

Cytosinium oxalate monohydrate

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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 = 0.050
 wR factor = 0.120
Data-to-parameter ratio = 22.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

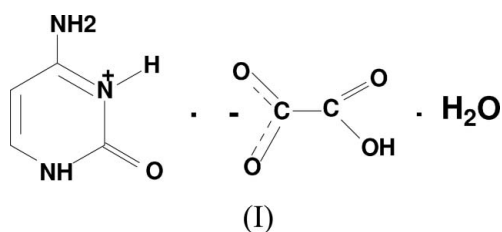
In the title compound, $\text{C}_4\text{H}_6\text{N}_3\text{O}^+ \cdot \text{C}_2\text{HO}_4^- \cdot \text{H}_2\text{O}$, the cytosine molecule is protonated and oxalic acid is in the monoionized state. The structure is stabilized by $\text{O}-\text{H} \cdots \text{O}$ and $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds, and van der Waals interactions. The water molecules are also found to mediate interactions between oxalate anions and cytosinium cations.

Comment

X-ray studies on crystalline complexes of amino acids with carboxylic acids have provided a wealth of information regarding intermolecular interactions and biomolecular aggregation patterns (Vijayan, 1988; Prasad & Vijayan, 1993). The crystal structures of glycinium oxalate (Subha Nandhini *et al.*, 2001a), sarcosinium oxalate monohydrate (Krishnakumar *et al.*, 1998) and L-alaninium oxalate (Subha Nandhini *et al.*, 2001b) have been elucidated.

This work is part of our research on structural studies of hybrid compounds based on 'organic matrix-inorganic acids' and 'organic matrix-organic acids': guaninium dinitrate hydrate (Bouchouit *et al.*, 2002), D-phenylglycinium nitrate (Bouchouit *et al.*, 2004), guaninium dihydrogenphosphite dihydrate (Bendheif *et al.*, 2003) and *m*-carboxyphenylammonium nitrate (Benali-Cherif *et al.*, 2002).

The present study reports the crystal structure of an 'organic matrix-organic acid' hybrid compound, (I), formed by reaction of cytosine with oxalic acid.



The asymmetric unit contains one cytosinium cation, one semi-oxalate anion and a water molecule. Cytosine is mono-protonated at atom N1 and oxalic acid is mono-deprotonated.

Geometrical parameters of the cytosinium cations are found to be in agreement with those of other similar structures of cytosinium nitrate (Cherouana *et al.*, 2003), cytosine (Barker & Marsh, 1964) and cytosine monohydrate (Jeffrey & Kinoshita, 1963).

The cytosinium cations is connected to HC_2O_4^- anions by six $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds (Table 1).

The semi-oxalate ions have a planar geometry. Bond distances around atom C3 indicate a carboxylate group with delocalization of the negative charge between atoms O3 and

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O4. Bond distances around atom C1 are consistent with a carboxylic acid group.

Water molecules play an important role in the cohesion and the stability of the crystal structure; they are involved in three hydrogen bonds connecting one oxalate anion and a cytosinium cation as donor (O1w—H2w··O2 and O1w—H1w··O7) and another oxalate anion as acceptor (O1w··H—O1) (Table 1). No hydrogen bonds were observed between water molecules.

Experimental

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

Crystal data

C₄H₆N₃O⁺·C₂H₂O₄⁻·H₂O
M_r = 219.16
 Monoclinic, *P*2₁/*c*
a = 3.6230 (3) Å
b = 11.9750 (2) Å
c = 20.2509 (2) Å
 β = 91.484 (3)°
V = 878.30 (7) Å³
Z = 4

D_x = 1.657 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 3139 reflections
 θ = 1.0–32.7°
 μ = 0.15 mm⁻¹
T = 293 (2) K
 Prism, colorless
 0.20 × 0.20 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
 φ scans
 12842 measured reflections
 3139 independent reflections
 2226 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.021
 θ_{\max} = 32.7°
h = -5 → 5
k = -18 → 18
l = -30 → 30

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.050
wR (*F*²) = 0.120
S = 1.03
 3139 reflections
 143 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 0.627P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.37 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.28 \text{ e } \text{Å}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N3—H3···O4	0.86	1.94	2.7874 (15)	170
N8—H8a···O3	0.86	1.87	2.7267 (17)	173
N8—H8b···O3 [‡]	0.86	2.10	2.7397 (15)	131
N8—H8b···O1 [‡]	0.86	2.58	3.4071 (17)	161
N1—H1···O2 ^{‡i}	0.86	2.09	2.9127 (16)	160
N1—H1···O4 ^{‡i}	0.86	2.37	2.9445 (16)	124
O1—H1a···O1w	0.82	1.76	2.5592 (16)	165
O1w—H2w···O2 ^{‡iii}	0.85 (1)	2.02 (1)	2.8322 (16)	159 (2)
O1w—H1w···O7 ^{‡iv}	0.85 (1)	1.98 (1)	2.8247 (16)	170 (2)

Symmetry codes: (i) -*x*, -*y* + 1, -*z*; (ii) -*x* + 1, *y* - ½, -*z* + ½; (iii) -*x* + 2, -*y* + 2, -*z*; (iv) *x*, -*y* + ½, *z* - ½.

All H atoms were located in Fourier maps; those attached to C and N were treated as riding on their parent atoms, with C—H = 0.93 and N—H = 0.86 Å and *U*_{iso} = 1.2*U*_{eq}(C,N). For the water molecule, the

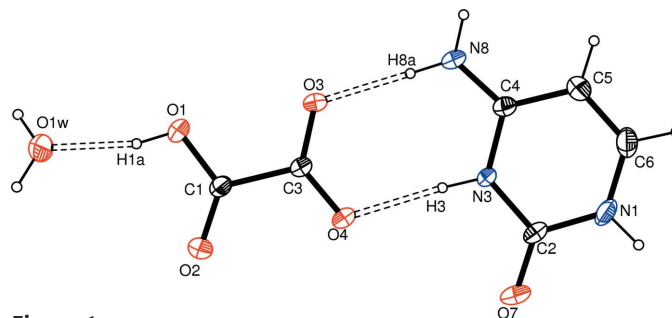


Figure 1
 ORTEP-3 (Farrugia, 1997) view of the title compound, with the atomic labelling scheme. Displacement are drawn at the 50% probability level. Hydrogen bonds are drawn as dashed lines.

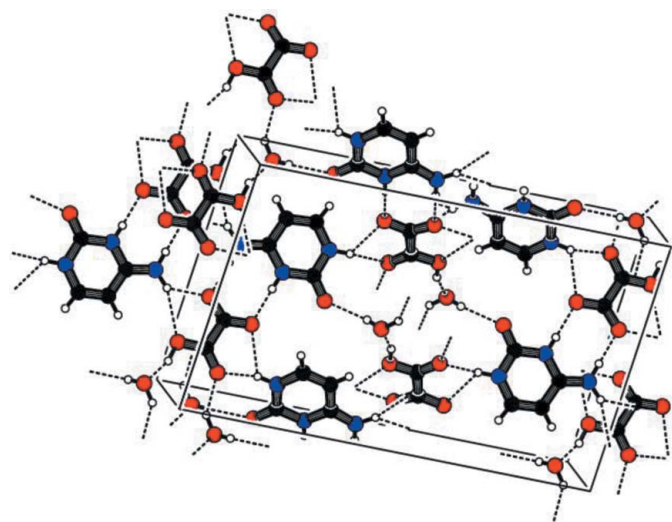


Figure 2
 PLATON (Spek, 2003) diagram of the layered packing in the title compound. Hydrogen bonds are drawn as dashed lines.

Ow—H and H···H distances were restrained to 0.85 (1) and 1.39 (2) Å, respectively, and the H atoms were refined with *U*_{iso} = 1.2*U*_{eq}(Ow).

Data collection: *KappaCCD Reference Manual* (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 *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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