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4,4′-Bipyridinium bis(3,5-dicarboxybenzoate) benzene-1,3,5-tricarboxylic acid hexahydrate

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The asymmetric unit of the title compound, $C_{10}H_{10}N_2^{2+}\cdot 2C_9H_5O_6^{-}\cdot C_9H_6O_6\cdot 6H_2O$, consists of half of a bipyridinium cation, one singly deprotonated 3,5-dicarboxybenzoate anion, one half of a benzene-1,3,5-tricarboxylic acid molecule and three water molecules that are linked by hydrogen bonds into a network structure. The two halves of the bipyridinium cation are related by an inversion centre and those of the benzene-1,3,5-tricarboxylic acid molecule by twofold rotation.

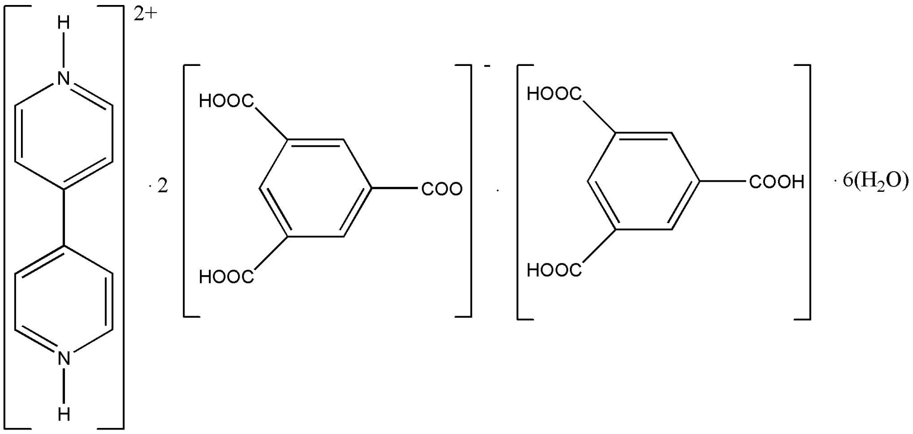
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.072
wR factor = 0.157
Data-to-parameter ratio = 11.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Much interest at present is focused on the construction of coordination polymers (Carlucci *et al.*, 1994; Munakata *et al.*, 1999; Hirsch *et al.*, 1997; Hoskins & Robson, 1990), and a large part of this interest has involved linear pyridyl-donor ligands; these include pyrazine (Carlucci *et al.*, 1995), 4,4′-bipyridine (Yaghi & Li, 1996) and longer bridges (Soma & Iwamoto, 1997). Bipyridine has been used extensively before (Huang & Xiong, 1997). We report here the structure of the title compound, (I), as part of further studies on coordination polymers constructed through hydrogen bonds with pyridyl-donor ligands.



(I)

Compound (I) consists of doubly protonated 4,4′-bipyridinium cations, singly deprotonated 3,5-dicarboxybenzoate anions, benzene-1,3,5-tricarboxylic acid molecules and water molecules (Fig. 1) that are linked by hydrogen bonds into a network structure (Fig. 2). There are many labile protons and a complex system of hydrogen bonds (Table 2) in this structure; the IR and NMR spectra are consistent with this. The two halves of the bipyridinium cation are related by an inversion centre and those of the benzene-1,3,5-tricarboxylic acid molecule by twofold rotation.

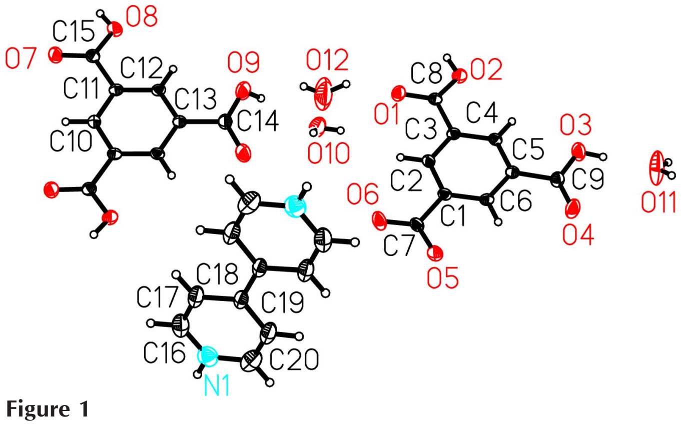


Figure 1
The structure of (I), with the atom numbering, showing displacement ellipsoids at the 50% probability level. Only one of the two sites for H9 is shown. Unlabelled atoms in the cation and acid molecule are generated from labelled atoms by the symmetry operations $(-x + \frac{3}{2}, -y + \frac{3}{2}, -z)$ and $(-x + 1, y, -z + \frac{3}{2})$.

Experimental

The title compound was synthesized by the hydrothermal method from a mixture of benzene-1,3,5-tricarboxylic acid (0.3 mmol), $La_2(SO_4)_3 \cdot 9H_2O$ (0.3 mmol), 4,4′-bipyridine (0.3 mmol) and water (8.0 ml) in a 15.0 ml Teflon-lined stainless steel reactor. The solution was heated at 423 K for 4 d. After reaction, the vessel was cooled slowly to room temperature to give yellow crystals. The prismatic crystals were collected, washed with distilled water and dried in air. The compound is soluble in dimethylformamide and begins to decompose at 393 K. IR (KBr pellet, 400–4000 cm^{-1}): 925.86, 1181.95, 1257.03, 1384.56, 1508.49, 1708.07, 3483.91 (*br*). ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.72 (*m*, 21H), 7.82 (*t*, 4H), 8.63 (*d*, 9H), 8.71 (*t*, 4 H).

Crystal data

$C_{10}H_{10}N_2^{2+} \cdot 2C_9H_5O_6^- \cdot C_9H_6O_6 \cdot 6H_2O$
$M_r = 894.69$
Monoclinic, $C2/c$
$a = 10.9217$ (7) Å
$b = 21.5274$ (17) Å
$c = 16.4036$ (11) Å
$\beta = 91.037$ (1)°
$V = 3856.1$ (5) Å^3
$Z = 4$

$D_x = 1.541$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3430 reflections
$\theta = 1.9$–25.1°
$\mu = 0.13$ mm^{-1}
$T = 298$ (2) K
Prism, yellow
0.39 × 0.20 × 0.14 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.97$, $T_{\max} = 0.98$
10 107 measured reflections

3430 independent reflections
3246 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\max} = 25.1°$
$h = -12 \rightarrow 12$
$k = -25 \rightarrow 25$
$l = -14 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.072$
$wR(F^2) = 0.157$
$S = 1.22$
3430 reflections
308 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0505P)^2 + 7.1401P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

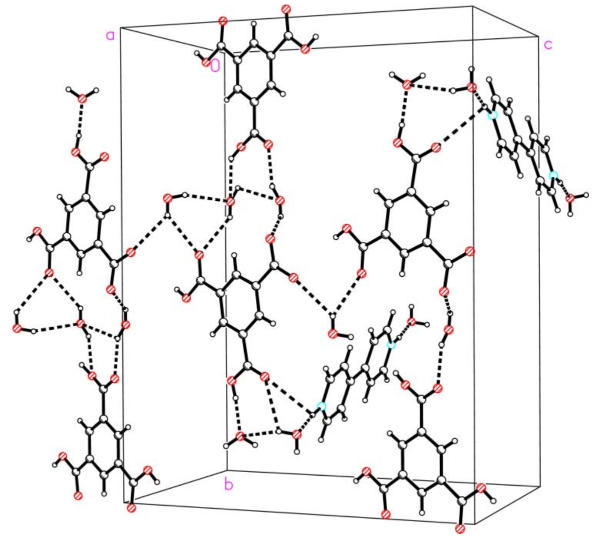


Figure 2
The three-dimensional network formed by hydrogen-bonding interactions in (I), shown as dashed lines. Only one of the two sites for H9 and hydrogen bonds involving it are shown.

Table 1
Selected geometric parameters (Å, °).

C3—C8	1.487 (3)	C16—N1	1.321 (5)
C8—O1	1.234 (3)	C20—N1	1.337 (5)
C8—O2	1.288 (3)		
O1—C8—O2	123.3 (2)	N1—C16—C17	120.5 (3)
O1—C8—C3	120.4 (2)	N1—C20—C19	119.8 (4)
O2—C8—C3	116.2 (2)	C16—N1—C20	121.3 (4)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O10—H10*A*···O7$^{\rm i}$	0.80 (3)	2.38 (4)	2.955 (4)	130 (5)
O10—H10*A*···O5$^{\rm ii}$	0.80 (3)	2.48 (4)	3.081 (4)	134 (5)
O11—H11*A*···O6$^{\rm iii}$	0.81 (3)	1.91 (3)	2.716 (4)	170 (5)
O11—H11*B*···O7$^{\rm iv}$	0.79 (3)	2.07 (3)	2.854 (4)	169 (5)
O2—H2*A*···O1$^{\rm v}$	0.82	1.88	2.700 (3)	176
O3—H3···O11	0.82	1.80	2.616 (4)	175
O8—H8···O5$^{\rm vi}$	0.82	1.66	2.476 (3)	171
O9—H9···O12	0.82	2.06	2.691 (4)	134
N1—H1···O10$^{\rm vii}$	0.86	1.87	2.727 (5)	173
O12—H12*A*···O9	0.81 (3)	1.99 (4)	2.691 (4)	145 (5)
O12—H12*B*···O1	0.81 (3)	2.39 (4)	2.963 (5)	128 (4)
O12—H12*B*···O6$^{\rm viii}$	0.81 (3)	2.42 (4)	3.072 (7)	137 (4)

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

Water H atoms were refined subject to the restraint O—H = 0.82 (3) Å. Other H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of 0.82 (O—H), 0.86 (N—H) and 0.93 Å (C—H), with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(parent atom). The presence of a peak in the difference Fourier map in a suitable location showed O9 to be protonated; however, due to the twofold symmetry, this site must be half occupied and the H atom disordered over the two sites. This H atom was included in the model as part of a rigid rotor, with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm O})$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve

Acta Cryst. (2005). E**61**, o1802–o1804 Li *et al.* • $C_{10}H_{10}N_2^{2+} \cdot 2C_9H_5O_6^- \cdot C_9H_6O_6 \cdot 6H_2O$ **o1803**

structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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