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5-Carboxy-1-carboxymethyl-2-oxidopyridinium

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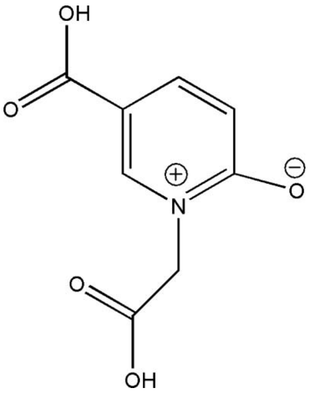
Key indicators: single-crystal X-ray study; *T* = 296 K; mean σ(C–C) = 0.002 Å; *R* factor = 0.036; *wR* factor = 0.106; data-to-parameter ratio = 11.0.

The title compound, $C_8H_7NO_5$, is a new betaine derivative obtained by the reaction of chloroacetic acid with 6-hydroxynicotinic acid under basic conditions. The molecule is planar except for the carboxymethyl group, which makes a dihedral angle of 77.40 (2)° with the pyridinium ring. The crystal structure is stabilized by intermolecular C—H⋯O and O—H⋯O hydrogen bonds to form a three-dimensional network.

Related literature

For related literature, see: Chen & Mak (1991); Gao *et al.* (2004); Tomono *et al.* (2005).



Experimental

Crystal data

$C_8H_7NO_5$
M_r = 197.15
Monoclinic, $P2_1/c$
a = 8.0116 (3) Å
b = 10.1247 (4) Å
c = 10.6618 (4) Å
β = 101.788 (2)°
V = 846.59 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.13 mm^{-1}
T = 296 (2) K
0.31 × 0.24 × 0.22 mm

Data collection

Bruker APEXII area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.960, T_{max} = 0.972
5747 measured reflections
1480 independent reflections
1311 reflections with $I > 2/s(I)$
R_{int} = 0.054

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.106
S = 1.09
1480 reflections
134 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1—H1*A*⋯O2^{i}	0.872 (17)	1.752 (18)	2.6219 (17)	176 (3)
O4—H4*A*⋯O3^{ii}	0.855 (16)	1.709 (18)	2.5411 (16)	164 (2)
C3—H3⋯O5^{iii}	0.93	2.56	3.4170 (17)	154
C7—H7*A*⋯O4^{iv}	0.97	2.55	3.3649 (19)	142

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2002); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: YM2052).

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supplementary materials

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5-Carboxy-1-carboxymethyl-2-oxidopyridinium

Y.-H. He and **Y.-L. Feng**

Comment

Pyridinium carboxylate salts, the analogue of betaine compounds are normally zwitterions containing a carboxylate group and a quaternary ammonium group. Owing to its versatile coordination behavior to metal ions, a large amount of betaine complexes have been reported,such as bis(pyridiniopropionato)disilver diperchlorate and dinitratobis(pyridiniopropionato)disilver(Chen & Mak, 1991), $Mg(C_7H_6NO_3)_2(H_2O)_4$(Gao *et al.*, 2004) and 3-Methoxy-carbonyl-1- methylpyridiniumbis(2-thioxo-1,3-dithiole-4,5-dithiolato) nickelate(II) (Tomono *et al.*, 2005). The title compound (1), is a dicarboxylic acid analogue of betaine (Fig.1). The 6-oxo-1,6-dihydropyridine-3-carboxylate fragment, O1/O2/O3/(C1—C6), is essentially planar with maximum deviation of 0.061 (1)Å for O2 atom from the least square plane and perpendicular to the acetate fragment, O4/O5/C8/C7, by 76.39 (7) Å.

The ^{1}H NMR spectrum reveals the hydroxyl is deprotonated and the two carboxyl are all protonated, which means the title compound is a traditional inner salt.

In the crystal structure, the molecules are linked by C—H···O and O—H···O intermolecular hydrogen bonds (symmetry codes as in table 2) to form a three dimensional network (Fig.2).

Experimental

The mixture of chloroacetic acid (2.84 g, 30 mmol) and 6-hydroxy-nicotinic acid (1.39 g, 10 mmol) was stirred under basic condition and refluxed at 90°C for 3 h, in which sodium hydroxide solution was added to keep the pH value around 11. Then the pH value was adjusted to about 3 by adding concentrated hydrochloric acid. Large quantity of light yellow precipitate was obtained with the yield of 90%.

Then colorless rhombus-shaped crystal of (I) were gained in the filtrate. And the melting point of the crystal is about 299°C.

Refinement

The H atoms bonded to C atoms were positioned geometrically [aromatic C—H 0.93 Å and aliphatic C—H = 0.97 Å, $U_{iso}(H) = 1.2U_{eq}(C)$]. The H atoms bonded to O atoms were located in a difference Fourier maps and refined with the O—H distance restrained to 0.82 (2)Å [$U_{iso}(H) = -1.5U_{eq}(O)$].

Figures

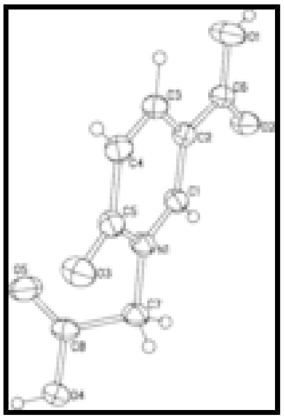

Fig. 1. A view of the molecule of (I), showing the atom-labelling scheme. displacement ellipsoids are shown at the 30% probability level.

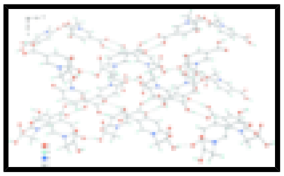

Fig. 2. A packing of (I) viewed down the *c* axis.

5-Carboxy-1-carboxymethyl-2-oxidopyridinium

Crystal data

$C_8H_7NO_5$

$M_r = 197.15$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 8.0116$ (3) Å

$b = 10.1247$ (4) Å

$c = 10.6618$ (4) Å

$\beta = 101.788$ (2)°

$V = 846.59$ (6) Å^3

$Z = 4$

$F_{000} = 408$

$D_x = 1.547$ Mg m^{-3}

Mo *K*α radiation
$\lambda = 0.71073$ Å

Cell parameters from 6859 reflections

$\theta = 2.6$–25.0°

$\mu = 0.13$ mm^{-1}

$T = 296$ (2) K

Block, colourless

0.31 × 0.24 × 0.22 mm

Data collection

Bruker APEX II area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293(2)$ K

ω scans

Absorption correction: empirical (using intensity measurements)
(SADABS; Sheldrick, 1996)

$T_{min} = 0.960$, $T_{max} = 0.972$

1480 independent reflections

1311 reflections with $I > 2/s(I)$

$R_{int} = 0.054$

$\theta_{max} = 25.0$°

$\theta_{min} = 2.6$°

$h = -9 \rightarrow 9$

$k = -12 \rightarrow 10$

5747 measured reflections

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.106$

$S = 1.09$

1480 reflections

134 parameters

2 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0568P)^2 + 0.1486P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = <0.003$

$\Delta\rho_{max} = 0.16$ e Å^{-3}

$\Delta\rho_{min} = -0.19$ e Å^{-3}

Extinction correction: SHELXL97, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.051 (6)

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 > 2sigma(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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.00147 (19)	0.14327 (14)	−0.09773 (12)	0.0710 (4)
H1A	−0.038 (3)	0.0630 (19)	−0.099 (3)	0.106*
O2	0.13230 (14)	0.09344 (11)	0.10199 (10)	0.0518 (3)
O3	0.39426 (15)	0.66491 (11)	0.08187 (10)	0.0549 (3)
O4	0.47211 (14)	0.65489 (12)	0.43812 (11)	0.0539 (4)
H4A	0.427 (3)	0.713 (2)	0.479 (2)	0.081*
O5	0.21283 (15)	0.62620 (16)	0.32046 (13)	0.0746 (5)
N1	0.33915 (15)	0.46367 (12)	0.15334 (11)	0.0396 (3)
C1	0.26468 (18)	0.34362 (14)	0.13670 (13)	0.0396 (4)
H1	0.2821	0.2842	0.2047	0.048*
C2	0.16493 (17)	0.30746 (15)	0.02314 (13)	0.0398 (4)
C3	0.13783 (18)	0.40021 (16)	−0.07807 (13)	0.0432 (4)
H3	0.0688	0.3781	−0.1564	0.052*
C4	0.21137 (19)	0.52053 (16)	−0.06178 (13)	0.0443 (4)

H4	0.1920	0.5803	−0.1294	0.053*
C5	0.31834 (18)	0.55812 (15)	0.05714 (13)	0.0409 (4)
C6	0.09656 (18)	0.17228 (16)	0.01153 (13)	0.0434 (4)
C7	0.44647 (19)	0.49939 (15)	0.27633 (13)	0.0441 (4)
H7B	0.5537	0.5348	0.2623	0.053*
H7A	0.4712	0.4209	0.3291	0.053*
C8	0.36079 (18)	0.60041 (16)	0.34566 (13)	0.0417 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0968 (10)	0.0518 (8)	0.0493 (7)	−0.0166 (7)	−0.0205 (6)	−0.0018 (6)
O2	0.0569 (7)	0.0487 (7)	0.0449 (6)	−0.0075 (5)	−0.0012 (5)	0.0029 (5)
O3	0.0720 (7)	0.0442 (7)	0.0446 (6)	−0.0102 (5)	0.0028 (5)	0.0066 (5)
O4	0.0523 (6)	0.0536 (8)	0.0500 (7)	0.0001 (5)	−0.0034 (5)	−0.0182 (5)
O5	0.0466 (7)	0.1110 (12)	0.0615 (8)	0.0029 (7)	0.0000 (5)	−0.0302 (8)
N1	0.0501 (7)	0.0360 (7)	0.0293 (6)	0.0008 (5)	−0.0001 (5)	0.0004 (5)
C1	0.0486 (8)	0.0361 (8)	0.0326 (7)	0.0035 (6)	0.0045 (6)	0.0012 (6)
C2	0.0419 (7)	0.0410 (8)	0.0349 (7)	0.0045 (6)	0.0038 (5)	−0.0037 (6)
C3	0.0457 (8)	0.0508 (10)	0.0303 (7)	0.0065 (7)	0.0012 (6)	−0.0025 (6)
C4	0.0523 (8)	0.0476 (9)	0.0310 (7)	0.0064 (7)	0.0040 (6)	0.0061 (6)
C5	0.0485 (8)	0.0394 (8)	0.0342 (7)	0.0033 (6)	0.0070 (6)	0.0031 (6)
C6	0.0457 (8)	0.0451 (9)	0.0362 (7)	0.0010 (6)	0.0013 (6)	−0.0049 (7)
C7	0.0537 (8)	0.0391 (9)	0.0334 (7)	0.0005 (6)	−0.0053 (6)	0.0006 (6)
C8	0.0455 (8)	0.0457 (9)	0.0312 (7)	−0.0078 (6)	0.0015 (6)	0.0011 (6)

Geometric parameters (Å, °)

O1—C6	1.2888 (18)	C1—H1	0.9300
O1—H1A	0.872 (17)	C2—C3	1.413 (2)
O2—C6	1.2396 (18)	C2—C6	1.470 (2)
O3—C5	1.2422 (19)	C3—C4	1.349 (2)
O4—C8	1.3086 (18)	C3—H3	0.9300
O4—H4A	0.855 (16)	C4—C5	1.429 (2)
O5—C8	1.1897 (19)	C4—H4	0.9300
N1—C1	1.3497 (19)	C7—C8	1.507 (2)
N1—C5	1.3872 (19)	C7—H7B	0.9700
N1—C7	1.4591 (17)	C7—H7A	0.9700
C1—C2	1.3577 (19)		
C6—O1—H1A	111.6 (18)	C5—C4—H4	119.3
C8—O4—H4A	112.2 (15)	O3—C5—N1	117.60 (13)
C1—N1—C5	122.72 (12)	O3—C5—C4	126.79 (14)
C1—N1—C7	120.32 (12)	N1—C5—C4	115.60 (13)
C5—N1—C7	116.96 (12)	O2—C6—O1	123.81 (15)
N1—C1—C2	121.59 (13)	O2—C6—C2	120.74 (13)
N1—C1—H1	119.2	O1—C6—C2	115.44 (14)
C2—C1—H1	119.2	N1—C7—C8	111.42 (12)
C1—C2—C3	118.19 (14)	N1—C7—H7B	109.3

C1—C2—C6	117.87 (13)	C8—C7—H7B	109.3
C3—C2—C6	123.90 (13)	N1—C7—H7A	109.3
C4—C3—C2	120.45 (13)	C8—C7—H7A	109.3
C4—C3—H3	119.8	H7B—C7—H7A	108.0
C2—C3—H3	119.8	O5—C8—O4	124.89 (15)
C3—C4—C5	121.44 (13)	O5—C8—C7	124.81 (14)
C3—C4—H4	119.3	O4—C8—C7	110.30 (12)

C5—N1—C1—C2	0.5 (2)	C3—C4—C5—O3	178.75 (15)
C7—N1—C1—C2	−179.65 (13)	C3—C4—C5—N1	−0.6 (2)
N1—C1—C2—C3	−1.1 (2)	C1—C2—C6—O2	−1.5 (2)
N1—C1—C2—C6	176.75 (12)	C3—C2—C6—O2	176.21 (13)
C1—C2—C3—C4	0.8 (2)	C1—C2—C6—O1	179.41 (13)
C6—C2—C3—C4	−176.91 (13)	C3—C2—C6—O1	−2.9 (2)
C2—C3—C4—C5	0.1 (2)	C1—N1—C7—C8	−108.72 (15)
C1—N1—C5—O3	−179.10 (13)	C5—N1—C7—C8	71.10 (16)
C7—N1—C5—O3	1.1 (2)	N1—C7—C8—O5	16.2 (2)
C1—N1—C5—C4	0.3 (2)	N1—C7—C8—O4	−164.33 (12)
C7—N1—C5—C4	−179.49 (12)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1A···O2^{i}	0.872 (17)	1.752 (18)	2.6219 (17)	176 (3)
O4—H4A···O3^{ii}	0.855 (16)	1.709 (18)	2.5411 (16)	164 (2)
C3—H3···O5^{iii}	0.93	2.56	3.4170 (17)	154
C7—H7A···O4^{iv}	0.97	2.55	3.3649 (19)	142

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

Fig. 1

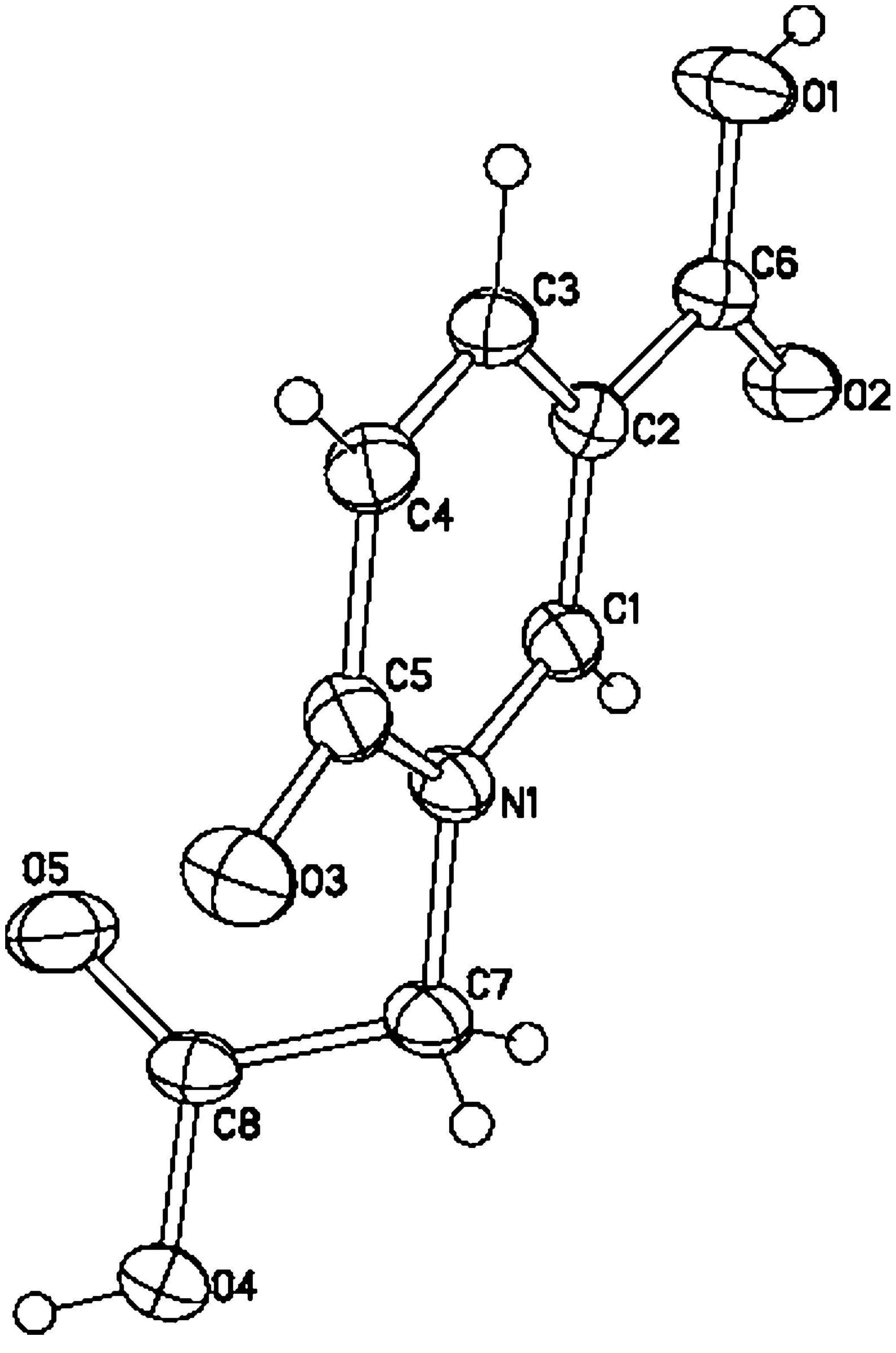

Fig. 2