Ethylammonium hydrogen oxalate–oxalic acid (2/1)

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The reaction between ethylamine and oxalic acid in water in a 1:1 molar ratio afforded the title salt, $C_2H_8N^+ \cdot C_2HO_4^- \cdot 0.5C_2H_2O_4$. The hydrogen oxalate anions interact through hydrogen bonding and are organized into a chains propagating along the c-axis direction. The chains are connected to the neighbouring cations and oxalic acid molecules by N—H···O and O—H···O hydrogen bonds and N···O dipole–dipole contacts, leading to a supramolecular three-dimensional network.

3D view
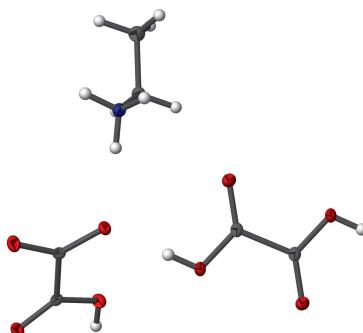
Chemical scheme
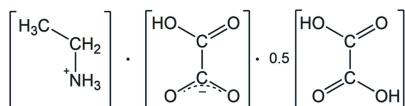
Structure description

Ammonium carboxylate networks obtained by mixing dicarboxylic acids with amines is of interest in the field of crystal engineering (Ballabh *et al.* 2002; Haynes & Pietersen, 2008; Dziuk *et al.* 2014*a*). These compounds exhibit a variety of structures that can lead, through non-covalent interactions (hydrogen bonding, π–π stacking, van der Waals and C—H···π contacts), to a large diversity of architectures and topologies. Dicarboxylic acids can act as polydirectional synthons, and amines, *via* the formation of ammonium, greatly increase the possible of linkages and interactions (Ivasenko & Perepichka, 2011; Yuge *et al.*, 2008; Lemmerer, 2011). To date, many examples of such crystalline networks from oxalic acid and hydrogen oxalate have been described, see for example: Dziuk *et al.* (2014*b,c*); Braga *et al.* (2013); Ejsmont (2006, 2007); Ejsmont & Zaleski (2006*a,b*); MacDonald *et al.* (2001). Our group has also contributed to this area by reporting recently two new structures of such compounds (Diallo *et al.*, 2015; Diop *et al.*, 2016). In a continuation of this work, we describe herein the synthesis and structure of the title salt **I**, isolated from an equimolar mixture of oxalic acid and ethylamine.

Compound **I** crystallizes in the monoclinic $C2/c$ space group with the asymmetric unit comprising of one ethylammonium cation ($C_2H_8N^+$), one hydrogen oxalate anion

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2$\cdots$O3^i	0.84	1.74	2.5717 (9)	173
N—H$A\cdots$O4	0.91	1.94	2.8472 (11)	177
N—H$B\cdots$O1^{ii}	0.91	2.04	2.9409 (11)	172
N—H$C\cdots$O6^{iii}	0.91	2.16	3.0400 (10)	163
O5—H5$\cdots$O4	0.84	1.68	2.5139 (10)	173

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

($C_2HO_4^-$) and a half-molecule of oxalic acid ($C_2H_2O_4$). The three components are linked together by several inter-molecular interactions (Table 1 and Fig. 1). The interatomic distances and angles of the ethylammonium cation are in the range of those previously measured for comparable salts (Ejsmont & Zaleski, 2006a; Ejsmont, 2006). Each $C_2H_8N^+$ cation is involved in N—H$\cdots$O hydrogen bonding with two distinct $C_2HO_4^-$ anions [N—H$A\cdots$O4 = 2.8472 (11) and N—H$B\cdots$O1 = 2.9409 (11) Å] and also with one neutral $C_2H_2O_4$ molecule [N—H$C\cdots$O6 = 3.0400 (10) Å]. These interactions are reinforced by van der Waals contacts involving $C_2H_8N^+$, and $C_2HO_4^-$ and $C_2H_2O_4$, respectively [N$\cdots$O3 = 2.8960 (11) and N$\cdots$O5 = 2.9423 (11) Å]. The hydrogen oxalate anion is twisted with an O3—C2—C1—O2 torsion angle of 168.94 (8)°. The C—C and C—O bond distances [C1—C2 = 1.5570 (13), C1—O1 = 1.2141 (12), C1—O2 = 1.3090 (11), C2—O3 = 1.2415 (11), C2—O4 = 1.2565 (12) Å] are similar to those observed in the literature for other organic salts containing this anion (Barnes, 2003; Essid *et al.*, 2013).

The hydrogen oxalate anions in **I** are linked into chains running parallel to the *c* axis by O2—H2$\cdots$O3 hydrogen bonds [2.5717 (9) Å]. Adjacent chains are bridged by neutral

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_2H_8N^+ \cdot C_2HO_4^- \cdot 0.5C_2H_2O_4$
M_r	360.28
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	100
a, b, c (Å)	21.1667 (8), 6.6243 (3), 11.3247 (4)
β (°)	91.509 (2)
V (Å^3)	1587.34 (11)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.14
Crystal size (mm)	0.47 × 0.3 × 0.17
Data collection	
Diffractometer	Bruker D8 Venture triumph Mo
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.712, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14201, 1829, 1624
R_{int}	0.027
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.075, 1.03
No. of reflections	1829
No. of parameters	113
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.50, −0.20

Computer programs: *APEX3* and *SAINT* (Bruker, 2014), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

oxalic acid molecules whose two OH groups participate in hydrogen-bonding interactions with two distinct hydrogen oxalate anions [O5—H5$\cdots$O4 = 2.5139 (10) Å], resulting in the formation of sheets. These sheets are stacked along the *b* axis with the ethylammonium cations intercalated between the sheets, generating a three-dimensional network (Fig. 2).

A search on the online portal of the Cambridge Structural Database (WebCSD; Thomas *et al.*, 2010) yielded 188 hits for ethylammonium salts and 25 hits for the hydrogen oxalate–oxalic acid combination.


Figure 1
View of the title salt showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dotted lines [symmetry codes: (i) $x, -y, \frac{1}{2} + z$; (ii) $1 - x, -y, 1 - z$; (iii) $1 - x, y, \frac{1}{2} - z$; (iv) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$].
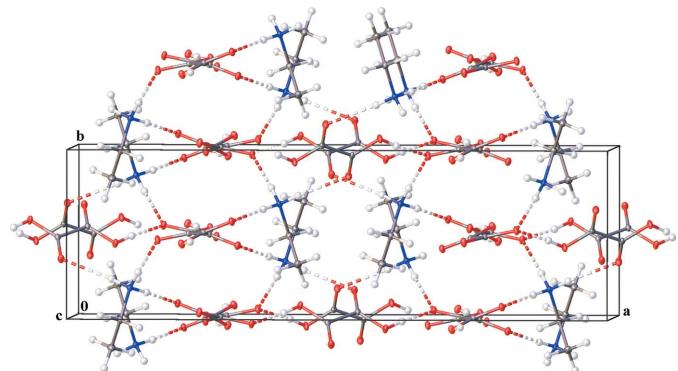

Figure 2
The packing, viewed along the *c* axis, showing the intermolecular hydrogen-bonding scheme (dashed lines) [colour code: C dark grey, H white, O red, N blue].

Synthesis and crystallization

All the chemicals were purchased from Aldrich (Germany) and used without further purification. The title compound was obtained by reacting equimolar amounts of oxalic acid (1.26 g, 0.02 mol) and ethylamine (50% in water, 2.6 ml, 0.02 mol), in 25 ml of water at 298 K. The resulting solution was allowed to evaporate at 338 K, leading after few days to colourless prismatic suitable for X-ray analysis.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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full crystallographic data

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Crystal data

$C_2H_8N^+ \cdot C_2HO_4^- \cdot 0.5C_2H_2O_4$
$M_r = 360.28$
Monoclinic, $C2/c$
$a = 21.1667 (8)$ Å
$b = 6.6243 (3)$ Å
$c = 11.3247 (4)$ Å
$\beta = 91.509 (2)°$
$V = 1587.34 (11)$ Å^3
$Z = 4$

$F(000) = 760$
$D_x = 1.508$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 7758 reflections
$\theta = 3.2–27.5°$
$\mu = 0.14$ mm^{-1}
$T = 100$ K
Prism, colourless
$0.47 \times 0.3 \times 0.17$ mm

Data collection

Bruker D8 Venture triumph Mo
   diffractometer
Radiation source: X-ray tube, Siemens KFF Mo
   2K-90C
TRIUMPH curved crystal monochromator
Detector resolution: 1024 x 1024 pixels mm^{-1}
φ and ω scans′
Absorption correction: multi-scan
   (SADABS; Bruker, 2014)

$T_{min} = 0.712$, $T_{max} = 0.746$
14201 measured reflections
1829 independent reflections
1624 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.2°$
$h = -27 \rightarrow 27$
$k = -8 \rightarrow 8$
$l = -14 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.075$
$S = 1.03$
1829 reflections
113 parameters
0 restraints

Hydrogen site location: inferred from
   neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0383P)^2 + 1.1891P]$
   where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.50$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}

Special details

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

Refinement. H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.99 Å (ethyl group) with $U_{iso}(H) = 1.2U_{eq}(C)$ or O—H = 0.84 Å (hydroxyl), N—H = 0.91 Å (ammonium) and C—H = 0.98 Å (methyl group) with $U_{iso}(H) = 1.5U_{eq}(O$ or N or C).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.75227 (4)	−0.01386 (14)	0.48767 (8)	0.01041 (19)
O1	0.80530 (3)	−0.07888 (11)	0.50554 (6)	0.01374 (16)
C2	0.72301 (4)	−0.00320 (14)	0.36024 (8)	0.01042 (19)
O2	0.71415 (3)	0.05216 (11)	0.56824 (6)	0.01410 (17)
H2	0.731311	0.037617	0.635430	0.021*
O3	0.76073 (3)	−0.03334 (11)	0.28000 (6)	0.01506 (17)
O4	0.66506 (3)	0.03493 (11)	0.34790 (6)	0.01416 (17)
N	0.61063 (4)	0.32342 (12)	0.18905 (7)	0.01222 (18)
HA	0.626827	0.230748	0.240865	0.018*
HB	0.639850	0.352637	0.134066	0.018*
HC	0.575304	0.272353	0.152545	0.018*
C4	0.59405 (5)	0.51142 (15)	0.25420 (9)	0.0146 (2)
H4A	0.630646	0.555335	0.304026	0.018*
H4B	0.558307	0.484025	0.306532	0.018*
C5	0.57599 (5)	0.67710 (16)	0.16787 (10)	0.0199 (2)
H5A	0.612135	0.708562	0.118768	0.030*
H5B	0.563719	0.798067	0.211491	0.030*
H5C	0.540406	0.632035	0.117391	0.030*
C3	0.52681 (4)	0.03067 (14)	0.45853 (8)	0.0111 (2)
O5	0.57859 (3)	−0.06835 (11)	0.48337 (6)	0.01553 (17)
H5	0.607761	−0.025239	0.441275	0.023*
O6	0.51865 (3)	0.15638 (11)	0.38186 (6)	0.01596 (17)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0115 (4)	0.0107 (4)	0.0091 (4)	−0.0012 (3)	0.0008 (3)	0.0006 (3)
O1	0.0110 (3)	0.0190 (4)	0.0111 (3)	0.0022 (3)	−0.0007 (2)	0.0001 (3)
C2	0.0111 (4)	0.0109 (4)	0.0092 (4)	0.0000 (3)	−0.0002 (3)	0.0009 (3)
O2	0.0135 (3)	0.0212 (4)	0.0076 (3)	0.0033 (3)	0.0003 (3)	−0.0010 (3)
O3	0.0112 (3)	0.0251 (4)	0.0090 (3)	0.0026 (3)	0.0014 (2)	−0.0004 (3)
O4	0.0094 (3)	0.0218 (4)	0.0113 (3)	0.0026 (3)	0.0007 (2)	0.0037 (3)
N	0.0109 (4)	0.0143 (4)	0.0114 (4)	−0.0009 (3)	−0.0008 (3)	0.0014 (3)
C4	0.0131 (5)	0.0162 (5)	0.0145 (5)	0.0005 (4)	0.0012 (4)	−0.0009 (4)
C5	0.0187 (5)	0.0164 (5)	0.0247 (5)	0.0010 (4)	0.0022 (4)	0.0048 (4)
C3	0.0102 (4)	0.0130 (4)	0.0100 (4)	−0.0011 (3)	0.0003 (3)	−0.0016 (3)
O5	0.0095 (3)	0.0216 (4)	0.0157 (4)	0.0027 (3)	0.0040 (3)	0.0060 (3)
O6	0.0126 (3)	0.0202 (4)	0.0152 (4)	0.0001 (3)	0.0012 (3)	0.0064 (3)

Geometric parameters (Å, °)

C1—O1	1.2141 (12)	C4—H4A	0.9900
C1—C2	1.5570 (13)	C4—H4B	0.9900
C1—O2	1.3090 (11)	C4—C5	1.5122 (14)
C2—O3	1.2415 (11)	C5—H5A	0.9800

C2—O4	1.2565 (12)	C5—H5B	0.9800
O2—H2	0.8400	C5—H5C	0.9800
N—HA	0.9100	C3—C3ⁱ	1.5467 (18)
N—HB	0.9100	C3—O5	1.3016 (12)
N—HC	0.9100	C3—O6	1.2121 (12)
N—C4	1.4940 (12)	O5—H5	0.8400
O1—C1—C2	120.93 (8)	N—C4—C5	110.14 (8)
O1—C1—O2	125.90 (9)	H4A—C4—H4B	108.1
O2—C1—C2	113.17 (8)	C5—C4—H4A	109.6
O3—C2—C1	115.04 (8)	C5—C4—H4B	109.6
O3—C2—O4	126.56 (9)	C4—C5—H5A	109.5
O4—C2—C1	118.40 (8)	C4—C5—H5B	109.5
C1—O2—H2	109.5	C4—C5—H5C	109.5
HA—N—HB	109.5	H5A—C5—H5B	109.5
HA—N—HC	109.5	H5A—C5—H5C	109.5
HB—N—HC	109.5	H5B—C5—H5C	109.5
C4—N—HA	109.5	O5—C3—C3ⁱ	111.32 (10)
C4—N—HB	109.5	O6—C3—C3ⁱ	121.50 (11)
C4—N—HC	109.5	O6—C3—O5	127.18 (9)
N—C4—H4A	109.6	C3—O5—H5	109.5
N—C4—H4B	109.6		
O1—C1—C2—O3	−11.28 (13)	O2—C1—C2—O3	168.94 (8)
O1—C1—C2—O4	169.03 (9)	O2—C1—C2—O4	−10.75 (12)

Symmetry code: (i) −x+1, −y, −z+1.

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O2—H2⋯O3ⁱⁱ	0.84	1.74	2.5717 (9)	173
N—H*A*⋯O4	0.91	1.94	2.8472 (11)	177
N—H*B*⋯O1ⁱⁱⁱ	0.91	2.04	2.9409 (11)	172
N—H*C*⋯O6ⁱᵛ	0.91	2.16	3.0400 (10)	163
O5—H5⋯O4	0.84	1.68	2.5139 (10)	173

Symmetry codes: (ii) *x*, −*y*, *z*+1/2; (iii) −*x*+3/2, *y*+1/2, −*z*+1/2; (iv) −*x*+1, *y*, −*z*+1/2.