organic compounds

Bis[(E)-4-(hydroxyiminomethyl)-pyridinium] oxalate

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The formula unit of the title compound, $2C_6H_7N_2O^+ \cdot C_2O_4^{2-}$, comprises two symmetry-equivalent 4-(hydroxyiminomethyl)-pyridinium cations on general positions, linked through hydrogen bonding *via* an oxalate anion that resides on a crystallographic centre of symmetry. The crystal structure consists of infinite chains of cations and oxalate anions directed by O—H···O and multicentre N—H···O intermolecular hydrogen-bonding interactions.

Related literature

For related literature, see: Martínez-Ripoll & Lorenz (1976*a*,*b*).
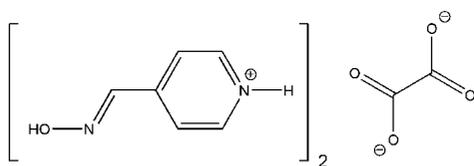
Experimental

Crystal data

$2C_6H_7N_2O^+ \cdot C_2O_4^{2-}$
$M_r = 334.30$
Monoclinic, $P2_1/c$
$a = 4.8895$ (2) Å
$b = 15.2920$ (5) Å
$c = 10.0491$ (4) Å
$\beta = 103.967$ (4)°
$V = 729.16$ (5) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.12$ mm^{-1}
$T = 113$ (2) K
$0.55 \times 0.11 \times 0.10$ mm

Data collection

Oxford Diffraction Sapphire2 CCD diffractometer
Absorption correction: multi-scan (*ABSPACK* in *CrysAlis RED*; Oxford Diffraction, 2006)
$T_{min} = 0.856$, $T_{max} = 0.990$
11067 measured reflections
1281 independent reflections
961 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.089$
$S = 1.04$
1281 reflections
110 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O71	0.88	1.84	2.660 (2)	154
N1—H1···O72[i]	0.88	2.30	2.897 (2)	126
O43—H43···O72[ii]	0.84	1.76	2.571 (2)	163

Symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (ii) $x - 1, y, z + 1$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2007); software used to prepare material for publication: *SHELXL97*.

References

Brandenburg, K. (2007). *DIAMOND*. Version 3.1e. Crystal Impact GbR, Bonn, Germany.
Martínez-Ripoll, M. & Lorenz, H. P. (1976*a*). *Acta Cryst.* B**32**, 2322–2325.
Martínez-Ripoll, M. & Lorenz, H. P. (1976*b*). *Acta Cryst.* B**32**, 2325–2328.
Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171.32.4. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

supporting information

Bis[(*E*)-4-(hydroxyiminomethyl)pyridinium] oxalate

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S1. Comment

Whereas the crystal structures of the (E)- and (Z)-isomers of pyridin-4-carbaldehyde oxime are known (Martínez-Ripoll & Lorenz, 1976*a*,b), no structural investigation of an (*E*)-pyridinium-4-carbaldehyde oxime salt has been reported yet (as far as we can ascertain). The free base (*E*)-pyridin-4-carbaldehyde oxime acts as hydrogen bonding donor and acceptor. This leads to the formation of infinite chains in the crystal structure, where one molecule is connected to a neighbouring molecule by an O—H···N hydrogen bond. Its protonated analoque, the pyridinium-4-carbaldehyde oxime cation is able to act as a twofold hydrogen bonding donor. Oxalate anions are well known as multiple hydrogen bonding acceptors. Herein we report the crystal and molecular structure of the oxalic acid salt of (*E*)-pyridinium-4-carbaldehyde oxime oxalate (Scheme 1).

An *ORTEP* diagram of the title compound is given in Fig. 1: selected geometric parameters are in table 1. The molecular geometry parameters are of usual order of magnitude and for the cation similar to its parent freebase compound (Martínez-Ripoll & Lorenz, 1976*a*). The bond length of the oxime group N42—C42 and O43—N42 are 1.274 (2) and 1.380 (2) Å, respectively. The C4—C41 bond is relatively short with 1.468 (2) Å due to partial delocalization of the oxime group with the pyridinium ring. Like the freebase (*E*)-pyridin-4-carbaldehyde oxime the cation of the title compound is not planar. The torsion angle of the N atom N42 of oxime group out of the plane of the pyridinium ring is 20.0 (2) °. The bond length of C7—C7i is relatively long with 1.563 (3) Å as expected for an oxalate anion.

The crystal structure of the title compound is given in Fig. 2 as a projection along the *a* axis direction. The O atom O43 of the oxime group of the pyridinium-4-carbaldehyde oxime cation is connected to O72 of the oxalate anion by a single hydrogen bond. The O43—H···O72 distance is 2.571 (2) Å indicating a moderate strong hydrogen bond. The N atom of the pyridinium ring is directed to the oxalate anion due to electrostatic interactions. The N1—H···O71 and N1—H···O72 is 2.660 (2) Å and 2.897 (2) Å, respectively. An increased hydrogen bond distance is indicative for multicentre bonding.

S2. Experimental

Pyridin-4-carbaldehyde oxime (Acros) was allowed to react with oxalyl dichloride (2:1 molar ratio) in dry tetrahydro-furan at ambient temperature. The resulting precipitate was filtered off, dried on air and dissolved in a mixture of di-methylformamide and water (1:1). This solution was allowed to evaporate slowly at room temperature. Single crystals of the title compound suitable for X-ray diffraction were obtained after two weeks.

S3. Refinement

The structure was refined by full-matrix least-squares refinement against F^2 using *SHELXL97* (Sheldrick, 1997). All non-hydrogen atoms were refined freely by using anisotropic displacement parameters. Hydrogen atoms were placed on geometrically calculated positions and refined with riding models in all cases with $U_{iso}(H) = 1.2$ (1.5 for hydroxy groups)
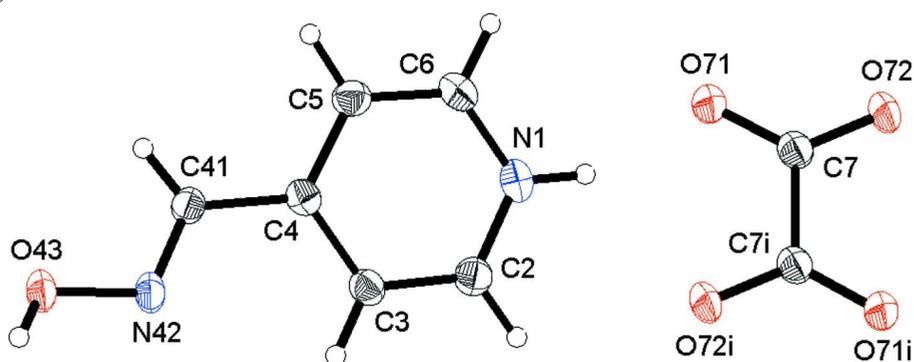
times $U_{eq}(C, N, O)$.

Figure 1

ORTEP diagram of the title compound. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are drawn at arbitrary size and symmetry generated atoms are labelled with a.
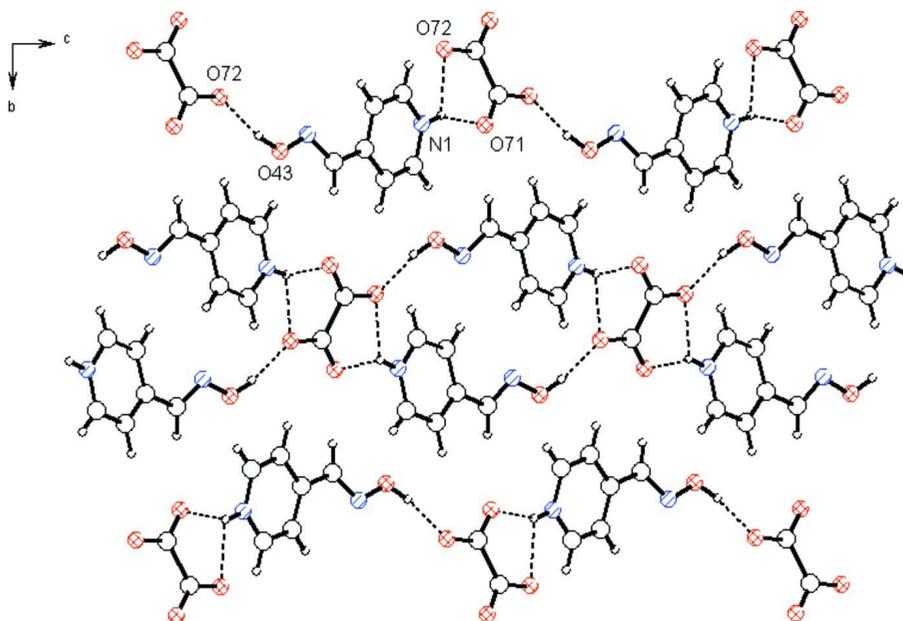
Figure 2

The crystal structure of the title compound viewed along the *a* axis direction. Hydrogen bonds are represented by dashed lines.

Bis[(*E*)-4-(hydroxyiminomethyl)pyridinium] oxalate

Crystal data

$2C_6H_7N_2O^+ \cdot C_2O_4^{2-}$	$V = 729.16 (5)$ Å^3
$M_r = 334.30$	$Z = 2$
Monoclinic, $P2_1/c$	$F(000) = 348$
Hall symbol: -P 2ybc	$D_x = 1.523$ Mg m^{-3}
$a = 4.8895 (2)$ Å	Melting point: not measured K
$b = 15.2920 (5)$ Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$c = 10.0491 (4)$ Å	Cell parameters from 3854 reflections
$\beta = 103.967 (4)°$	$\theta = 2.5–36.5°$

$\mu = 0.12$ mm^{-1}	Needle, colourless
$T = 113$ K	$0.55 \times 0.11 \times 0.10$ mm

Data collection

Oxford Diffraction Sapphire2 CCD diffractometer	$T_{min} = 0.856$, $T_{max} = 0.990$
Radiation source: Enhance (Mo) X-ray Source	11067 measured reflections
Graphite monochromator	1281 independent reflections
Detector resolution: 8.4171 pixels mm^{-1}	961 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.051$
Absorption correction: multi-scan (ABSPACK in *CrysAlis RED*; Oxford Diffraction, 2006)	$\theta_{max} = 25.0°$, $\theta_{min} = 3.4°$
	$h = -5 \rightarrow 5$
	$k = -18 \rightarrow 18$
	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.032$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.089$	
$S = 1.04$	H-atom parameters constrained
1281 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0522P)^2 + 0.0471P]$
110 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.23$ e Å^{-3}
	$\Delta\rho_{min} = -0.23$ e Å^{-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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.6117 (3)	0.60445 (9)	0.71059 (13)	0.0247 (4)
H1	0.7064	0.5883	0.6505	0.030*
N42	0.1137 (3)	0.62604 (9)	1.08097 (13)	0.0241 (3)
C2	0.4916 (3)	0.54332 (11)	0.77268 (16)	0.0243 (4)
H2	0.5118	0.4833	0.7528	0.029*
C3	0.3397 (3)	0.56697 (11)	0.86471 (16)	0.0225 (4)
H3	0.2507	0.5235	0.9072	0.027*
C4	0.3160 (3)	0.65497 (10)	0.89594 (15)	0.0204 (4)
C5	0.4469 (3)	0.71665 (10)	0.83047 (16)	0.0245 (4)
H5	0.4357	0.7771	0.8503	0.029*
C6	0.5916 (3)	0.68968 (11)	0.73751 (16)	0.0257 (4)
H6	0.6787	0.7317	0.6915	0.031*
C41	0.1582 (3)	0.68277 (10)	0.99568 (15)	0.0224 (4)

H41	0.0914	0.7411	0.9966	0.027*
O43	−0.0394 (3)	0.65975 (7)	1.16792 (12)	0.0293 (3)
H43	−0.0141	0.6286	1.2387	0.044*
O71	0.8730 (2)	0.60681 (7)	0.50707 (11)	0.0301 (3)
O72	1.1057 (2)	0.54797 (7)	0.36342 (11)	0.0292 (3)
C7	0.9929 (3)	0.54522 (10)	0.46309 (16)	0.0225 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O43	0.0383 (7)	0.0282 (7)	0.0282 (7)	0.0070 (5)	0.0211 (6)	0.0022 (5)
N1	0.0233 (8)	0.0312 (8)	0.0215 (7)	0.0015 (6)	0.0089 (6)	−0.0007 (6)
N42	0.0256 (8)	0.0262 (8)	0.0236 (7)	0.0039 (6)	0.0123 (6)	−0.0010 (6)
C2	0.0249 (9)	0.0242 (9)	0.0237 (9)	0.0009 (7)	0.0057 (7)	0.0007 (7)
C3	0.0236 (9)	0.0235 (9)	0.0213 (8)	0.0008 (7)	0.0073 (7)	0.0031 (7)
C4	0.0191 (8)	0.0245 (9)	0.0169 (8)	0.0019 (7)	0.0030 (7)	0.0032 (6)
C5	0.0276 (9)	0.0212 (9)	0.0247 (9)	0.0002 (7)	0.0064 (7)	0.0024 (7)
C6	0.0260 (9)	0.0288 (9)	0.0234 (9)	−0.0033 (8)	0.0080 (7)	0.0035 (7)
C41	0.0242 (9)	0.0218 (9)	0.0220 (9)	0.0027 (7)	0.0072 (7)	−0.0003 (6)
O71	0.0411 (7)	0.0239 (6)	0.0315 (7)	0.0038 (5)	0.0210 (6)	0.0022 (5)
O72	0.0382 (7)	0.0292 (7)	0.0268 (6)	0.0032 (5)	0.0207 (6)	0.0038 (5)
C7	0.0226 (9)	0.0249 (9)	0.0207 (8)	−0.0035 (7)	0.0064 (7)	−0.0019 (7)

Geometric parameters (Å, º)

O43—N42	1.380 (2)	C4—C5	1.391 (2)
O43—H43	0.8400	C4—C41	1.468 (2)
N1—C2	1.336 (2)	C5—C6	1.364 (2)
N1—C6	1.340 (2)	C5—H5	0.9500
N1—H1	0.8800	C6—H6	0.9500
N42—C41	1.274 (2)	C41—H41	0.9500
C2—C3	1.367 (2)	O71—C7	1.246 (2)
C2—H2	0.9500	O72—C7	1.255 (2)
C3—C4	1.393 (2)	C7—C7^i	1.563 (3)
C3—H3	0.9500		
N42—O43—H43	109.5	C3—C4—C41	121.31 (14)
C2—N1—C6	121.63 (14)	C6—C5—C4	119.51 (15)
C2—N1—H1	119.2	C6—C5—H5	120.2
C6—N1—H1	119.2	C4—C5—H5	120.2
C41—N42—O43	112.22 (13)	N1—C6—C5	120.53 (15)
N1—C2—C3	120.17 (15)	N1—C6—H6	119.7
N1—C2—H2	119.9	C5—C6—H6	119.7
C3—C2—H2	119.9	N42—C41—C4	117.73 (14)
C2—C3—C4	119.75 (15)	N42—C41—H41	121.1
C2—C3—H3	120.1	C4—C41—H41	121.1
C4—C3—H3	120.1	O71—C7—O72	126.36 (15)
C5—C4—C3	118.40 (15)	O71—C7—C7^i	118.13 (17)

C5—C4—C41	120.30 (15)	O72—C7—C7^i	115.51 (17)
C6—N1—C2—C3	1.1 (2)	C2—N1—C6—C5	0.2 (2)
N1—C2—C3—C4	−1.5 (2)	C4—C5—C6—N1	−1.0 (2)
C2—C3—C4—C5	0.7 (2)	O43—N42—C41—C4	−179.24 (12)
C2—C3—C4—C41	−179.11 (14)	C5—C4—C41—N42	−159.83 (16)
C3—C4—C5—C6	0.5 (2)	C3—C4—C41—N42	20.0 (2)
C41—C4—C5—C6	−179.66 (14)		

Symmetry code: (i) −*x*+2, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O71	0.88	1.84	2.660 (2)	154
N1—H1···O72^i	0.88	2.30	2.897 (2)	126
O43—H43···O72^{ii}	0.84	1.76	2.571 (2)	163

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