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Ammonium 3-cyano-4-(dicyanomethylene)-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate monohydrate

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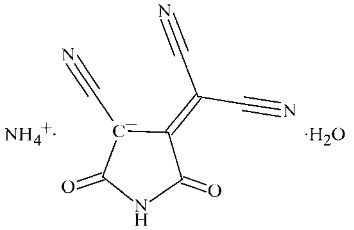
Each anion of the title salt, $NH_4^+\cdot C_8HN_4O_2^-\cdot H_2O$, is linked by two N—H···O hydrogen bonds to another anion, thus forming an essentially planar centrosymmetric dimer. The dimers are considered to be molecular building blocks of an anionic wall. The building blocks form infinite ribbons *via* –C—N···N—C– dipole–dipole and π–π interactions. Adjacent ribbons are stacked by means of π–π interactions, thus forming an anionic wall. Neighbouring walls are connected by $(NH_4^+\ldots H_2O)_n$ chains running along the *b* axis.

Comment

Recently, in the exploration and crystal engineering of novel π–π-stacking organic anions, we have determined and reported the structures of three organic salts. All three salts have the same anion, namely 3-cyano-4-(dicyanomethylene)-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate, (I), but different cations, *e.g.* potassium, (II) (Tafeenko *et al.*, 2003), *N*,*N*-dimethylanilinium, (III) (Tafeenko, Peschar *et al.*, 2004), and *N*-methylpyridinium, (IV) (Tafeenko, Nikolaev *et al.*, 2004), and show different types of molecular packing and aggregation.

In the potassium salt, (II), the anions are connected *via* the cyano groups (π–π and dipole–dipole interactions) of the dicyanomethylene moieties. A novel type of aggregation of anion (I) was found in salt (IV). All anions of (IV) are arranged as dimers *via* two N—H···O hydrogen bonds and form one-dimensional columns parallel to the *b* axis, as a result of π–π interactions. Each dianionic stack has eight neighbouring stacks of cations and is not connected directly to other dianionic stacks. However, as the dimers have a cyanomethylene moiety on both sides, cyano–cyano-type interactions may lead to the formation of ribbons and, assuming π–π interactions between adjacent ribbons, to larger assemblies. In this paper, we report the structure of the ammonium hydrate salt, (V), of anion (I), which exhibits the intermolecular forces between anions that were found in both (II) and (IV).



(V)

The geometry of anion (I) in the title salt (Fig. 1) is essentially the same as in the structures of (II)–(IV). Each anion is linked by two N—H···O hydrogen bonds to another anion, thus forming a centrosymmetric dimer. Adjacent dimers are connected by (–C—N)···(N—C–)* dipole–dipole and π–π interactions, thus forming infinite essentially planar ribbons (Fig. 2); the angle between two adjacent molecules in

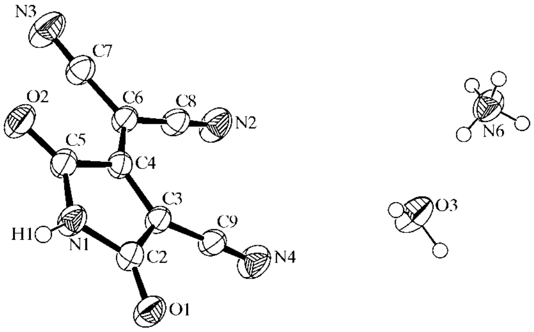


Figure 1
A view of the title salt, (V), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

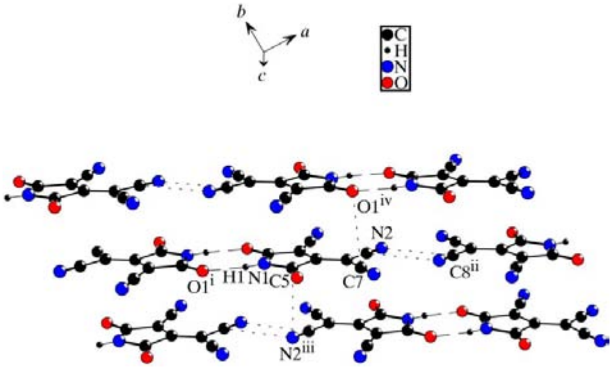


Figure 2
The arrangement of the centrosymmetric anionic dimers (blocks) in ribbons. Adjacent blocks in each ribbon are connected by –CN···NC*– dipole–dipole and π–π interactions. The N2···C8^{ii} distance is 3.370 (3) Å. Adjacent ribbons are interconnected *via* π–π interactions, forming an anionic wall. The interplanar distance is 3.34 Å. The shortest distances between atoms in adjacent layers are C5···N2^{iii} of 3.246 (3) Å and C7···O1^{iv} of 3.314 (3) Å. [Symmetry codes: (i) $-x, 2-y, 1-z$; (ii) $2-x, 1-y, 1-z$; (iii) $1-x, 1-y, 1-z$; (iv) $1-x, 2-y, 1-z$.]

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the ribbon is 0.00 (3)°, and the deviations of the atoms from the plane running through three adjacent [*e.g.* (x, y, z), $(-x, 2-y, 1-z)$ and $(2-x, 1-y, 1-z)$] five-membered rings are within 0.033 (1) and −0.022 (1) Å. The angle which the $-C(CN)_2$ group makes with the five-membered ring is 3.03 (8)°, demonstrating a small twist from planarity about the C4—C6 bond.

The cyano–cyano interaction can be found in many crystals of molecules containing a cyano group, but in only a few of them does this interaction result in a planar configuration (Allen, 2002). Since each ribbon interacts with two adjacent ribbons by means of π–π interactions, we can consider the dimers to be molecular building blocks of anionic walls (Fig. 2). The ribbons of adjacent walls are not parallel (Fig. 3) but form a dihedral angle of 53.70 (4)°.

Besides the structural evidence of π–π interactions, a difference in colour can also be observed between the salt in solution and in the solid form. In water or any organic solution (*e.g.* acetonitrile), all known salts with the anion in question have a vivid yellow colour, while in the solid state, the ammonium salt is dark red.

Two H atoms of the ammonium cation and the lone pair of the O atom of the water molecule form $(NH_4^+\ldots H_2O)_n$ chains (Fig. 3) which run strictly along the *b* axis. The other two H atoms of the ammonium cation and the two H atoms of the water molecule join adjacent anionic walls together *via* hydrogen bonds (Table 1 and Fig. 3). In our opinion, the water molecules play an important role in this type of aggregation of anion (I) in the solid state. Although the stability of the anionic wall is mainly provided by the mutual attraction of cations and anions, the integration of the water molecules in the cationic chain, owing to the hydrogen bonds, makes this attraction more evenly distributed. From this point of view, a wall-type aggregation of anion (I) may also be expected in other salts containing hydrophilic cations, for instance, alkaline earth salts.

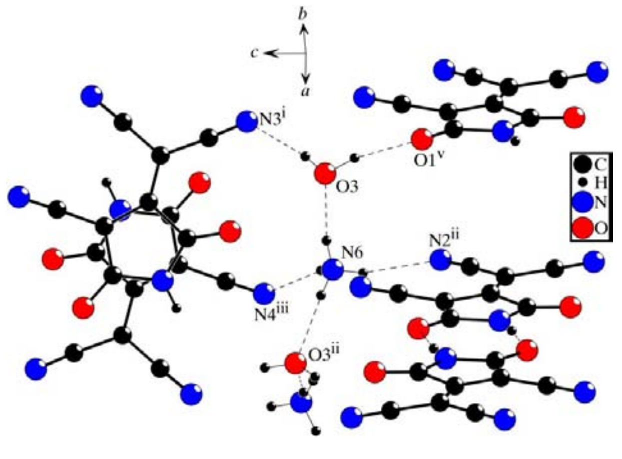

Figure 3
Part of the crystal structure of (V), showing the key hydrogen bonds for the molecular arrangement in the crystal as dashed lines. Symmetry codes are listed in Table 1.

Experimental

The synthesis of the title salt was carried out in the same way as for (II)–(IV) (see *Comment*). The starting compound, 2,2,3,3-tetracyanocyclopropanecarboxylic acid, was synthesized from α-chloroketone and TCNE (ethylene-1,1,2,2-tetracarbonitrile). The title salt, (V), was obtained by mixing ammonium iodide with 2,2,3,3-tetracyanocyclopropanecarboxylic acid. The reaction was carried out in water–propan-2-ol (1:1) solvent at room temperature. Dark-red crystals of (V) were collected from the reaction mixture by filtration and drying.

Crystal data

$NH_4^+\cdot C_8HN_4O_2^-\cdot H_2O$
$M_r = 221.19$
Monoclinic, $P2_1/n$
$a = 7.2618$ (11) Å
$b = 7.5232$ (12) Å
$c = 19.033$ (5) Å
$\beta = 92.745$ (10)°
$V = 1038.6$ (4) Å^3
$Z = 4$
$D_x = 1.415$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 35$–45°
$\mu = 0.96$ mm^{-1}
$T = 291$ (2) K
Prism, dark red
0.15 × 0.13 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non–profiled ω scans
2129 measured reflections
2069 independent reflections
1787 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.040$
$\theta_{\max} = 72.9°$
$h = -9 \rightarrow 8$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 23$
2 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.104$
$S = 1.08$
2069 reflections
173 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0538P)^2 + 0.228P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N6—H61···O3	0.87 (3)	2.05 (3)	2.905 (3)	169 (2)
O3—H3···N3^{i}	0.83 (3)	2.24 (3)	3.059 (2)	170 (3)
O3—H31···O1^{ii}	0.92 (3)	1.93 (3)	2.8338 (18)	167 (2)
N1—H1···O1^{iii}	0.91 (2)	1.92 (2)	2.8136 (16)	171 (2)
N6—H62···O3^{iv}	0.94 (3)	2.04 (3)	2.920 (2)	156 (3)
N6—H63···N2^{iv}	0.85 (3)	2.24 (3)	3.034 (2)	156 (3)
N6—H6···N4^{v}	0.89 (3)	2.21 (3)	3.011 (2)	150 (2)

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

The positions of the H atoms were determined from a Fourier difference map and their coordinates were refined freely with isotropic displacement parameters. The $U_{\rm iso}$ value for atom H1, which is involved in strong dimers to form a hydrogen bond, is 0.055 (5) Å^2, and the $U_{\rm iso}$ value for atom H61 is 0.072 (7) Å^2. For all other H atoms, $U_{\rm iso}$(H) values range from 0.098 (9) to 0.116 (11) Å^2.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2000) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1520). Services for accessing these data are described at the back of the journal.

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