | 177 (2) |
| N9—H9⋯O12 | 1.01 (2) | 1.73 (2) | 2.741 (2) | 178.4 (14) |
| N9—H9⋯O13 | 1.01 (2) | 2.34 (3) | 2.966 (2) | 118.8 (18) |
| O1W—H11⋯O23 | 0.87 (3) | 2.16 (3) | 2.989 (2) | 159 (2) |
| O1W—H12⋯O12 | 0.91 (4) | 1.95 (4) | 2.853 (2) | 174 (2) |
| N2—H21⋯O21 | 0.91 (2) | 1.99 (2) | 2.887 (2) | 171 (2) |
| N2—H22⋯O23[i] | 0.88 (3) | 2.00 (3) | 2.884 (2) | 174 (3) |
| O2W—H23⋯O1W[ii] | 0.84 (3) | 1.80 (3) | 2.643 (2) | 174 (3) |
| O2W—H24⋯O13 | 0.85 (3) | 1.91 (3) | 2.756 (2) | 176 (2) |
| C8—H8⋯O11[ii] | 0.91 (2) | 2.49 (2) | 3.267 (2) | 143.5 (17) |

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

All H atoms were refined isotropically.

Data collection: *KappaCCD* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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