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2,2′-Bipyridin-1-ium hemioxalate oxalic acid monohydrate

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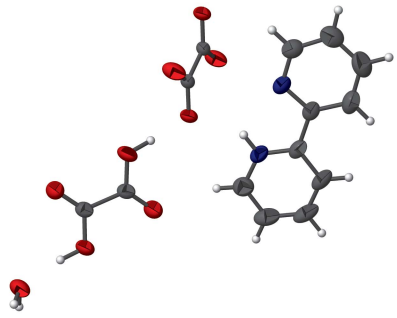
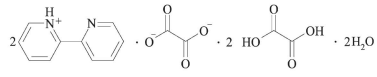
Structural data: full structural data are available from iucrdata.iucr.org

The asymmetric unit of the title compound, $C_{10}H_9N_2^+\cdot 0.5C_2O_4^{2-}\cdot C_2H_2O_4\cdot H_2O$, consists of a 2,2′-bipyridinium cation, half an oxalate dianion, one oxalic acid and one water molecule. One N atom in 2,2′-bipyridine is unprotonated, while the second is protonated and forms an N—H···O hydrogen bond. In the crystal, the anions are connected with surrounding acid molecules and water molecules by strong near-linear O—H···O hydrogen bonds. The water molecules are located between the anions and oxalic acids; their O atoms participate as donors and acceptors, respectively, in O—H···O hydrogen bonds, which form sheets arranged parallel to the *ac* plane.

3D view



Chemical scheme



Structure description

Hydrogen bonds are one of the most important intermolecular interactions in structural chemistry (Desiraju, 2013). The strong interactions between cations and anions have been studied extensively for use in supramolecular chemistry and crystal engineering. Carboxylic acids, especially in hydrates, form strong interactions that may strongly influence the different forms of structures, usually forming supramolecular synthons (Dziuk *et al.*, 2014*a*,*b*, 2017; Braga *et al.*, 2013; Ejsmont & Zaleski, 2006). 2,2′-Bipyridine derivatives are classical bidentate chelating heterocyclic ligands (Steel, 1996) employed in transition metal catalysis and inorganic syntheses (*e.g.* aluminium-initiated polymerization; Blau, 1888; Mardare & Matyjaszewski, 1994) because of their robust redox stability and ease of functionalization (Kaes *et al.*, 2000). Many complexes with 2,2′-bipyridine have distinctive optical properties and are used in studies of electron and energy transfer, catalysis and supramolecular chemistry (Balzani *et al.*, 2006). Their use as building blocks for the construction of efficient molecular and macromolecular nonlinear optical chromophores is an area of great interest (Coe *et al.*, 2005). 2,2′-Bipyridine

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

D—H···A	D—H	H···A	D···A	D—H···A
O7—H7A···O2^{i}	0.84	1.99	2.8192 (12)	170
N1—H1···O1	0.86	1.99	2.7586 (13)	148
O4—H4···O1	0.94	1.64	2.5795 (11)	176
O4—H4···O2	0.94	2.62	3.2259 (12)	122
O6—H6···O7	0.92	1.63	2.5467 (11)	169
O7—H7B···O2^{ii}	0.93	1.75	2.6802 (12)	174
C8—H8···O3	0.93	2.52	3.3132 (18)	144
C10—H10···O7^{iii}	0.93	2.43	3.2562 (17)	148
C13—H13···O6^{iv}	0.93	2.59	3.3876 (16)	144

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

has been used for more than a century as common chelating ligand in analytical, organometallic and coordination chemistry (Steel, 1996).

The crystal structure of the title hydrated salt, (I), consists of a 2,2′-bipyridinium cation, half an oxalate anion, one oxalic acid and one water molecule (Fig. 1). The oxalate anion is planar with an inversion center at the mid-point of the C—C bond. One nitrogen atom in the 2,2′-bipyridinium cation is unprotonated while second one is protonated and forms a strong N—H···O hydrogen bond. In the crystal, two different types of strong hydrogen bonds are observed: N—H···O and O—H···O (Table 1, Fig. 2). The anions are connected with the cations and surrounding acid molecules and water molecules by strong near-linear O—H···O hydrogen bonds. The water molecules are located between the anions and oxalic acid molecules; their O atoms participate as donors and acceptors, respectively, in O—H···O hydrogen bonds, which form sheets arranged parallel to the *ac* plane.

Synthesis and crystallization

Crystals were grown at room temperature by slow evaporation of an aqueous solution containing 2,2′-bipyridine and oxalic acid in a 1:1 stoichiometric ratio.

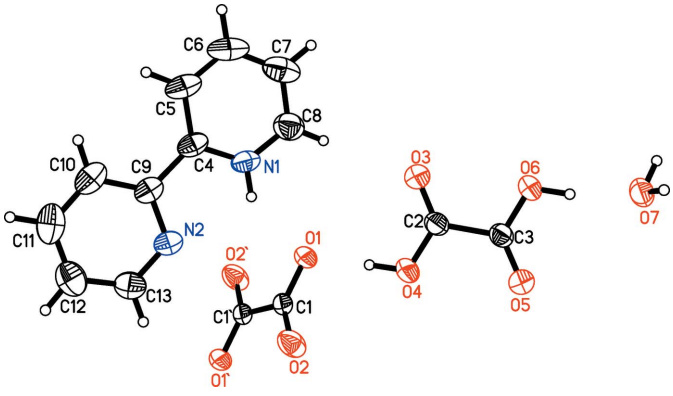


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{10}H_9N_2^+ \cdot 0.5C_2O_4^{2-} \cdot C_2H_2O_4 \cdot H_2O$
M_r	309.25
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	293
a, b, c (Å)	7.2618 (4), 8.9419 (6), 11.0001 (7)
α, β, γ (°)	85.545 (5), 86.177 (5), 75.248 (5)
V (Å^3)	687.84 (8)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.12
Crystal size (mm)	0.4 × 0.35 × 0.3
Data collection	
Diffractometer	Oxford Diffraction Xcalibur
Absorption correction	–
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4712, 2648, 2054
R_{int}	0.016
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.089, 1.04
No. of reflections	2648
No. of parameters	200
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.16, −0.16

Computer programs: *CrysAlis CCD* (Oxford Diffraction, 2008), *SHELXS2014* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) and *SHELXTL* (Sheldrick, 2008).

Refinement

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

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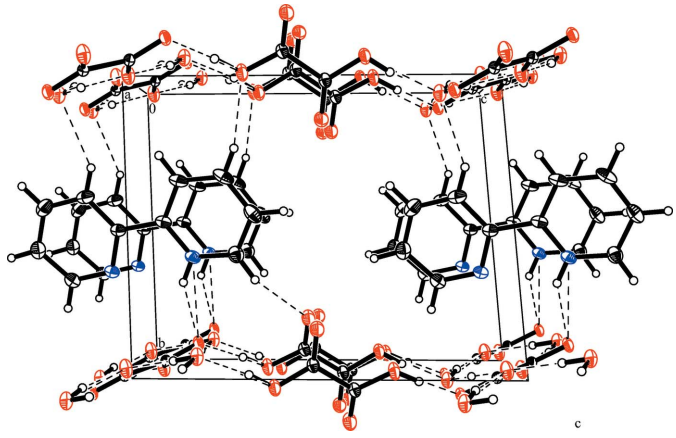

Figure 2
The packing viewed along the *b* axis, showing the hydrogen-bonding scheme (dashed lines).

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full crystallographic data

IUCrData (2018). **3**, x181219 [https://doi.org/10.1107/S2414314618012191]

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Crystal data

$C_{10}H_9N_2^+·0.5C_2O_4^{2-}·C_2H_2O_4·H_2O$
M_r = 309.25
Triclinic, $P\overline{1}$
a = 7.2618 (4) Å
b = 8.9419 (6) Å
c = 11.0001 (7) Å
α = 85.545 (5)°
β = 86.177 (5)°
γ = 75.248 (5)°
V = 687.84 (8) Å^3
Z = 2
$F(000)$ = 322
D_x = 1.493 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4712 reflections
θ = 3.1–26.0°
μ = 0.12 mm^{-1}
T = 293 K
Plate, pink
0.4 × 0.35 × 0.3 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 1024 x 1024 with blocks 2 x 2 pixels mm^{-1}
ω–scan
4712 measured reflections
2648 independent reflections
2054 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
θ_{max} = 26.0°, θ_{min} = 3.1°
h = −8→8
k = −9→11
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.089
S = 1.04
2648 reflections
200 parameters
0 restraints
Hydrogen site location: difference Fourier map
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.051P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}
Extinction correction: SHELXL2014 (Sheldrick, 2015b), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.138 (7)

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. All H atoms were located in a difference map and set to this position. During refinement they were treated as riding on their parent N, O and C atoms, with and U_{iso} (H) = 1.2U_{eq}(C, N, O).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.49365 (11)	0.08583 (10)	0.85141 (7)	0.0386 (2)
N1	0.27452 (14)	0.38740 (12)	0.84585 (10)	0.0408 (3)
H1	0.3370	0.2997	0.8775	0.049*
C1	0.56889 (16)	0.02093 (13)	0.94780 (10)	0.0294 (3)
O2	0.74212 (11)	−0.01433 (10)	0.96493 (8)	0.0465 (3)
N2	0.38268 (15)	0.33461 (12)	1.07479 (10)	0.0406 (3)
C2	0.68092 (17)	0.05604 (14)	0.56545 (11)	0.0349 (3)
O3	0.55452 (14)	0.17018 (12)	0.54737 (8)	0.0594 (3)
C3	0.80116 (17)	−0.03224 (15)	0.46116 (10)	0.0339 (3)
O4	0.73101 (12)	−0.00942 (11)	0.67194 (7)	0.0470 (3)
H4	0.6457	0.0297	0.7370	0.056*
C4	0.21997 (17)	0.50713 (14)	0.91815 (12)	0.0389 (3)
C5	0.11417 (19)	0.64602 (15)	0.86672 (15)	0.0510 (4)
H5	0.0713	0.7310	0.9141	0.061*
O5	0.91375 (13)	−0.15528 (11)	0.47742 (8)	0.0506 (3)
C6	0.0722 (2)	0.65872 (18)	0.74540 (17)	0.0589 (4)
H6A	0.0006	0.7522	0.7113	0.071*
O6	0.76264 (12)	0.04452 (10)	0.35664 (7)	0.0453 (3)
H6	0.8398	−0.0028	0.2934	0.054*
C7	0.1354 (2)	0.53431 (19)	0.67463 (15)	0.0591 (4)
H7	0.1098	0.5430	0.5923	0.071*
O7	0.94612 (12)	−0.06711 (10)	0.16511 (7)	0.0440 (3)
H7A	1.0359	−0.0334	0.1317	0.053*
H7B	0.8673	−0.0478	0.0991	0.053*
C8	0.2373 (2)	0.39662 (18)	0.72765 (14)	0.0524 (4)
H8	0.2802	0.3104	0.6817	0.063*
C9	0.27939 (17)	0.47844 (14)	1.04566 (12)	0.0377 (3)
C10	0.2316 (2)	0.59226 (17)	1.12833 (15)	0.0546 (4)
H10	0.1623	0.6917	1.1047	0.066*
C11	0.2885 (2)	0.5560 (2)	1.24680 (16)	0.0633 (4)
H11	0.2570	0.6305	1.3043	0.076*
C12	0.3922 (2)	0.40849 (19)	1.27819 (14)	0.0563 (4)
H12	0.4313	0.3805	1.3574	0.068*
C13	0.43656 (19)	0.30303 (16)	1.18919 (13)	0.0481 (4)
H13	0.5086	0.2037	1.2104	0.058*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0423 (5)	0.0424 (5)	0.0235 (4)	0.0008 (4)	0.0009 (4)	0.0047 (4)
N1	0.0347 (6)	0.0340 (6)	0.0480 (7)	0.0002 (5)	−0.0044 (5)	0.0057 (5)
C1	0.0346 (7)	0.0280 (6)	0.0231 (6)	−0.0036 (5)	0.0005 (5)	−0.0022 (5)
O2	0.0339 (5)	0.0719 (7)	0.0328 (5)	−0.0137 (5)	−0.0012 (4)	0.0040 (4)
N2	0.0397 (6)	0.0320 (6)	0.0479 (7)	−0.0060 (5)	−0.0037 (5)	0.0025 (5)
C2	0.0320 (6)	0.0421 (7)	0.0286 (6)	−0.0071 (6)	−0.0025 (5)	0.0027 (5)

O3	0.0621 (6)	0.0590 (7)	0.0374 (6)	0.0187 (5)	0.0016 (5)	0.0013 (5)
C3	0.0303 (6)	0.0421 (8)	0.0287 (6)	−0.0083 (6)	−0.0030 (5)	0.0007 (5)
O4	0.0449 (5)	0.0603 (6)	0.0252 (5)	0.0035 (4)	0.0024 (4)	0.0038 (4)
C4	0.0279 (6)	0.0304 (7)	0.0561 (9)	−0.0064 (5)	0.0018 (6)	0.0043 (6)
C5	0.0404 (7)	0.0320 (8)	0.0755 (11)	−0.0041 (6)	−0.0029 (7)	0.0109 (7)
O5	0.0542 (6)	0.0474 (6)	0.0384 (5)	0.0080 (5)	−0.0009 (4)	−0.0006 (4)
C6	0.0400 (8)	0.0480 (10)	0.0833 (12)	−0.0080 (7)	−0.0128 (8)	0.0285 (8)
O6	0.0493 (5)	0.0512 (6)	0.0265 (5)	0.0015 (4)	0.0015 (4)	0.0022 (4)
C7	0.0470 (9)	0.0685 (11)	0.0592 (10)	−0.0142 (8)	−0.0145 (7)	0.0217 (8)
O7	0.0389 (5)	0.0597 (6)	0.0311 (5)	−0.0090 (4)	0.0007 (4)	−0.0025 (4)
C8	0.0464 (8)	0.0574 (9)	0.0501 (9)	−0.0077 (7)	−0.0067 (7)	0.0024 (7)
C9	0.0296 (6)	0.0324 (7)	0.0507 (8)	−0.0092 (5)	0.0029 (5)	0.0001 (6)
C10	0.0519 (9)	0.0371 (8)	0.0727 (11)	−0.0077 (7)	0.0052 (8)	−0.0087 (7)
C11	0.0676 (10)	0.0655 (11)	0.0637 (11)	−0.0268 (9)	0.0104 (8)	−0.0241 (8)
C12	0.0579 (9)	0.0687 (11)	0.0495 (9)	−0.0289 (8)	−0.0027 (7)	−0.0048 (8)
C13	0.0468 (8)	0.0463 (8)	0.0518 (9)	−0.0137 (7)	−0.0076 (7)	0.0051 (7)

Geometric parameters (Å, º)

O1—C1	1.2569 (13)	C5—H5	0.9300
N1—C8	1.3375 (17)	C6—C7	1.371 (2)
N1—C4	1.3453 (17)	C6—H6A	0.9300
N1—H1	0.8600	O6—H6	0.9224
C1—O2	1.2401 (13)	C7—C8	1.3733 (19)
C1—C1^{i}	1.559 (2)	C7—H7	0.9300
N2—C13	1.3306 (16)	O7—H7A	0.8379
N2—C9	1.3402 (15)	O7—H7B	0.9327
C2—O3	1.1997 (14)	C8—H8	0.9300
C2—O4	1.2996 (13)	C9—C10	1.380 (2)
C2—C3	1.5355 (18)	C10—C11	1.383 (2)
C3—O5	1.2007 (14)	C10—H10	0.9300
C3—O6	1.3014 (13)	C11—C12	1.373 (2)
O4—H4	0.9417	C11—H11	0.9300
C4—C5	1.3841 (17)	C12—C13	1.378 (2)
C4—C9	1.4791 (19)	C12—H12	0.9300
C5—C6	1.378 (2)	C13—H13	0.9300
C8—N1—C4	123.91 (11)	C3—O6—H6	112.1
C8—N1—H1	118.0	C6—C7—C8	118.73 (15)
C4—N1—H1	118.0	C6—C7—H7	120.6
O2—C1—O1	125.34 (10)	C8—C7—H7	120.6
O2—C1—C1^{i}	118.21 (12)	H7A—O7—H7B	98.0
O1—C1—C1^{i}	116.44 (12)	N1—C8—C7	119.56 (14)
C13—N2—C9	117.25 (12)	N1—C8—H8	120.2
O3—C2—O4	125.59 (12)	C7—C8—H8	120.2
O3—C2—C3	122.43 (11)	N2—C9—C10	122.62 (13)
O4—C2—C3	111.97 (10)	N2—C9—C4	115.25 (12)
O5—C3—O6	126.36 (12)	C10—C9—C4	122.13 (12)

O5—C3—C2	122.97 (11)	C9—C10—C11	118.92 (14)
O6—C3—C2	110.67 (11)	C9—C10—H10	120.5
C2—O4—H4	114.2	C11—C10—H10	120.5
N1—C4—C5	117.27 (13)	C12—C11—C10	118.99 (14)
N1—C4—C9	116.89 (11)	C12—C11—H11	120.5
C5—C4—C9	125.84 (13)	C10—C11—H11	120.5
C6—C5—C4	120.14 (15)	C11—C12—C13	118.18 (15)
C6—C5—H5	119.9	C11—C12—H12	120.9
C4—C5—H5	119.9	C13—C12—H12	120.9
C7—C6—C5	120.36 (13)	N2—C13—C12	124.03 (13)
C7—C6—H6A	119.8	N2—C13—H13	118.0
C5—C6—H6A	119.8	C12—C13—H13	118.0

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H7*A*···O2^{ii}	0.84	1.99	2.8192 (12)	170
N1—H1···O1	0.86	1.99	2.7586 (13)	148
O4—H4···O1	0.94	1.64	2.5795 (11)	176
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C8—H8···O3	0.93	2.52	3.3132 (18)	144
C10—H10···O7^{iv}	0.93	2.43	3.2562 (17)	148
C13—H13···O6^{v}	0.93	2.59	3.3876 (16)	144

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