

4-(4-Pyridyl)pyridinium 3',4,4'-tricarboxyphenyl-3-carboxylate dihydrate

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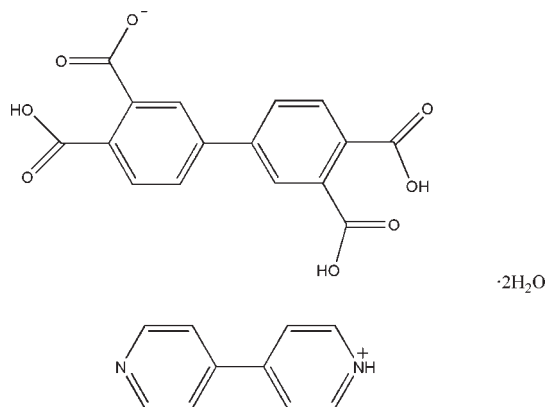
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.039; wR factor = 0.112; data-to-parameter ratio = 11.4.

In the title compound, $\text{C}_{10}\text{H}_9\text{N}_2^+ \cdot \text{C}_{16}\text{H}_9\text{O}_8^- \cdot 2\text{H}_2\text{O}$, both the cation and anion possess crystallographically imposed centres of symmetry, causing the nitrogen-bound H atom in the 4-(4-pyridyl)pyridinium cation and the acidic H atom of the carboxylate groups at the 3 and 3' positions in the anion to be disordered over two positions with equal occupancies. In the crystal packing, the cations, anions and water molecules are connected by $\text{O}-\text{H} \cdots \text{O}$, $\text{C}-\text{H} \cdots \text{O}$ and $\text{N}-\text{H} \cdots \text{N}$ hydrogen bonds, forming layers parallel to $(2\bar{1}0)$. These layer are further connected into a three-dimensional supramolecular network by $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds involving the water molecules as H-atom donors and by weak $\pi-\pi$ stacking interactions between neighbouring benzene and pyridine rings, with centroid-centroid distances of 3.756 (5) Å.

Related literature

For related structures, see: Wang *et al.* (2006, 2007); Yang *et al.* (2007).



Experimental

Crystal data

$\text{C}_{10}\text{H}_9\text{N}_2^+ \cdot \text{C}_{16}\text{H}_9\text{O}_8^- \cdot 2\text{H}_2\text{O}$
 $M_r = 522.46$
 Triclinic, $P\bar{1}$
 $a = 7.1955$ (8) Å
 $b = 8.935$ (1) Å
 $c = 9.8847$ (11) Å
 $\alpha = 90.7920$ (11)°
 $\beta = 106.4850$ (13)°

$\gamma = 107.1180$ (15)°
 $V = 579.09$ (11) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 0.12$ mm⁻¹
 $T = 296$ K
 $0.23 \times 0.21 \times 0.19$ mm

Data collection

Bruker APEXII area-detector diffractometer
 2990 measured reflections

2050 independent reflections
 1818 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.014$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.112$
 $S = 1.03$
 2050 reflections
 180 parameters
 3 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.32$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.25$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N1}-\text{H1A} \cdots \text{N1}^{\text{i}}$	0.92 (2)	1.89 (2)	2.814 (3)	177 (4)
$\text{O4}-\text{H4A} \cdots \text{O1W}$	0.82	1.75	2.5657 (19)	176
$\text{O1W}-\text{H1W} \cdots \text{O1}^{\text{ii}}$	0.83	1.86	2.642 (2)	157
$\text{O1W}-\text{H2W} \cdots \text{O3}^{\text{iii}}$	0.84	2.03	2.841 (2)	165
$\text{O2}-\text{H2A} \cdots \text{O2}^{\text{iv}}$	0.91 (2)	1.54 (2)	2.446 (3)	173 (7)
$\text{C3}-\text{H3} \cdots \text{O1}^{\text{v}}$	0.93	2.54	3.270 (2)	135
$\text{C13}-\text{H13} \cdots \text{O2}^{\text{vi}}$	0.93	2.57	3.448 (2)	159
$\text{C9}-\text{H9} \cdots \text{O2}^{\text{vii}}$	0.93	2.36	3.246 (2)	160

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

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); 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: RZ2388).

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supplementary materials

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4-(4-Pyridyl)pyridinium 3',4,4'-tricarboxybiphenyl-3-carboxylate dihydrate

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Comment

In recent years, research on coordination polymers has made considerable progress in the fields of supramolecular chemistry and crystal engineering, because of their intriguing structural motifs and functional properties, such as molecular adsorption, magnetism, and luminescence. In general, hydrogen bonding interactions between ligands are specific and directional. In this context, biphenyl-3,3',4,4'-tetracarboxylic acid and 4,4'-bipyridine are excellent candidates for the construction of three-dimensional network motifs (Wang *et al.*, 2006; Wang *et al.*, 2007; Yang *et al.*, 2007). Recently, we obtained the title compound under hydrothermal conditions and report its crystal structure here.

The asymmetric unit of the title compound contains one half of a monoprotic 4-4'-bipyridinium cation, one half of a 3-3'-4-tricarboxybiphenyl-4'-carboxylate anion and a water molecule, with both cation and anion possessing crystallographically imposed centre of symmetry (Fig. 1). As a result, the H1A nitrogen-bound hydrogen atom in the cation and acidic H2A hydrogen atom in the anion are disordered over two positions with site occupancies of 0.5. Bond lengths and angles are unexceptional. In the crystal packing (Fig. 2), cations, anions and lattice water molecules are linked by intermolecular O—H...O, C—H...O and N—H...N hydrogen bonds (Table 1) into layers parallel to (2 $\bar{1}$ 0). The layers are further connected into a three-dimensional network by O—H...O hydrogen bonds involving the water molecules as H-donors and by weak π - π stacking interactions involving neighbouring benzene and pyridine rings, with centroid-to-centroid distances of 3.756 (5) Å.

Experimental

A mixture of 4,4'-bipyridine (0.078 g, 0.5 mmol), 4-4'-dicarboxybiphenyl-3-3'-dicarboxylic acid (0.165 g; 0.5 mmol), water (10 mL) was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (25 mL capacity). The autoclave was heated and maintained at 433K for 3 days, and then cooled to room temperature at 5K h⁻¹ to obtain colourless block crystals suitable for X-ray analysis.

Refinement

Water H atoms were located in a difference Fourier map and refined with the O—H distance restrained to 0.84 Å and with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O})$. The H atom bound to the N1 nitrogen atom in the cation and the carboxylic H atoms were refined with distance restraints of N—H = 0.90 Å and O—H = 0.90 Å, respectively. The H1A and H2A hydrogen atoms are disordered over two centrosymmetrically related positions and were therefore refined with site occupancies of 0.5. All other H atoms were placed at calculated positions and treated as riding on the parent atoms, with C—H = 0.93 Å, and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$.

Figures

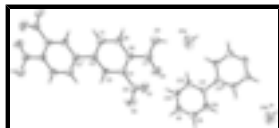


Fig. 1. The molecular structure of the title compound showing the atomic-numbering scheme and 50% probability ellipsoids. Only one position of the disordered H atoms in the cation and anion is shown. Symmetry codes: (i) 1-x, 2-y, -z; (ii) 2-x, -y, 1-z; (iii) -x, 1-y, -z.

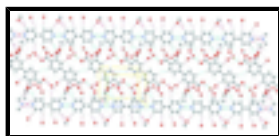


Fig. 2. Partial packing diagram of the title compound showing the layered network formed by intermolecular O—H...O, C—H...O and N—H...N hydrogen bonds (dashed lines). Both positions of the disordered H atoms in the cation and anions are shown.

4-(4-Pyridyl)pyridinium 3',4,4'-tricarboxybiphenyl-3-carboxylate dihydrate

Crystal data

$C_{10}H_9N_2^+ \cdot C_{16}H_9O_8^- \cdot 2H_2O$

$M_r = 522.46$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 7.1955$ (8) Å

$b = 8.935$ (1) Å

$c = 9.8847$ (11) Å

$\alpha = 90.7920$ (11)°

$\beta = 106.4850$ (13)°

$\gamma = 107.1180$ (15)°

$V = 579.09$ (11) Å³

$Z = 1$

$F(000) = 272$

$D_x = 1.498$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2061 reflections

$\theta = 2.4$ – 28.2 °

$\mu = 0.12$ mm⁻¹

$T = 296$ K

Block, colourless

$0.23 \times 0.21 \times 0.19$ mm

Data collection

Bruker APEXII area-detector diffractometer

Radiation source: fine-focus sealed tube

graphite

φ and ω scan

2990 measured reflections

2050 independent reflections

1818 reflections with $I > 2\sigma(I)$

$R_{int} = 0.014$

$\theta_{max} = 25.2$ °, $\theta_{min} = 2.2$ °

$h = -7$ → 8

$k = -10$ → 9

$l = -11$ → 11

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.112$

$S = 1.03$

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

$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2 + 0.2257P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

2050 reflections	$\Delta\rho_{\max} = 0.32 \text{ e } \text{\AA}^{-3}$
180 parameters	$\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$
3 restraints	Extinction correction: <i>SHELXL97</i> (Sheldrick, 2008), $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.071 (9)

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. 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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.4881 (3)	1.01415 (19)	0.18864 (18)	0.0405 (4)	
H1	0.5318	1.1230	0.2095	0.049*	
C2	0.4740 (2)	0.94960 (17)	0.05542 (16)	0.0321 (4)	
C3	0.4103 (3)	0.78512 (18)	0.03012 (17)	0.0361 (4)	
H3	0.4008	0.7393	-0.0576	0.043*	
C4	0.3611 (2)	0.68843 (17)	0.13133 (17)	0.0333 (4)	
C5	0.3102 (3)	0.51258 (19)	0.09704 (18)	0.0397 (4)	
C6	0.3725 (2)	0.75584 (18)	0.26291 (16)	0.0344 (4)	
C7	0.3003 (3)	0.65386 (19)	0.36673 (18)	0.0389 (4)	
C8	0.4384 (3)	0.91911 (19)	0.28990 (18)	0.0407 (4)	
H8	0.4490	0.9650	0.3779	0.049*	
C9	0.9236 (3)	-0.1318 (2)	0.19327 (19)	0.0447 (4)	
H9	0.8726	-0.2254	0.1336	0.054*	
C10	0.9232 (3)	-0.13691 (19)	0.33220 (18)	0.0412 (4)	
H10	0.8722	-0.2331	0.3647	0.049*	
C11	0.9987 (2)	0.00096 (18)	0.42445 (17)	0.0351 (4)	
C12	1.0714 (3)	0.1400 (2)	0.3674 (2)	0.0490 (5)	
H12	1.1234	0.2355	0.4243	0.059*	
C13	1.0666 (3)	0.1367 (2)	0.2273 (2)	0.0524 (5)	
H13	1.1151	0.2311	0.1914	0.063*	
N1	0.9947 (2)	0.00297 (17)	0.14119 (15)	0.0428 (4)	
H1A	0.997 (7)	0.004 (5)	0.049 (2)	0.051*	0.50
O1	0.4404 (2)	0.44851 (15)	0.14281 (16)	0.0572 (4)	
O3	0.1949 (2)	0.51807 (15)	0.33352 (14)	0.0596 (4)	
O4	0.3524 (3)	0.72538 (16)	0.49433 (14)	0.0647 (5)	
H4A	0.3092	0.6627	0.5465	0.097*	

supplementary materials

O1W	0.2145 (3)	0.5413 (2)	0.66452 (17)	0.0799 (6)	
H1W	0.3004	0.5290	0.7356	0.120*	
H2W	0.1031	0.5241	0.6817	0.120*	
O2	0.1336 (2)	0.43770 (14)	0.01377 (15)	0.0520 (4)	
H2A	0.040 (8)	0.490 (8)	0.001 (8)	0.078*	0.50

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0520 (10)	0.0255 (8)	0.0388 (9)	0.0025 (7)	0.0159 (8)	-0.0015 (7)
C2	0.0325 (8)	0.0276 (8)	0.0339 (8)	0.0060 (6)	0.0100 (6)	0.0017 (6)
C3	0.0467 (9)	0.0279 (8)	0.0327 (8)	0.0081 (7)	0.0141 (7)	-0.0006 (6)
C4	0.0346 (8)	0.0277 (8)	0.0352 (8)	0.0066 (6)	0.0102 (6)	0.0025 (6)
C5	0.0549 (10)	0.0293 (8)	0.0396 (9)	0.0115 (8)	0.0231 (8)	0.0057 (7)
C6	0.0353 (8)	0.0308 (8)	0.0339 (8)	0.0054 (6)	0.0104 (7)	0.0027 (6)
C7	0.0447 (9)	0.0324 (8)	0.0376 (9)	0.0063 (7)	0.0152 (7)	0.0023 (7)
C8	0.0526 (10)	0.0325 (8)	0.0323 (9)	0.0041 (7)	0.0153 (7)	-0.0022 (7)
C9	0.0530 (11)	0.0371 (9)	0.0421 (10)	0.0122 (8)	0.0135 (8)	-0.0016 (7)
C10	0.0513 (10)	0.0285 (8)	0.0431 (10)	0.0093 (7)	0.0163 (8)	0.0035 (7)
C11	0.0373 (8)	0.0286 (8)	0.0391 (9)	0.0092 (6)	0.0119 (7)	0.0039 (6)
C12	0.0691 (13)	0.0293 (9)	0.0425 (10)	0.0041 (8)	0.0190 (9)	0.0022 (7)
C13	0.0714 (13)	0.0379 (10)	0.0451 (10)	0.0079 (9)	0.0226 (9)	0.0093 (8)
N1	0.0516 (9)	0.0454 (8)	0.0332 (8)	0.0152 (7)	0.0151 (7)	0.0064 (6)
O1	0.0725 (10)	0.0442 (7)	0.0666 (9)	0.0307 (7)	0.0254 (7)	0.0142 (6)
O3	0.0830 (10)	0.0355 (7)	0.0522 (8)	-0.0054 (7)	0.0330 (7)	0.0011 (6)
O4	0.0976 (11)	0.0443 (8)	0.0368 (7)	-0.0065 (7)	0.0266 (7)	0.0019 (6)
O1W	0.0693 (10)	0.0986 (13)	0.0630 (10)	0.0071 (9)	0.0252 (8)	0.0340 (9)
O2	0.0599 (9)	0.0273 (6)	0.0601 (8)	0.0046 (6)	0.0146 (7)	-0.0086 (6)

Geometric parameters (\AA , $^\circ$)

C1—C8	1.378 (2)	C9—N1	1.334 (2)
C1—C2	1.395 (2)	C9—C10	1.375 (3)
C1—H1	0.9300	C9—H9	0.9300
C2—C3	1.400 (2)	C10—C11	1.392 (2)
C2—C2 ⁱ	1.488 (3)	C10—H10	0.9300
C3—C4	1.385 (2)	C11—C12	1.392 (2)
C3—H3	0.9300	C11—C11 ⁱⁱ	1.489 (3)
C4—C6	1.397 (2)	C12—C13	1.375 (3)
C4—C5	1.514 (2)	C12—H12	0.9300
C5—O1	1.222 (2)	C13—N1	1.334 (2)
C5—O2	1.277 (2)	C13—H13	0.9300
C6—C8	1.391 (2)	N1—H1A	0.921 (18)
C6—C7	1.484 (2)	O4—H4A	0.8200
C7—O3	1.209 (2)	O1W—H1W	0.8263
C7—O4	1.307 (2)	O1W—H2W	0.8370
C8—H8	0.9300	O2—H2A	0.911 (19)
C8—C1—C2	121.02 (15)	C6—C8—H8	119.4

C8—C1—H1	119.5	N1—C9—C10	122.24 (16)
C2—C1—H1	119.5	N1—C9—H9	118.9
C1—C2—C3	117.26 (15)	C10—C9—H9	118.9
C1—C2—C2 ⁱ	121.74 (17)	C9—C10—C11	120.39 (16)
C3—C2—C2 ⁱ	121.00 (17)	C9—C10—H10	119.8
C4—C3—C2	122.24 (15)	C11—C10—H10	119.8
C4—C3—H3	118.9	C10—C11—C12	116.23 (16)
C2—C3—H3	118.9	C10—C11—C11 ⁱⁱ	121.63 (18)
C3—C4—C6	119.43 (14)	C12—C11—C11 ⁱⁱ	122.14 (18)
C3—C4—C5	117.83 (14)	C13—C12—C11	120.36 (16)
C6—C4—C5	122.62 (14)	C13—C12—H12	119.8
O1—C5—O2	122.14 (16)	C11—C12—H12	119.8
O1—C5—C4	119.75 (16)	N1—C13—C12	122.31 (17)
O2—C5—C4	117.99 (15)	N1—C13—H13	118.8
C8—C6—C4	118.80 (15)	C12—C13—H13	118.8
C8—C6—C7	121.15 (14)	C13—N1—C9	118.47 (15)
C4—C6—C7	119.90 (14)	C13—N1—H1A	120 (3)
O3—C7—O4	123.27 (16)	C9—N1—H1A	121 (3)
O3—C7—C6	122.33 (15)	C7—O4—H4A	109.5
O4—C7—C6	114.33 (14)	H1W—O1W—H2W	109.1
C1—C8—C6	121.24 (15)	C5—O2—H2A	115 (5)
C1—C8—H8	119.4		

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1A \cdots N1 ⁱⁱⁱ	0.92 (2)	1.89 (2)	2.814 (3)	177 (4)
O4—H4A \cdots O1W	0.82	1.75	2.5657 (19)	176.
O1W—H1W \cdots O1 ^{iv}	0.83	1.86	2.642 (2)	157.
O1W—H2W \cdots O3 ^v	0.84	2.03	2.841 (2)	165.
O2—H2A \cdots O2 ^{vi}	0.91 (2)	1.54 (2)	2.446 (3)	173 (7)
C3—H3 \cdots O1 ^{vii}	0.93	2.54	3.270 (2)	135.
C13—H13 \cdots O2 ^{viii}	0.93	2.57	3.448 (2)	159.
C9—H9 \cdots O2 ^{ix}	0.93	2.36	3.246 (2)	160.

Symmetry codes: (iii) $-x+2, -y, -z$; (iv) $-x+1, -y+1, -z+1$; (v) $-x, -y+1, -z+1$; (vi) $-x, -y+1, -z$; (vii) $-x+1, -y+1, -z$; (viii) $x+1, y, z$; (ix) $-x+1, -y, -z$.

Fig. 1

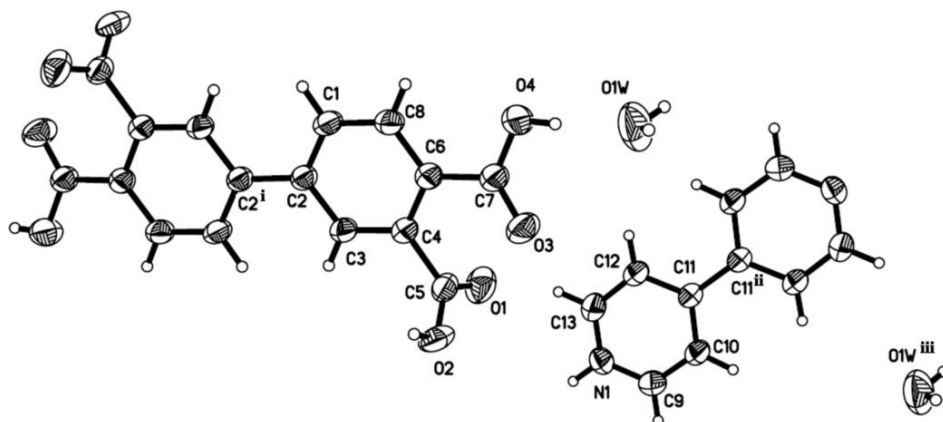


Fig. 2

