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Pyridine-2-carboxamidrazonium hydrogenoxalate

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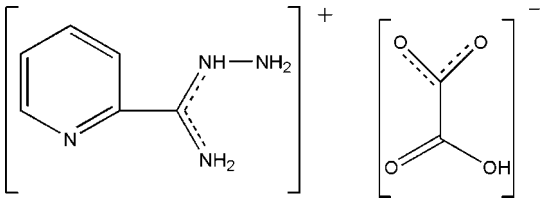
Key indicators: single-crystal X-ray study; T = 299 K; mean σ(C–C) = 0.004 Å; R factor = 0.058; wR factor = 0.137; data-to-parameter ratio = 15.2.

In the title structure, $C_6H_9N_4^+\cdot C_2HO_4^-$, there are O—H···O, N—H···N and N—H···O hydrogen bonds that form a three-dimensional network. The hydrogenoxalate anions are bonded by O—H···O hydrogen bonds to form chains parallel to the b axis. The pyridine-2-carboxamidrazonium cations are linked by the N—H···N bonds into dimeric centrosymmetric entities with an $R_2^2(10)$ motif. These dimers are connected to hydrogenoxalates *via* N—H···O hydrogen bonds. In addition, there is a weak C—H···O hydrogen bond, as well as a C—H···π interaction with the 2-pyridyl ring [C—H···*Cg*: C—H = 0.93 Å, H···*Cg* = 2.90 Å, C···*Cg* = 3.581 (3) Å and C—H···*Cg* = 131°; *Cg* is the centroid of the 2-pyridyl ring at ($\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{3}{2}-z$)]. It is interesting to note that the two NH_2 groups in the structure occur both in planar and pyramidal arrangements.

Related literature

For related literature, see: Banachiewicz & Banachiewicz (2004); Case (1965); Ejsmont (2007); Krishnakumar *et al.* (2002); Subha Nandhini *et al.* (2001); Etter *et al.* (1990).



Experimental

Crystal data

$C_6H_9N_4^+\cdot C_2HO_4^-$
M_r = 226.20
Monoclinic, $C2/c$
a = 26.634 (3) Å
b = 5.6454 (7) Å
c = 18.337 (2) Å
β = 131.030 (2)°
V = 2079.9 (4) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 299 (2) K
0.24 × 0.24 × 0.12 mm

Data collection

Bruker APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.972, T_{max} = 0.986
9695 measured reflections
2470 independent reflections
1649 reflections with $I > 2\sigma(I)$
R_{int} = 0.091

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.137
S = 0.99
2470 reflections
163 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···N4^{i}	0.871 (10)	2.277 (15)	3.051 (3)	148 (2)
N2—H2B···O4^{ii}	0.870 (10)	2.018 (11)	2.874 (2)	168 (2)
N4—H4A···O4^{iii}	0.904 (9)	2.145 (12)	3.016 (2)	162 (2)
N4—H4B···O1^{iv}	0.891 (9)	2.120 (10)	3.002 (2)	171 (2)
O2—H2C···O3^{v}	0.837 (10)	1.713 (10)	2.550 (2)	179 (4)
N3—H3···O3	0.882 (9)	1.930 (12)	2.766 (2)	158 (2)
N3—H3···O1	0.882 (9)	2.59 (2)	3.129 (2)	120.3 (17)
C4—H4···O4^{ii}	0.93	2.42	3.221 (4)	144

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FB2050).

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supplementary materials

Acta Cryst. (2007). E**63**, o3215 [**doi:10.1107/S160053680702822X**]

Pyridine-2-carboxamidrazonium hydrogenoxalate

M. Wang, B. Hu, X.-Y. Wang, C.-G. Wang and M.-N. Cao

Comment

Pyridinecarboxamidrazones are well studied, due to their high antituberculosis activities (Banachiewicz *et al.*, 2004). As a part of our investigation of the reactions of 2-pyridinecarboxamidrazone with dicarboxylic acids, we report the crystal structure of the title compound, (I).

Unlike other similar semi-oxalate complexes (Krishnakumar *et al.*, 2002; Subha Nandhini *et al.*, 2001; Ejsmont, 2007) the hydrogenoxalate ion in (I) is not planar. The dihedral angle O1—C8—C9—O3 is 14.49 (16)°. In the cation, the dihedral angle N2—C1—C2—N1 is −151.1 (2)°.

Experimental

The 2-pyridinecarboxamidrazone was prepared as described by Case (1965). A solution of oxalic acid dihydrate (0.126 g, 1 mmol) in ethanol (15 ml) was added to the solution of 2-pyridinecarboxamidrazone (0.136 g, 1 mmol) in ethanol (15 ml). The suspension was stirred for one hour at room temperature and filtrated, the light yellow solution was allowed to stand at room temperature, then light yellow well shaped crystals with typical dimensions about 1/2*x* 1 *x* 1 mm were obtained after about one week.

Refinement

All the H-atoms were discernible in the difference Fourier map. H atoms bound to C atoms were included in calculated positions and allowed to ride during refinement, with C—H = 0.93 Å, and U_{iso}(H) = 1.2U_{eq}(C). H atoms bound to O or N atoms were refined with restraints for O—H = 0.82 (1) Å, N(sp^2-state)-H = 0.86 (1) Å, N(sp^3-state)-H = 0.89 (1) Å, and U_{iso}(H) = 1.5U_{eq}(O, N).

Figures

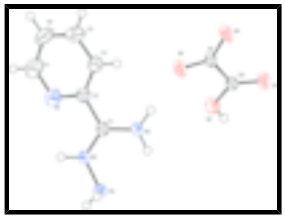

Fig. 1. The title molecules of the asymmetric unit with displacement ellipsoids drawn at the 50% probability level.

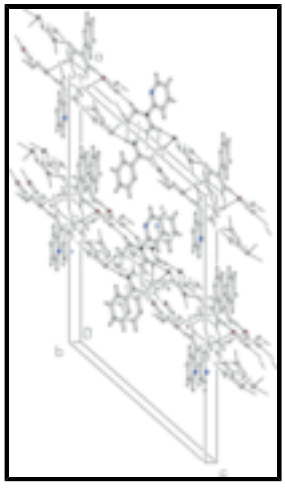

Fig. 2. Packing diagram of the title molecule viewed down the *b* axis, showing the formation of columns.

Pyridine-2-carboxamidrazonium hydrogenoxalate

Crystal data

$C_6H_9N_4^+ \cdot C_2HO_4^-$	F_{000} = 944
M_r = 226.20	D_x = 1.445 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 1565 reflections
a = 26.634 (3) Å	θ = 3.0–22.8º
b = 5.6454 (7) Å	μ = 0.12 mm^{-1}
c = 18.337 (2) Å	*T* = 299 (2) K
β = 131.030 (2)º	Plate, light yellow
V = 2079.9 (4) Å^3	0.24 × 0.24 × 0.12 mm
Z = 8	

Data collection

Bruker APEX CCD area-detector diffractometer	2470 independent reflections
Radiation source: fine-focus sealed tube	1649 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.091
T = 299(2) K	θ_{max} = 28.0º
φ and ω scans	θ_{min} = 2.0º
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	*h* = −34→34
T_{min} = 0.972, T_{max} = 0.986	*k* = −7→7
9695 measured reflections	*l* = −24→21

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods

Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.058$	Hydrogen site location: difference Fourier map
$wR(F^2) = 0.137$	H atoms treated by a mixture of independent and constrained refinement
$S = 0.99$	$w = 1/[\sigma^2(F_o^2) + (0.061P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
2470 reflections	$(\Delta/\sigma)_{max} < 0.001$
163 parameters	$\Delta\rho_{max} = 0.32$ e Å^{-3}
6 restraints	$\Delta\rho_{min} = -0.32$ e Å^{-3}
22 constraints	Extinction correction: none

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 $F^2 > 2\text{sigma}(F^2)$ 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	0.19244 (10)	0.5643 (4)	0.56883 (16)	0.0487 (6)
N2	0.06855 (10)	0.6941 (3)	0.58191 (15)	0.0361 (5)
H2A	0.0365 (9)	0.797 (3)	0.5560 (16)	0.043*
H2B	0.0798 (11)	0.609 (4)	0.6303 (12)	0.043*
N3	0.07582 (9)	0.7962 (3)	0.46892 (14)	0.0299 (4)
H3	0.0878 (10)	0.761 (4)	0.4353 (14)	0.036*
N4	0.02341 (9)	0.9613 (3)	0.42661 (13)	0.0298 (4)
H4A	−0.0122 (8)	0.887 (4)	0.3731 (11)	0.036*
H4B	0.0319 (11)	1.073 (3)	0.4017 (15)	0.036*
C1	0.09544 (10)	0.6720 (3)	0.54292 (15)	0.0259 (5)
C2	0.15045 (10)	0.5003 (4)	0.58226 (15)	0.0304 (5)
C4	0.15572 (11)	0.2932 (4)	0.62603 (16)	0.0339 (5)
H4	0.1258	0.2573	0.6347	0.041*
C5	0.20684 (12)	0.1395 (4)	0.65693 (18)	0.0446 (6)
H5	0.2114	−0.0039	0.6857	0.054*
C6	0.25023 (13)	0.2003 (5)	0.6447 (2)	0.0542 (8)
H6	0.2852	0.1002	0.6657	0.065*
C7	0.24161 (14)	0.4136 (5)	0.6005 (2)	0.0624 (8)
H7	0.2716	0.4538	0.5925	0.075*
O1	0.06808 (8)	0.3398 (2)	0.36510 (12)	0.0411 (4)
O2	0.09533 (8)	0.1966 (2)	0.28170 (12)	0.0367 (4)
H2C	0.0937 (12)	0.061 (2)	0.2986 (17)	0.044*

O3	0.08940 (9)	0.7835 (2)	0.33181 (13)	0.0412 (4)
O4	0.08870 (8)	0.6301 (2)	0.21993 (12)	0.0379 (4)
C8	0.08279 (10)	0.3658 (3)	0.31594 (15)	0.0247 (4)
C9	0.08774 (10)	0.6146 (3)	0.28618 (15)	0.0253 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0439 (12)	0.0554 (14)	0.0590 (15)	0.0103 (10)	0.0391 (12)	0.0110 (11)
N2	0.0506 (12)	0.0368 (11)	0.0381 (12)	0.0156 (9)	0.0367 (11)	0.0144 (9)
N3	0.0409 (10)	0.0308 (9)	0.0322 (10)	0.0089 (8)	0.0301 (9)	0.0058 (8)
N4	0.0398 (10)	0.0260 (9)	0.0305 (11)	0.0060 (8)	0.0261 (9)	0.0054 (8)
C1	0.0311 (11)	0.0245 (10)	0.0250 (11)	−0.0007 (8)	0.0196 (9)	−0.0023 (9)
C2	0.0320 (11)	0.0309 (11)	0.0280 (12)	0.0029 (9)	0.0197 (10)	−0.0018 (9)
C4	0.0371 (12)	0.0324 (11)	0.0340 (13)	0.0007 (10)	0.0242 (11)	−0.0020 (10)
C5	0.0458 (14)	0.0320 (12)	0.0431 (15)	0.0079 (11)	0.0236 (13)	0.0038 (11)
C6	0.0442 (15)	0.0547 (17)	0.0614 (19)	0.0198 (13)	0.0337 (15)	0.0057 (15)
C7	0.0500 (16)	0.074 (2)	0.079 (2)	0.0152 (15)	0.0497 (17)	0.0138 (17)
O1	0.0732 (12)	0.0269 (8)	0.0515 (11)	−0.0049 (8)	0.0533 (11)	−0.0008 (7)
O2	0.0617 (11)	0.0166 (7)	0.0540 (11)	0.0023 (7)	0.0476 (10)	0.0019 (7)
O3	0.0825 (12)	0.0186 (7)	0.0527 (11)	0.0015 (8)	0.0575 (10)	−0.0015 (7)
O4	0.0702 (11)	0.0256 (8)	0.0444 (10)	0.0013 (7)	0.0490 (10)	0.0016 (7)
C8	0.0320 (11)	0.0209 (9)	0.0259 (11)	−0.0005 (8)	0.0211 (10)	−0.0009 (9)
C9	0.0351 (11)	0.0203 (10)	0.0312 (12)	0.0026 (8)	0.0263 (10)	0.0030 (9)

Geometric parameters (Å, °)

N1—C7	1.333 (3)	C4—H4	0.9300
N1—C2	1.343 (3)	C5—C6	1.358 (4)
N2—C1	1.308 (3)	C5—H5	0.9300
N2—H2A	0.871 (10)	C6—C7	1.384 (4)
N2—H2B	0.870 (10)	C6—H6	0.9300
N3—C1	1.294 (3)	C7—H7	0.9300
N3—N4	1.413 (2)	O1—C8	1.205 (2)
N3—H3	0.882 (9)	O2—C8	1.301 (2)
N4—H4A	0.904 (9)	O2—H2C	0.837 (10)
N4—H4B	0.891 (9)	O3—C9	1.250 (2)
C1—C2	1.489 (3)	O4—C9	1.235 (2)
C2—C4	1.372 (3)	C8—C9	1.543 (3)
C4—C5	1.384 (3)		
C7—N1—C2	116.5 (2)	C5—C4—H4	121.0
C1—N2—H2A	117.2 (16)	C6—C5—C4	119.3 (2)
C1—N2—H2B	124.0 (16)	C6—C5—H5	120.4
H2A—N2—H2B	119 (2)	C4—C5—H5	120.4
C1—N3—N4	120.41 (17)	C5—C6—C7	119.0 (2)
C1—N3—H3	122.0 (15)	C5—C6—H6	120.5
N4—N3—H3	116.3 (15)	C7—C6—H6	120.5
N3—N4—H4A	104.2 (14)	N1—C7—C6	123.3 (3)

N3—N4—H4B	105.0 (14)	N1—C7—H7	118.4
H4A—N4—H4B	102 (2)	C6—C7—H7	118.4
N3—C1—N2	122.16 (19)	C8—O2—H2C	113.5 (17)
N3—C1—C2	116.87 (18)	O1—C8—O2	125.73 (18)
N2—C1—C2	120.97 (19)	O1—C8—C9	121.40 (17)
N1—C2—C4	124.0 (2)	O2—C8—C9	112.87 (17)
N1—C2—C1	114.14 (19)	O4—C9—O3	126.15 (19)
C4—C2—C1	121.87 (19)	O4—C9—C8	118.31 (17)
C2—C4—C5	118.0 (2)	O3—C9—C8	115.53 (18)
C2—C4—H4	121.0		
N4—N3—C1—N2	−0.5 (3)	C1—C2—C4—C5	177.4 (2)
N4—N3—C1—C2	179.35 (18)	C2—C4—C5—C6	1.3 (4)
C7—N1—C2—C4	0.2 (4)	C4—C5—C6—C7	−0.8 (4)
C7—N1—C2—C1	−178.3 (2)	C2—N1—C7—C6	0.4 (5)
N3—C1—C2—N1	29.1 (3)	C5—C6—C7—N1	−0.1 (5)
N2—C1—C2—N1	−151.0 (2)	O1—C8—C9—O4	−164.6 (2)
N3—C1—C2—C4	−149.4 (2)	O2—C8—C9—O4	14.7 (3)
N2—C1—C2—C4	30.5 (3)	O1—C8—C9—O3	14.3 (3)
N1—C2—C4—C5	−1.0 (4)	O2—C8—C9—O3	−166.32 (19)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2A···N4^{i}	0.871 (10)	2.277 (15)	3.051 (3)	148 (2)
N2—H2B···O4^{ii}	0.870 (10)	2.018 (11)	2.874 (2)	168 (2)
N4—H4A···O4^{iii}	0.904 (9)	2.145 (12)	3.016 (2)	162 (2)
N4—H4B···O1^{iv}	0.891 (9)	2.120 (10)	3.002 (2)	171 (2)
O2—H2C···O3^{v}	0.837 (10)	1.713 (10)	2.550 (2)	179 (4)
N3—H3···O3	0.882 (9)	1.930 (12)	2.766 (2)	158 (2)
N3—H3···O1	0.882 (9)	2.59 (2)	3.129 (2)	120.3 (17)
C4—H4···O4^{ii}	0.93	2.42	3.221 (4)	144

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

Fig. 1

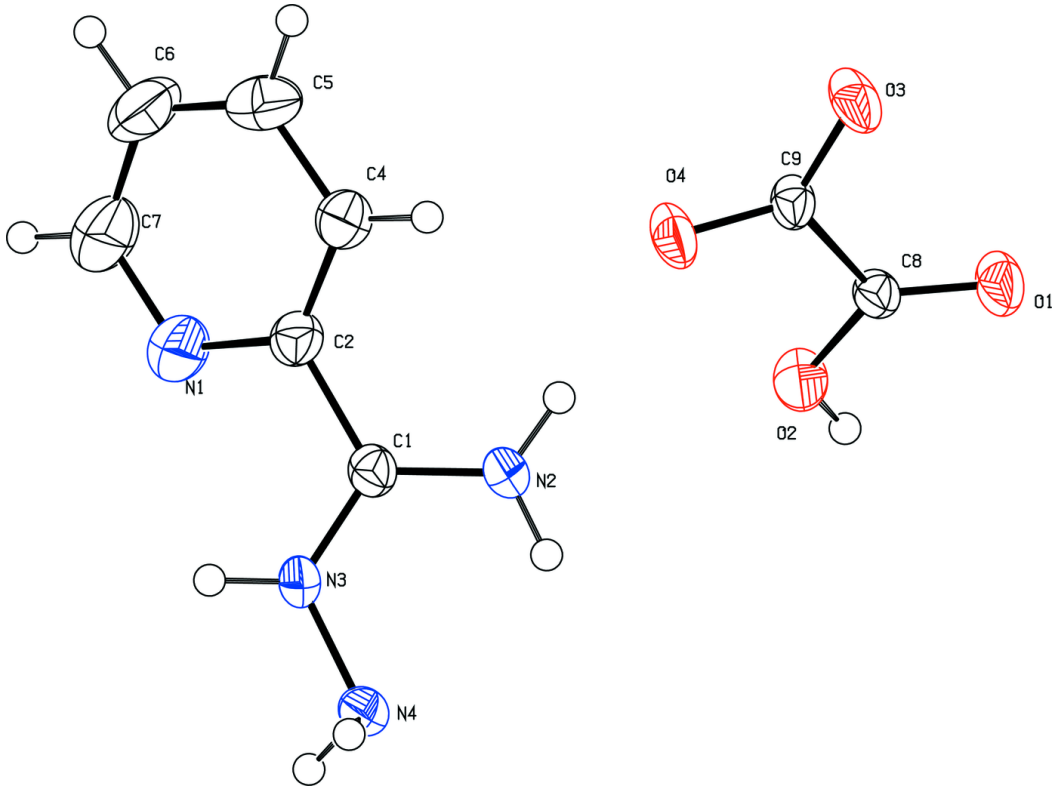

Fig. 2