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Ammonium violurate: a compact structure with extensive hydrogen bonding in three dimensions

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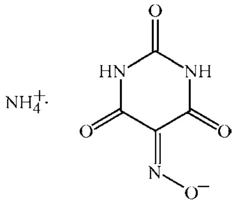
The title compound [systematic name: ammonium pyrimidine-2,4-5,6(1*H*,3*H*)-tetrone 5-oximate], $NH_4^+\cdot C_4H_2N_3O_4^-$, crystallizes from water in the triclinic space group $P\overline{1}$ and is isomorphous with a known rubidium complex [Gillier (1965). *Bull. Soc. Chim. Fr.* pp. 2373–2384]. The principal feature of the structure is hydrogen bonding; each ammonium H atom acts as a bifurcated donor and three of the four violurate O atoms are bifurcated acceptors, with the fourth acting as a trifurcated acceptor. The pattern of hydrogen bonding around the cation is very similar to the rubidium coordination environment in the related structure. The violurate anions pack as hydrogen-bonded crinkled tapes, which are linked and separated by the ammonium cations to give a compact three-dimensional structure.

Comment

Violuric acid is a derivative of barbituric acid, having an isonitroso substituent at the 4-position on the barbiturate ring. We are interested in the structures of barbituric acid and its derivatives (Nichol & Clegg, 2005*a*,*b*, 2007) and of their *s*-block coordination complexes (Nichol & Clegg, 2006*b*). Additionally, we have reported a definitive redetermination of violuric acid monohydrate (Nichol & Clegg, 2005*d*), a second polymorph of violuric acid monohydrate (Guille *et al.*, 2007) and the structure of violuric acid methanol solvate (Nichol & Clegg, 2005*c*).

Complexes of violuric acid with potassium, rubidium (Gillier, 1965) and strontium (Hamelin, 1976) are already known. The isonitroso substituent allows greater scope for coordination when compared with unsubstituted barbituric acid, and it also introduces two extra hydrogen-bonding acceptors. We have also been investigating the influence of weak hydrogen bonding in organic complexes of these barbiturate derivatives using a counter-ion that forms no intermolecular classical hydrogen bonds (Nichol & Clegg, 2006*a*), and we wished to investigate the hydrogen bonding in an organic complex in which classical hydrogen bonding is expected to be dominant. The ammonium salt of violuric acid, (I), is a logical choice for study since the NH_4^+ cation has four hydrogen-bond donor sites. Additionally, the crystal structure of ammonium barbiturate has already been reported (Craven, 1964), giving us a useful comparison structure.



(I)

The asymmetric unit of (I) is presented in Fig. 1. The salt crystallizes from aqueous solution in the $P\overline{1}$ space group and has $Z' = 1$. A search of the Cambridge Structural Database (Version 5.28 plus two updates; Allen, 2002) shows that this compound is isostructural with the rubidium complex determined by Gillier (1965), the ammonium and rubidium cations being approximately the same size. The C, N and O atoms of the violurate ring form a planar skeleton (r.m.s. deviation 0.0075 Å) and the isonitroso group is almost coplanar with the ring (the r.m.s. deviation for all non-H atoms is 0.1965 Å). The isonitroso group is ordered, disorder of this group being occasionally seen in violurate crystal structures. Bond lengths are listed in Table 1 and are largely unexceptional. At 1.351 (3) Å, the $C{=}N$ bond is longer than that observed in neutral violuric acid monohydrate (1.295 Å; Nichol & Clegg, 2005*d*), whilst the N—O bond, at 1.265 (3) Å, is shorter than that observed for N—OH (1.346 Å); this is consistent with what would be expected upon deprotonation of the OH group. The two C—C bond lengths are similar to those found in neutral violuric acid. The ammonium cation is regular tetrahedral, as expected, and the freely refined N—H distances range from 0.91 (4) to 0.95 (3) Å, with no significant angular distortions from ideal geometry.

The violurate anion has five potential hydrogen-bonding acceptor sites and two donor sites, with an additional four donor sites in the ammonium cation. Indeed, this hydrogen-bonding arrangement is a rather good match for the rubidium coordination in the known isomorphous complex. Table 2

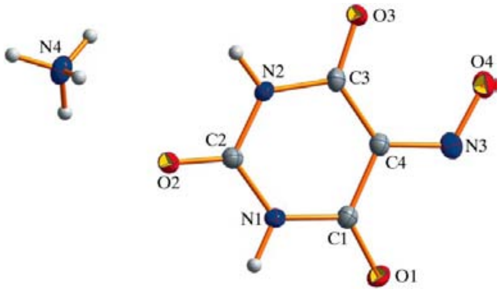


Figure 1
The asymmetric unit of (I), showing 50% probability displacement ellipsoids and H atoms as small spheres.

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gives details of the hydrogen-bonding geometry, Fig. 2 gives a pictorial representation of how the ammonium cation interacts with the violurate anion, and Fig. 3 shows both the hydrogen bonding in (I) and the rubidium coordination in the related structure. This shows that all the hydrogen-bonding interactions are replicated as Rb···O contacts in the coordination complex, two additional Rb···O and Rb···N contacts (one each) probably resulting from the nondirectional Coulombic nature of the metal–ligand bonds, which are not found in the more directional hydrogen-bonding interactions.

In the hydrogen-bonding analysis, each H atom of the ammonium cation acts as a bifurcated donor, whilst the O atoms of the violurate anion are a mixture of bifurcated and trifurcated acceptors. Hydrogen bonding consists of a combination of short strong almost-linear interactions with long, weak and very bent interactions. This is in contrast to ammonium barbiturate, where the hydrogen bonding is much more conventional in length and direction. Firstly, there are the 'standard' hydrogen bonds found in the $R_2^2(8)$ motif (Bernstein *et al.*, 1995), involving N—H···O interactions about a crystallographic inversion centre, which link the violurate anions to form a tape. This is a very common motif in the packing of molecules of this type and they are indicated by dotted lines (shown in blue in the electronic version of the paper). Secondly, there are the longer interactions between the ammonium cation and the oxygen acceptors of the violurate anion. These are denoted by five-dash lines (orange in the electronic version) and range from the reasonably short and linear (N4—H1···O4$^{\rm iii}$) to the incredibly long (N4—H4···O1$^{\rm i}$) and the extremely bent (N4—H3···O4$^{\rm ii}$) (symmetry codes as in Table 2). Most are of the form $D(3)$, although the bifurcated H3 atom forms an $R_1^2(6)$ motif with atoms O3 and O4 as acceptors. Finally, there is a long N4–

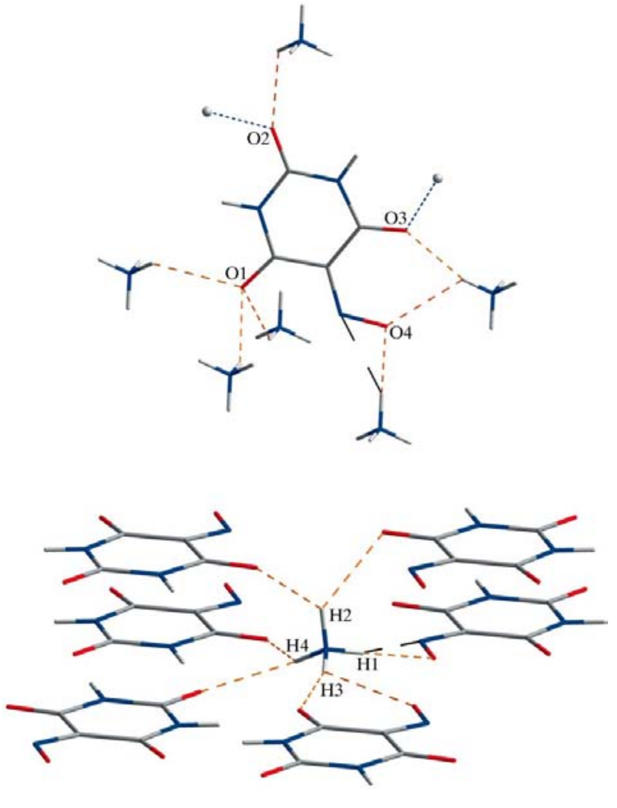

Figure 2
The hydrogen-bonding environment of one ammonium cation (top) and one violurate anion (bottom) in (I). Dotted lines (blue in the electronic version of the paper) indicate the hydrogen bonds linking the violurate anions into a tape, five-dash lines (orange in the electronic version) indicate the N—H···O bonds from ammonium, and long-dash lines (black in the electronic version) indicate the N—H···N bonds.

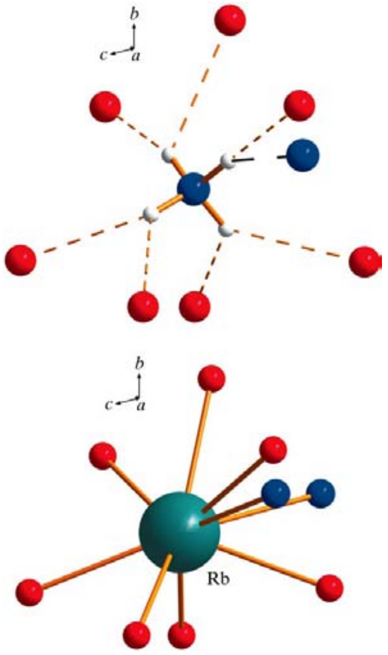

Figure 3
A comparison of the hydrogen-bonding environment of (I) with the coordination environment of the known rubidium complex. The two are very similar.

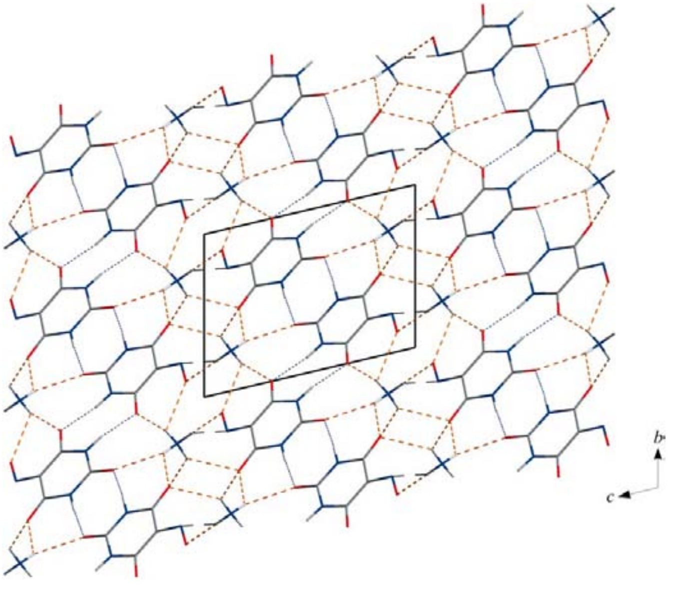

Figure 4
A projection along the *a* axis of (I).

$H1\cdots N3^{iii}$ interaction, which is denoted by a long-dashed line (black in the electronic version). The relative orientation suggests minimal interaction between the H atom and the acceptor lone pair, and so this is a very weak interaction, forming an $R_1^2(3)$ interaction with atom O4 as the other acceptor. Fig. 4 shows an *a*-axis projection revealing the web of hydrogen bonds that hold the violurate anions together into tapes and which link these tapes *via* the ammonium cation to form the three-dimensional structure.

The crystal packing of (I) shares some similarities with the crystal packing of ammonium barbiturate. A projection along the *ab* diagonal is given in Fig. 5. The ammonium ion lies out of the plane of the violurate tapes and keeps the tapes approximately 4.8 Å apart, which is much larger than the separation of 3.25 Å seen in ammonium barbiturate; there is thus no π–π stacking in ammonium violurate. Hydrogen bonding of the ammonium cations to the violurate tapes completes the three-dimensional framework in this crystal structure.

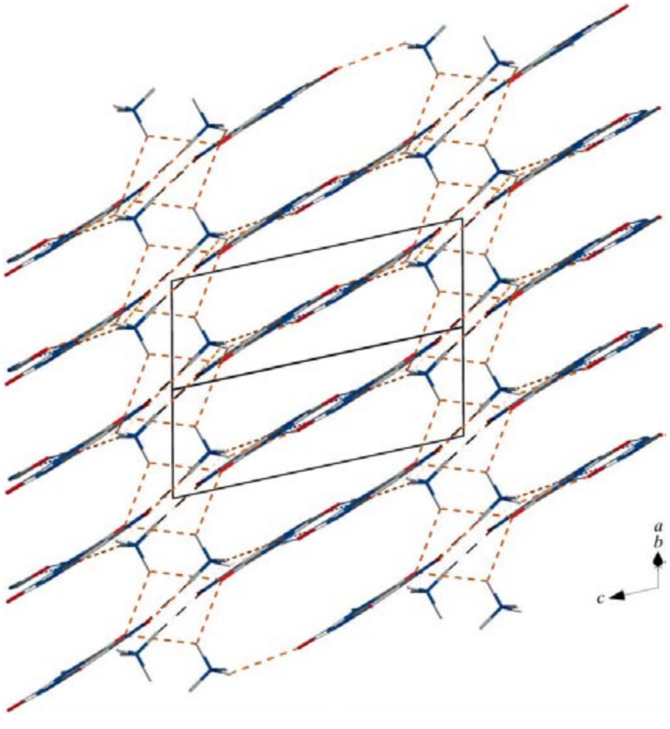

Figure 5
A projection along the *ab* diagonal of (I). Ammonium $N-H\cdots O$ interactions are indicated by short-dash lines and $N-H\cdots N$ interactions are indicated by long-dash lines.

Experimental

Ammonium carbonate (0.08 g, 1 mmol) was added to a pale-yellow solution of violuric acid (0.17 g, 1 mmol) dissolved in 10 ml of hot distilled water. The solution instantly turned purple. Overnight standing at room temperature resulted in a powder-like mass of very small violet crystals of (I) (mass 0.123 g, yield 70%). CHN analysis found: C 27.33, H 3.54, N 31.68%; $C_4H_6N_4O_4$ requires: C 27.58, H 3.45, N 32.18%.

Crystal data

$NH_4^+\cdot C_4H_2N_3O_4^-$
$M_r = 174.13$
Triclinic, $P\bar{1}$
$a = 4.8087$ (6) Å
$b = 7.4678$ (10) Å
$c = 9.5748$ (11) Å
$\alpha = 101.734$ (13)°
$\beta = 93.643$ (14)°
$\gamma = 105.869$ (11)°
$V = 321.22$ (8) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.16$ mm^{-1}
$T = 120$ (2) K
0.06 × 0.04 × 0.01 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.920$, $T_{max} = 0.998$
7149 measured reflections
1466 independent reflections
1102 reflections with $I > 2\sigma(I)$
$R_{int} = 0.067$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.133$
$S = 1.03$
1466 reflections
133 parameters
All H-atom parameters refined
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Table 1
Selected geometric parameters (Å).

O1—C1	1.229 (3)	N2—C2	1.359 (3)
O2—C2	1.228 (3)	N2—C3	1.389 (3)
O3—C3	1.237 (3)	N3—C4	1.351 (3)
O4—N3	1.265 (3)	C1—C4	1.456 (3)
N1—C1	1.392 (3)	C3—C4	1.439 (3)
N1—C2	1.356 (3)		

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1N\cdots O2^{i}$	0.96 (3)	1.81 (3)	2.772 (2)	175 (3)
$N2-H2N\cdots O3^{ii}$	0.90 (3)	1.91 (3)	2.805 (3)	172 (3)
$N4-H1\cdots O4^{iii}$	0.93 (4)	1.84 (4)	2.765 (3)	178 (3)
$N4-H1\cdots N3^{iii}$	0.93 (4)	2.41 (4)	3.249 (3)	150 (3)
$N4-H2\cdots O1^{iv}$	0.95 (3)	2.20 (3)	2.898 (3)	130 (3)
$N4-H2\cdots O1^{v}$	0.95 (3)	2.36 (3)	3.010 (3)	125 (2)
$N4-H3\cdots O3^{ii}$	0.91 (4)	2.06 (4)	2.947 (3)	165 (3)
$N4-H3\cdots O4^{ii}$	0.91 (4)	2.45 (4)	3.007 (3)	120 (3)
$N4-H4\cdots O2$	0.93 (4)	2.38 (4)	3.048 (3)	129 (3)
$N4-H4\cdots O1^{i}$	0.93 (4)	2.58 (4)	3.293 (3)	134 (3)

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

All H atoms were located in a difference map and were freely refined. N—H distances are in the range 0.90 (3)–0.96 (3) Å. All U_{iso}(H) values were freely refined.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg & Putz, 2004); software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3165). Services for accessing these data are described at the back of the journal.

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