

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

3-Cyanoanilinium hydrogen oxalate hemihydrate

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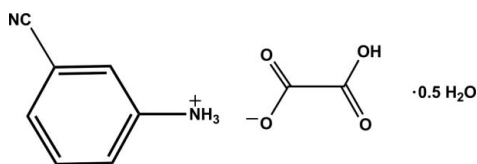
Received 26 April 2012; accepted 3 May 2012

Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.054; wR factor = 0.156; data-to-parameter ratio = 17.2.

In the title hydrated molecular salt, $\text{C}_7\text{H}_7\text{N}_2^+\cdot\text{C}_2\text{HO}_4^-\cdot 0.5\text{H}_2\text{O}$, contains a 3-cyanoanilinium cation, a hydrogen oxalate anion and half a water molecule in an asymmetric unit. The dihedral angle between the $\text{CO}_2(\text{H})$ and CO_2 planes of the hydrogen oxalate ion is $7.96(1)^\circ$. In the crystal, the components are linked by $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds, forming a layer lying parallel to the ac plane.

Related literature

For the properties of related compounds, see: Chen *et al.* (2000); Liu *et al.* (1999); Zhao *et al.* (2003). For the structures of related compounds, see: Dai & Chen (2011); Xu *et al.* (2011); Zheng (2011).



Experimental

Crystal data

$\text{C}_7\text{H}_7\text{N}_2^+\cdot\text{C}_2\text{HO}_4^-\cdot 0.5\text{H}_2\text{O}$
 $M_r = 217.18$
Monoclinic, $P2_1/c$
 $a = 15.1221(7)$ Å
 $b = 5.6518(1)$ Å

$c = 13.6926(6)$ Å
 $\beta = 113.22(4)^\circ$
 $V = 1075.5(3)$ Å³
 $Z = 4$
Mo $K\alpha$ radiation

$\mu = 0.11$ mm⁻¹
 $T = 173$ K

0.10 × 0.05 × 0.05 mm

Data collection

Rigaku Mercury2 (2 × 2 bin mode) diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
 $T_{\min} = 0.910$, $T_{\max} = 1.000$

7209 measured reflections
2446 independent reflections
1906 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$
 $wR(F^2) = 0.156$
 $S = 1.07$
2446 reflections
142 parameters

5 restraints
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.28$ e Å⁻³
 $\Delta\rho_{\min} = -0.24$ e Å⁻³

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

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1W}-\text{H1WA}\cdots\text{O1}^{\text{i}}$	0.82	1.96	2.767 (2)	166
$\text{N1}-\text{H1A}\cdots\text{O1}^{\text{ii}}$	0.89	1.91	2.797 (2)	172
$\text{N1}-\text{H1C}\cdots\text{O2}^{\text{iii}}$	0.89	1.96	2.778 (2)	152
$\text{O3}-\text{H3}\cdots\text{O2}^{\text{iii}}$	0.82	1.74	2.559 (2)	178
$\text{N1}-\text{H1B}\cdots\text{O1W}$	0.89	1.91	2.788 (2)	167

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

This work was supported by a start-up Grant from Southeast University, People's Republic of China.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2542).

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supporting information

Acta Cryst. (2012). E68, o1678 [doi:10.1107/S1600536812019824]

3-Cyanoanilinium hydrogen oxalate hemihydrate

Xin-Yuan Chen

S1. Comment

Salts of amide attracted more attention as phase transition dielectric materials for its application in micro-electronics, memory storage (Chen *et al.*, 2000; Liu, *et al.* 1999; Zhao, *et al.* 2003). With the purpose of obtaining phase transition crystals of 3-aminobenzonitrile salts, its interaction with various acids has been studied and we have elaborated a serie of new materials with this organic molecule (Dai & Chen 2011; Xu, *et al.* 2011; Zheng 2011). In this paper, we describe the crystal structure of the title compound.

The asymmetric unit is composed of a 3-cyanoanilinium cation, a carboxyformate anion, and a half molecule of water (Fig. 1). The geometric parameters of the title compound agree well with reported similar structure (Dai & Chen 2011). The cation is almost planar (r.m.s. deviation 0.0062 Å, benzene ring as the best plane).

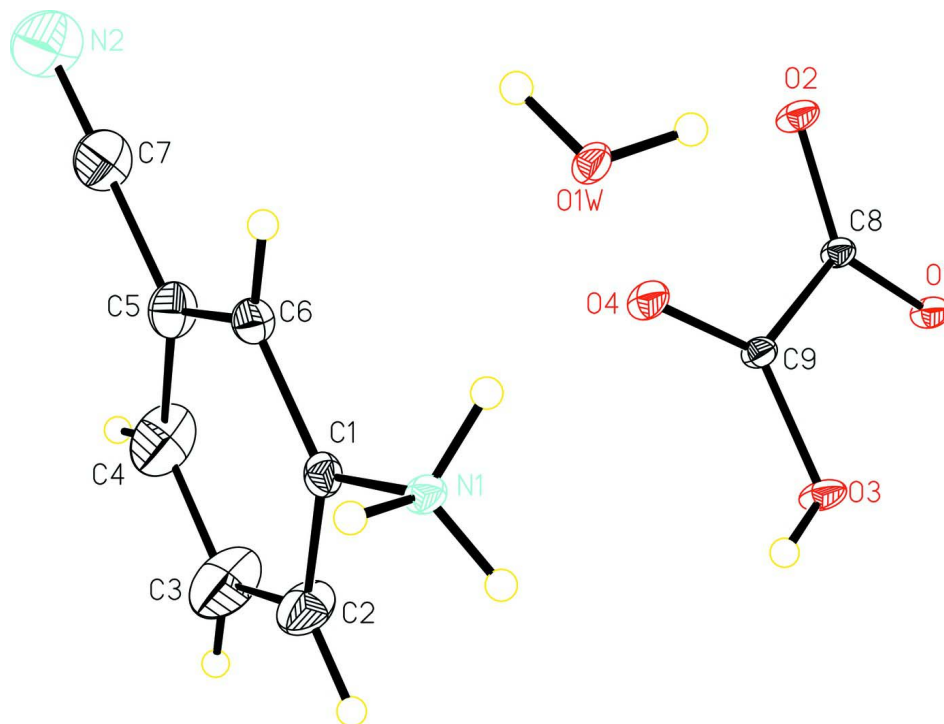
The cations are surrounded by the anions and water molecules *via* hydrogen bonds which play an important role in stabilizing the crystal structure. In the crystal structure, all the amino H atoms are involved in N—H \cdots O hydrogen bonds with carboxyformate anion and water molecule with the distances of 2.797 (2) Å, 2.778 (2) Å and 2.788 (2) Å, respectively. In addition, the H atoms of water molecule and carboxyformate anion are involved in the O—H \cdots O H-bonding interactions. In the crystal structure, those H-bonds link the ionic units into a two-dimensional sheets parallel to the *ac* plane (Table 1 and Fig. 2).

S2. Experimental

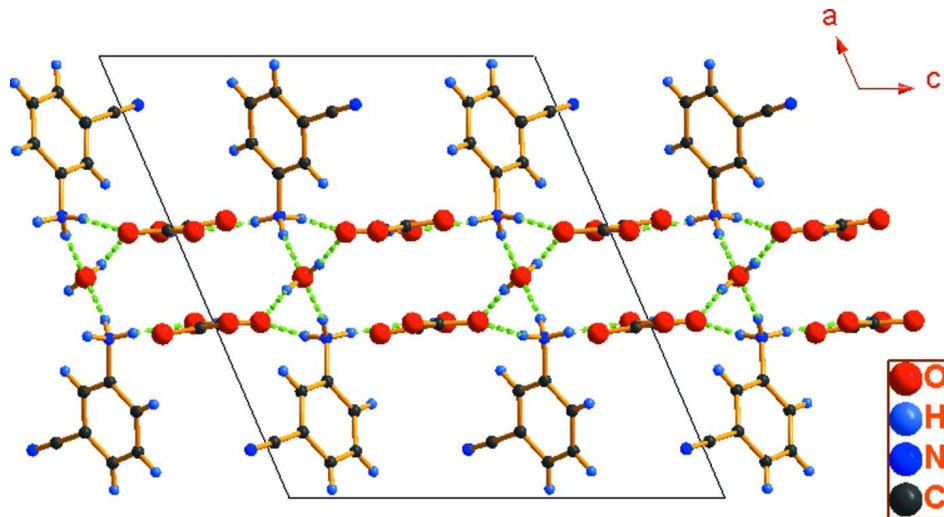
The commercial 3-aminobenzonitrile (3 mmol, 324 mg) and oxalic acid (3 mmol, 270 mg) were dissolved in 50 ml water/MeOH solution (1:1 *v/v*). The solvent was slowly evaporated in air affording colourless block-shaped crystals of the title compound suitable for X-ray analysis.

S3. Refinement

The H atoms were included in the refinement at geometrically idealized positions and treated in riding mode with O—H = 0.82 Å, N—H = 0.89 Å and C—H = 0.93 Å, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{O/N})$; a rotating-group model was used for the $-\text{NH}_3$ group.

**Figure 1**

A view of the title compound with the atomic numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

**Figure 2**

The crystal packing of the title compound viewing along the *b*-axis, showing the two-dimensional hydrogen-bonded network.

3-Cyanoanilinium hydrogen oxalate hemihydrate

Crystal data

 $C_7H_7N_2^+ \cdot C_2HO_4^- \cdot 0.5H_2O$ $M_r = 217.18$ Monoclinic, $P2_1/c$ Hall symbol: $-P\ 2_1c$ $a = 15.1221\ (7)\ \text{\AA}$ $b = 5.6518\ (1)\ \text{\AA}$ $c = 13.6926\ (6)\ \text{\AA}$ $\beta = 113.22\ (4)^\circ$ $V = 1075.5\ (3)\ \text{\AA}^3$ $Z = 4$ $F(000) = 452$ $D_x = 1.341\ \text{Mg m}^{-3}$ Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2446 reflections

 $\theta = 2.9\text{--}27.5^\circ$ $\mu = 0.11\ \text{mm}^{-1}$ $T = 173\ \text{K}$

Block, colorless

 $0.10 \times 0.05 \times 0.05\ \text{mm}$

Data collection

Rigaku Mercury2 (2x2 bin mode)
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 13.6612 pixels mm^{-1}

CCD profile fitting scans

Absorption correction: multi-scan

(CrystalClear; Rigaku, 2005)

 $T_{\min} = 0.910$, $T_{\max} = 1.000$

7209 measured reflections

2446 independent reflections

1906 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.034$ $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.9^\circ$ $h = -18 \rightarrow 19$ $k = -7 \rightarrow 7$ $l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.054$ $wR(F^2) = 0.156$ $S = 1.07$

2446 reflections

142 parameters

5 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0872P)^2 + 0.1364P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.28\ \text{e \AA}^{-3}$ $\Delta\rho_{\min} = -0.24\ \text{e \AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1W	0.5000	0.3943 (3)	0.7500	0.0237 (4)
H1WA	0.4708	0.3063	0.6999	0.036*
N1	0.63809 (11)	0.7280 (2)	0.75668 (11)	0.0247 (4)
H1A	0.6328	0.8305	0.8034	0.037*

H1B	0.5962	0.6106	0.7469	0.037*
H1C	0.6258	0.8012	0.6952	0.037*
C1	0.73556 (13)	0.6324 (3)	0.79701 (14)	0.0278 (4)
C6	0.75806 (14)	0.4443 (3)	0.86683 (15)	0.0312 (4)
H6A	0.7120	0.3818	0.8888	0.037*
C5	0.85041 (16)	0.3490 (4)	0.90408 (18)	0.0449 (6)
C7	0.87338 (18)	0.1547 (5)	0.9797 (2)	0.0579 (7)
C3	0.8941 (2)	0.6365 (8)	0.8017 (3)	0.0843 (11)
H3A	0.9400	0.7024	0.7805	0.101*
C2	0.80292 (17)	0.7312 (5)	0.7645 (2)	0.0547 (7)
H2A	0.7870	0.8596	0.7183	0.066*
N2	0.89001 (19)	0.0051 (5)	1.0408 (2)	0.0826 (9)
C4	0.9188 (2)	0.4440 (7)	0.8704 (2)	0.0730 (9)
H4A	0.9802	0.3793	0.8937	0.088*
O1	0.60131 (9)	-0.0466 (2)	0.39238 (9)	0.0266 (3)
O2	0.60400 (10)	-0.1979 (2)	0.54425 (9)	0.0294 (3)
O3	0.60355 (10)	0.3895 (2)	0.46709 (9)	0.0302 (3)
H3	0.6034	0.5206	0.4927	0.045*
O4	0.62804 (10)	0.2420 (2)	0.62874 (9)	0.0298 (3)
C9	0.61454 (12)	0.2186 (3)	0.53599 (13)	0.0216 (4)
C8	0.60611 (12)	-0.0294 (3)	0.48550 (13)	0.0210 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1W	0.0349 (10)	0.0193 (8)	0.0149 (8)	0.000	0.0076 (7)	0.000
N1	0.0353 (9)	0.0215 (7)	0.0201 (7)	-0.0007 (6)	0.0140 (6)	-0.0001 (6)
C1	0.0285 (10)	0.0333 (10)	0.0223 (8)	-0.0041 (7)	0.0107 (7)	-0.0045 (7)
C6	0.0315 (10)	0.0308 (10)	0.0305 (10)	-0.0006 (7)	0.0115 (8)	-0.0024 (8)
C5	0.0347 (12)	0.0507 (14)	0.0439 (13)	0.0079 (10)	0.0097 (9)	0.0010 (10)
C7	0.0420 (14)	0.0564 (16)	0.0646 (17)	0.0147 (11)	0.0097 (12)	0.0095 (14)
C3	0.0396 (16)	0.146 (3)	0.076 (2)	0.0062 (17)	0.0328 (15)	0.039 (2)
C2	0.0386 (13)	0.0800 (19)	0.0483 (14)	-0.0052 (11)	0.0200 (11)	0.0215 (13)
N2	0.0643 (16)	0.0727 (18)	0.092 (2)	0.0214 (13)	0.0107 (14)	0.0307 (15)
C4	0.0335 (14)	0.118 (3)	0.0714 (19)	0.0210 (15)	0.0244 (13)	0.0192 (19)
O1	0.0457 (8)	0.0193 (6)	0.0186 (6)	-0.0043 (5)	0.0168 (5)	-0.0029 (5)
O2	0.0541 (9)	0.0158 (6)	0.0209 (6)	-0.0013 (5)	0.0177 (6)	0.0005 (5)
O3	0.0592 (9)	0.0138 (6)	0.0219 (6)	-0.0003 (5)	0.0205 (6)	0.0005 (5)
O4	0.0505 (9)	0.0228 (7)	0.0177 (6)	-0.0020 (5)	0.0154 (5)	-0.0032 (5)
C9	0.0320 (9)	0.0166 (8)	0.0170 (8)	-0.0012 (6)	0.0105 (7)	0.0001 (6)
C8	0.0304 (9)	0.0158 (8)	0.0176 (8)	-0.0006 (6)	0.0104 (6)	0.0000 (6)

Geometric parameters (Å, °)

O1W—H1WA	0.8207	C3—C2	1.376 (4)
N1—C1	1.459 (2)	C3—C4	1.389 (5)
N1—H1A	0.8900	C3—H3A	0.9300
N1—H1B	0.8900	C2—H2A	0.9300

N1—H1C	0.8900	C4—H4A	0.9300
C1—C6	1.380 (3)	O1—C8	1.2521 (19)
C1—C2	1.380 (3)	O2—C8	1.255 (2)
C6—C5	1.392 (3)	O3—C9	1.314 (2)
C6—H6A	0.9300	O3—H3	0.8205
C5—C4	1.395 (4)	O4—C9	1.211 (2)
C5—C7	1.454 (4)	C9—C8	1.546 (2)
C7—N2	1.146 (4)		
C1—N1—H1A	109.5	C2—C3—C4	121.2 (3)
C1—N1—H1B	109.5	C2—C3—H3A	119.4
H1A—N1—H1B	109.5	C4—C3—H3A	119.4
C1—N1—H1C	109.5	C3—C2—C1	118.8 (2)
H1A—N1—H1C	109.5	C3—C2—H2A	120.6
H1B—N1—H1C	109.5	C1—C2—H2A	120.6
C6—C1—C2	121.57 (19)	C3—C4—C5	119.3 (2)
C6—C1—N1	118.97 (16)	C3—C4—H4A	120.3
C2—C1—N1	119.46 (18)	C5—C4—H4A	120.3
C1—C6—C5	119.32 (19)	C9—O3—H3	112.2
C1—C6—H6A	120.3	O4—C9—O3	126.41 (15)
C5—C6—H6A	120.3	O4—C9—C8	121.21 (15)
C6—C5—C4	119.8 (2)	O3—C9—C8	112.36 (13)
C6—C5—C7	118.5 (2)	O1—C8—O2	125.99 (15)
C4—C5—C7	121.7 (2)	O1—C8—C9	119.18 (14)
N2—C7—C5	177.9 (3)	O2—C8—C9	114.83 (14)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1WA \cdots O1 ⁱ	0.82	1.96	2.767 (2)	166
N1—H1A \cdots O1 ⁱⁱ	0.89	1.91	2.797 (2)	172
N1—H1C \cdots O2 ⁱⁱⁱ	0.89	1.96	2.778 (2)	152
O3—H3 \cdots O2 ⁱⁱⁱ	0.82	1.74	2.559 (2)	178
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