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# Hydrogen bonding in creatininium nitrate

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**Key indicators**

Single-crystal X-ray study
$T$ = 293 K
Mean $\sigma$(C–C) = 0.002 Å
Disorder in main residue
$R$ factor = 0.040
$wR$ factor = 0.110
Data-to-parameter ratio = 18.8

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



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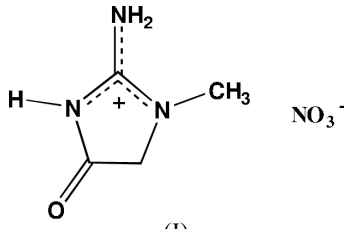
In the title compound, $C_4H_8N_3O^+\cdot NO_3^-$, creatininium cations and nitrate anions are linked to each other through strong hydrogen bonds, formed by all H atoms covalently bonded to the N atoms. Short contacts are also observed between the anions. This complex three-dimensional network of hydrogen bonds ensures the cohesion of the ionic structure.

## Comment

Studies of organic–inorganic hybrid materials, including amino acids and various inorganic acids (Benali-Cherif *et al.*, 2004; Bouchouit *et al.*, 2002; Benali-Cherif, Bendheif *et al.*, 2003), have received a great deal of attention in recent years, because of their electrical, magnetic and optical properties (Kagan *et al.*, 1999; Hill, 1998).




(I)

Hydrogen bonds in hybrid compounds are of interest because of their widespread biological occurrence. For example, hydrogen bonds between phosphate groups and histidine imidazolyl groups are involved in the active-site substrate-binding mechanism of ribonuclease (Richards *et al.*, 1972) and in the regulation of the oxygen affinity of deoxyhaemoglobin by 2,3-diphosphoglycerate (Perutz & Ten Eyck, 1972). The potential importance of hydrogen bonding in the structure and function of biomolecules is well established (Jeffrey & Saenger, 1991). In particular, N—H···O hydrogen bonds are predominant in determining the formation of secondary structure elements in proteins, and base-pairing in nucleic acids and their biomolecular interactions.

Creatinine is formed by the metabolism of phosphocreatine, a high-energy molecule which provides a rapid supply of ATP to muscles. Phosphocreatine is converted spontaneously to creatinine on a regular basis. Consequently, creatinine is released into the blood and excreted by the kidneys as a metabolic waste product.

The present structure analysis of creatininium 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; Cherouana *et al.*,

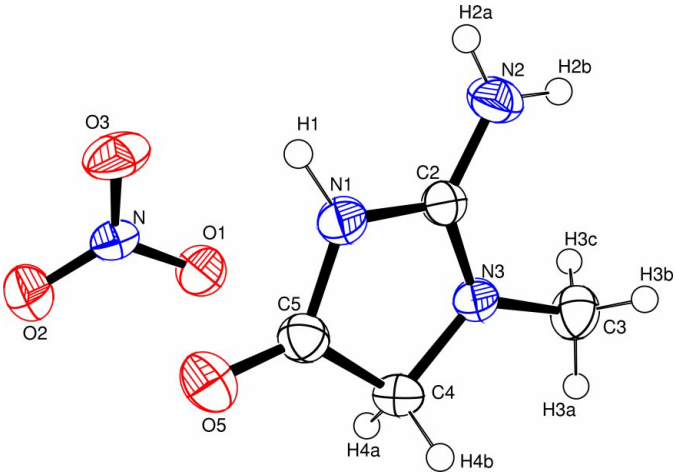



**Figure 1**
A view of (I), with the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Only one disorder component is shown.

2002; Benali-Cherif, Bendheif *et al.*, 2002; Benali-Cherif, Cherouana *et al.*, 2002; Cherouana, Bendjeddou *et al.*, 2003; Bendjeddou *et al.*, 2003).

In the present study, only the imino group of the imidazolyl moiety (atom N1) in creatinine is protonated, which confirms the possibility of the existence of creatinine and creatininium cations in various tautomeric forms in aqueous solution. This is discussed and quantified in the light of the interpretation of the solution acidity effect on $^{1}$H, $^{13}$C and $^{14}$N NMR chemical shifts (Kotsyubynskyy *et al.*, 2004).

The bond distances in the imidazolyl ring of (I) are, in general, not significantly different from those found in similar hybrid compounds containing protonated imidazolyl moieties. The creatininium ring is planar, as expected, with a mean deviation from planarity of less than 0.0017 Å.

The two N—O distances involving atoms O2 and O3 are slightly shorter than the third one with atom O1. Usually, in similar hybrid compounds, the opposite is observed, for example in D-phenylglycinium nitrate (Bouchouit *et al.*, 2004) and cytosinium nitrate (Cherouana, Bouchouit *et al.*, 2003). The O—N—O angles range from 118.94 (11) to 121.60 (12)°. The bond distances and angles of the creatininium residue agree with those found in the literature.

The asymmetric unit of (I) contains a monoprotonated creatininium cation and a nitrate anion. The crystal structure of (I) is built up from intricate cation–anion hydrogen bonds, resulting in a two-dimensional network parallel to the *bc* plane (Fig. 2).

The cation–anion N—H···O interactions form zigzag chains (Fig. 3) extending along the *b* axis, the strongest being that between atoms N2 and O3 (Table 1).

In the crystal packing of (I), there are also anion–anion interactions *via* O···O short contacts, the strongest being that between atoms O3 and O1 [O3···O1$^{i}$ = 2.961 (2) Å; symmetry code: (i) $x, -y+\frac{1}{2}, z+\frac{1}{2}$]. This interaction contributes to the cohesion of the crystal.

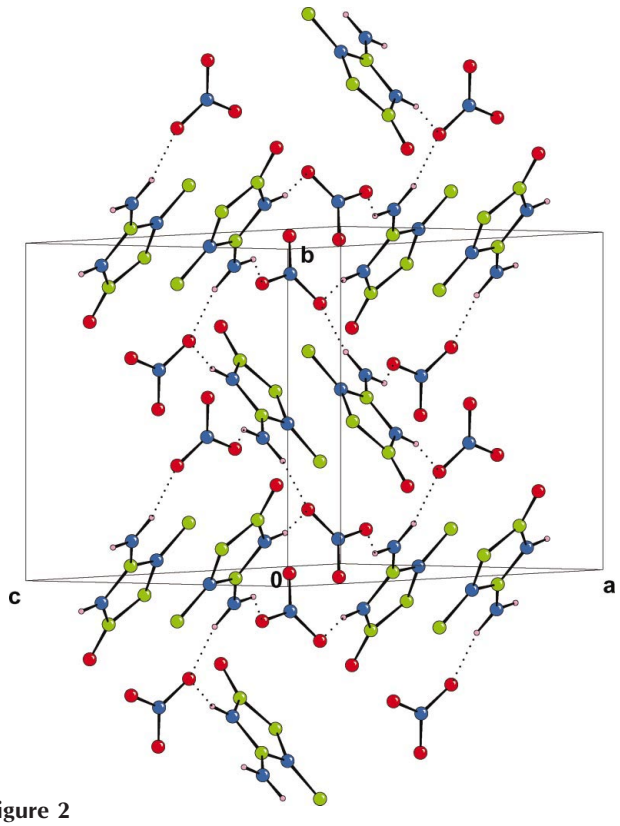



**Figure 2**
A view of the N—H···O hydrogen-bond (dotted lines) network. H atoms attached to C atoms have been omitted for clarity.

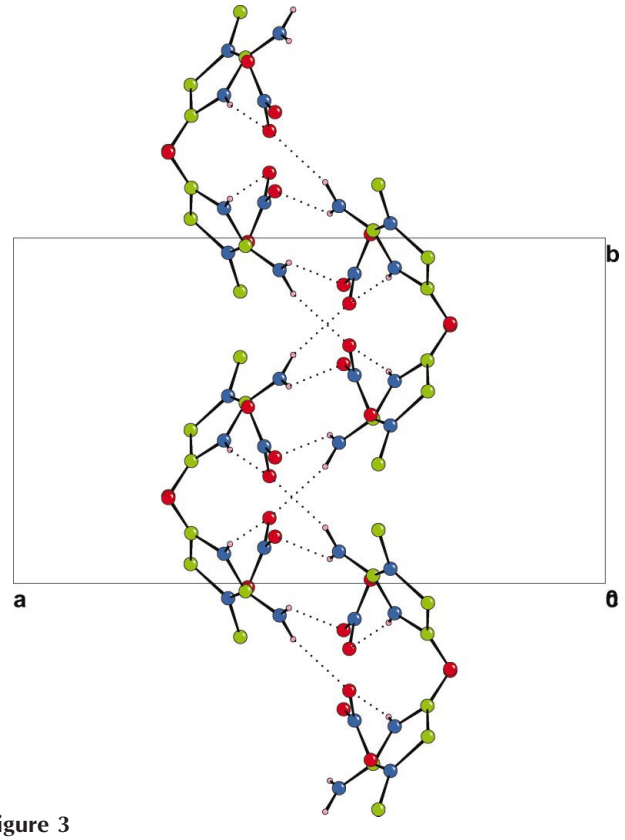



**Figure 3**
A view of (I), showing the zigzag chains formed by the N—H···O hydrogen bonds (dotted lines), extending along the *b* axis.

## Experimental

The title compound, (I), was crystallized by the slow evaporation of an aqueous solution of creatinine and nitric acid in a 1:1 stoichiometric ratio.

*Crystal data*

$C_4H_8N_3O^+\cdot NO_3^-$
$M_r$ = 176.14
Orthorhombic, *Pbca*
$a$ = 16.6509 (3) Å
$b$ = 9.7336 (2) Å
$c$ = 8.9989 (3) Å
$V$ = 1458.48 (6) Å$^3$
$Z$ = 8
$D_x$ = 1.604 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 12 577 reflections
$\theta$ = 5.8–30°
$\mu$ = 0.14 mm$^{-1}$
$T$ = 293 (2) K
Needle, colourless
0.30 × 0.10 × 0.10 mm

*Data collection*

Nonius KappaCCD area-detector diffractometer
$\varphi$ scans
Absorption correction: none
12 577 measured reflections
2102 independent reflections
1473 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.057
$\theta_{max}$ = 30.0°
$h = -23 \rightarrow 23$
$k = -13 \rightarrow 11$
$l = -12 \rightarrow 12$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.110
$S$ = 1.02
2102 reflections
112 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0578P)^2 + 0.0648P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.0001$
$\Delta\rho_{max}$ = 0.25 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.24 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1···O1$^{i}$ | 0.870 (17) | 1.977 (18) | 2.8381 (16) | 170.1 (15) |
| N1—H1···O2$^{i}$ | 0.870 (17) | 2.621 (16) | 3.2031 (17) | 125.3 (12) |
| N1—H1···N$^{i}$ | 0.870 (17) | 2.657 (17) | 3.4493 (15) | 152.1 (13) |
| N2—H2$A$···O1$^{ii}$ | 0.86 | 2.16 | 2.9022 (16) | 144 |
| N2—H2$B$···O3$^{iii}$ | 0.86 | 2.14 | 2.8222 (16) | 136 |
| N2—H2$B$···O2$^{i}$ | 0.86 | 2.56 | 3.2380 (19) | 136 |

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

All H atoms were located in Fourier difference maps. Methyl H atoms were refined as an idealized methyl group disordered over two positions with occupancies of 0.5. The H atom on atom N1 was refined freely. The remaining H atoms were treated as riding, with C—H distances in the range 0.96–0.97 Å and with $U_{iso}$(H) = 1.2$U_{eq}$(C,N), except for the disordered methyl H atoms, where $U_{iso}$(H) = 1.5$U_{eq}$(C).

Data collection: *KappaCCD Server Software* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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