

2,2'-[*p*-Phenylenebis(methylideneazane-diy)]dipyridinium bis(hydrogensulfate) dihydrate

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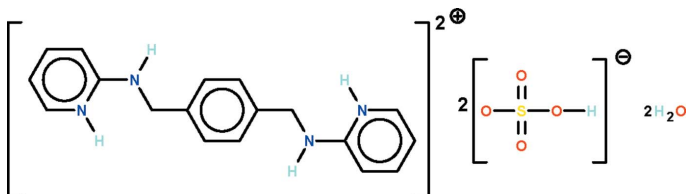
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.040; wR factor = 0.143; data-to-parameter ratio = 15.3.

The cation of the title salt, $\text{C}_{18}\text{H}_{20}\text{N}_4^{2+} \cdot 2\text{HSO}_4^- \cdot 2\text{H}_2\text{O}$, lies on a center of inversion with the mid-point directly in the middle of the *p*-phenylene ring. Within the hydrogensulfate ion, the S—O(H) bond is the longest of the S—O bonds. The dihedral angle between the central and terminal ring of the cation is $78.6(2)^\circ$. In the crystal, the cation, anion and water molecule interact by O—H...O and N—H...O hydrogen bonds, generating a three-dimensional network.

Related literature

For the synthesis and structure of 1,4-bis(pyridine-2-amino-methyl)benzene, see: Zou *et al.* (2003).



Experimental

Crystal data

$\text{C}_{18}\text{H}_{20}\text{N}_4^{2+} \cdot 2\text{HSO}_4^- \cdot 2\text{H}_2\text{O}$ $c = 9.5113(5)$ Å
 $M_r = 522.55$ $\alpha = 97.648(2)^\circ$
 Triclinic, $P\bar{1}$ $\beta = 92.340(2)^\circ$
 $a = 7.1718(5)$ Å $\gamma = 114.005(2)^\circ$
 $b = 9.3010(7)$ Å $V = 571.25(7)$ Å³

$Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 0.30$ mm⁻¹

$T = 293$ K
 $0.25 \times 0.21 \times 0.18$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\text{min}} = 0.930$, $T_{\text{max}} = 0.949$

5648 measured reflections
 2583 independent reflections
 1624 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.143$
 $S = 1.14$
 2583 reflections
 169 parameters
 5 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.48$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.42$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H3...O1w ⁱ	0.84 (1)	1.75 (1)	2.592 (4)	178 (5)
O1w—H11...O2	0.84 (1)	1.93 (2)	2.749 (3)	164 (5)
O1w—H12...O4 ⁱⁱ	0.84 (1)	1.98 (1)	2.813 (3)	174 (5)
N2—H2...O1	0.89 (1)	2.02 (2)	2.844 (3)	154 (3)
N1—H1...O4 ⁱⁱⁱ	0.88 (1)	2.03 (1)	2.903 (3)	170 (3)

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2312).

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supplementary materials

Acta Cryst. (2010). E66, o3300 [doi:10.1107/S1600536810047999]

2,2'-[*p*-Phenylenebis(methylideneazanediy)]dipyridinium bis(hydrogensulfate) dihydrate

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Comment

The synthesis complements other reports of the coordinating ability of 1,4-bis(2-pyridylaminomethyl)benzene, a relatively flexible *N*-donor ligand having aromatic as well as aliphatic donor sites. The structure of the neutral ligand has been reported (Zou *et al.*, 2003). Protonation by a strong acid, sulfuric acid, occurs at both pyridyl nitrogen atoms to yield the hydrogensulfate salt, $C_{18}H_{20}N_4^{2+} \cdot 2(HSO_4)^- \cdot 2H_2O$ (Scheme I, Fig. 1). The cation lies on a center-of-inversion with the mid-point directly in the middle of the *p*-phenylene ring. The hydrogensulfate anion bears a hydrogen atom, so that the S–O_H bond is the longest of the S–O bonds. The cation, anion and water molecule interact by O–H \cdots O and N–H \cdots O hydrogen bonds to generate a three-dimensional network (Table 1).

Experimental

1,4-Bis(2-pyridylaminomethyl)benzene (10 mmol, 2.90 g) was dissolved in methanol (50 ml). Strong sulfuric acid was added until the pH was 3. The solution was filtered; colorless crystals were isolated after several days.

Refinement

Carbon-bound hydrogen atoms were placed in calculated positions (C–H 0.93–0.97 Å) and were included in the refinement in the riding model approximation, with $U(H)$ set to $1.2U_{eq}(C)$. The amino/ammonium and water H atoms were located in a difference Fourier map, and were refined with distance restraints of N–H 0.88 ± 0.01 and O–H $0.84 + 0.01$ Å; their temperature factors were refined.

Figures

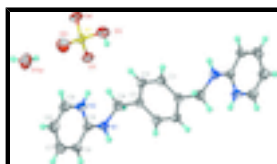


Fig. 1. Thermal ellipsoid plot (Barbour, 2001) of $C_{18}H_{20}N_4^{2+} \cdot 2(HSO_4)^- \cdot 2H_2O$ at the 50% probability level; hydrogen atoms are drawn as spheres of arbitrary radius. The cation lies on a center-of-inversion.

2,2'-[*p*-Phenylenebis(methylideneazanediy)]dipyridinium bis(hydrogensulfate) dihydrate

Crystal data

$C_{18}H_{20}N_4^{2+} \cdot 2HSO_4^- \cdot 2H_2O$

$M_r = 522.55$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$Z = 1$

$F(000) = 274$

$D_x = 1.519 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

supplementary materials

$a = 7.1718$ (5) Å
 $b = 9.3010$ (7) Å
 $c = 9.5113$ (5) Å
 $\alpha = 97.648$ (2)°
 $\beta = 92.340$ (2)°
 $\gamma = 114.005$ (2)°
 $V = 571.25$ (7) Å³

Cell parameters from 3948 reflections

$\theta = 3.1$ – 27.4 °
 $\mu = 0.30$ mm⁻¹
 $T = 293$ K
Prism, colorless
 $0.25 \times 0.21 \times 0.18$ mm

Data collection

Rigaku R-Axis RAPID
diffractometer

Radiation source: fine-focus sealed tube
graphite

Detector resolution: 10.000 pixels mm⁻¹
 ω scans

Absorption correction: multi-scan
(*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.930$, $T_{\max} = 0.949$

5648 measured reflections

2583 independent reflections

1624 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\max} = 27.4$ °, $\theta_{\min} = 3.1$ °

$h = -9 \rightarrow 8$

$k = -12 \rightarrow 12$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.143$

$S = 1.14$

2583 reflections

169 parameters

5 restraints

Primary atom site location: structure-invariant direct methods

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

$w = 1/[\sigma^2(F_o^2) + (0.0586P)^2 + 0.3231P]$

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

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

$\Delta\rho_{\max} = 0.48$ e Å⁻³

$\Delta\rho_{\min} = -0.42$ e Å⁻³

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.19334 (11)	0.92763 (8)	0.76081 (7)	0.0379 (2)
O1	0.1234 (3)	0.7575 (2)	0.7264 (2)	0.0508 (5)
O2	0.2506 (5)	0.9842 (3)	0.9097 (2)	0.0767 (8)
O3	0.3889 (4)	1.0040 (3)	0.6846 (3)	0.0627 (7)
H3	0.481 (5)	0.981 (5)	0.719 (4)	0.094*
O4	0.0542 (3)	0.9850 (3)	0.7002 (3)	0.0566 (6)
O1W	0.3282 (4)	1.0635 (4)	1.2016 (3)	0.0730 (8)
H11	0.286 (7)	1.023 (6)	1.1157 (19)	0.110*
H12	0.218 (4)	1.055 (6)	1.235 (5)	0.110*

N1	0.1175 (4)	0.3172 (3)	0.7485 (2)	0.0418 (6)
H1	0.112 (5)	0.220 (2)	0.740 (4)	0.063*
N2	0.2258 (4)	0.5652 (3)	0.8961 (2)	0.0388 (5)
H2	0.202 (5)	0.606 (4)	0.821 (2)	0.058*
C1	0.5953 (5)	0.6591 (3)	0.4870 (3)	0.0409 (7)
H1A	0.6588	0.7665	0.4787	0.049*
C2	0.4067 (5)	0.6003 (3)	0.5401 (3)	0.0417 (7)
H2A	0.3444	0.6687	0.5668	0.050*
C3	0.3092 (4)	0.4410 (3)	0.5541 (3)	0.0363 (6)
C4	0.1038 (5)	0.3747 (4)	0.6143 (3)	0.0432 (7)
H4A	0.0537	0.4573	0.6301	0.052*
H4B	0.0057	0.2875	0.5452	0.052*
C5	0.1854 (4)	0.4078 (3)	0.8764 (3)	0.0342 (6)
C6	0.2159 (4)	0.3435 (4)	0.9964 (3)	0.0407 (6)
H6	0.1907	0.2362	0.9874	0.049*
C7	0.2830 (5)	0.4399 (4)	1.1269 (3)	0.0492 (8)
H7	0.3020	0.3970	1.2064	0.059*
C8	0.3230 (5)	0.6011 (4)	1.1422 (3)	0.0502 (8)
H8	0.3689	0.6664	1.2308	0.060*
C9	0.2939 (4)	0.6600 (4)	1.0261 (3)	0.0453 (7)
H9	0.3206	0.7676	1.0345	0.054*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0398 (4)	0.0353 (4)	0.0421 (4)	0.0194 (3)	0.0045 (3)	0.0058 (3)
O1	0.0561 (13)	0.0329 (11)	0.0647 (14)	0.0198 (10)	0.0081 (10)	0.0079 (9)
O2	0.106 (2)	0.0816 (19)	0.0359 (13)	0.0403 (17)	-0.0082 (12)	-0.0100 (11)
O3	0.0481 (14)	0.0637 (16)	0.0861 (18)	0.0248 (12)	0.0202 (12)	0.0361 (13)
O4	0.0494 (13)	0.0527 (14)	0.0795 (16)	0.0314 (11)	0.0020 (11)	0.0175 (11)
O1W	0.0499 (15)	0.116 (2)	0.0588 (16)	0.0458 (16)	-0.0023 (12)	-0.0032 (15)
N1	0.0508 (15)	0.0357 (13)	0.0414 (13)	0.0204 (12)	0.0084 (10)	0.0059 (10)
N2	0.0420 (13)	0.0386 (14)	0.0403 (13)	0.0204 (11)	0.0020 (10)	0.0096 (10)
C1	0.0555 (18)	0.0352 (15)	0.0354 (15)	0.0226 (13)	0.0055 (12)	0.0047 (11)
C2	0.0557 (18)	0.0433 (17)	0.0371 (15)	0.0322 (15)	0.0059 (12)	0.0042 (12)
C3	0.0449 (16)	0.0423 (16)	0.0243 (13)	0.0220 (13)	0.0009 (10)	0.0025 (10)
C4	0.0469 (17)	0.0506 (18)	0.0346 (15)	0.0241 (14)	0.0008 (11)	0.0033 (12)
C5	0.0284 (13)	0.0360 (15)	0.0400 (15)	0.0138 (11)	0.0075 (10)	0.0096 (11)
C6	0.0418 (16)	0.0412 (16)	0.0472 (17)	0.0216 (13)	0.0103 (12)	0.0187 (12)
C7	0.0398 (16)	0.073 (2)	0.0443 (17)	0.0278 (15)	0.0096 (12)	0.0258 (15)
C8	0.0475 (18)	0.060 (2)	0.0428 (17)	0.0244 (16)	0.0010 (13)	0.0023 (14)
C9	0.0443 (17)	0.0401 (17)	0.0500 (17)	0.0184 (13)	0.0012 (13)	0.0009 (13)

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

S1—O2	1.425 (2)	C1—H1A	0.9300
S1—O1	1.437 (2)	C2—C3	1.385 (4)
S1—O4	1.443 (2)	C2—H2A	0.9300

supplementary materials

S1—O3	1.551 (2)	C3—C1 ⁱ	1.390 (4)
O3—H3	0.84 (1)	C3—C4	1.517 (4)
O1W—H11	0.84 (1)	C4—H4A	0.9700
O1W—H12	0.84 (1)	C4—H4B	0.9700
N1—C5	1.331 (4)	C5—C6	1.406 (4)
N1—C4	1.462 (4)	C6—C7	1.371 (4)
N1—H1	0.88 (1)	C6—H6	0.9300
N2—C5	1.356 (3)	C7—C8	1.394 (5)
N2—C9	1.362 (4)	C7—H7	0.9300
N2—H2	0.89 (1)	C8—C9	1.341 (4)
C1—C2	1.382 (4)	C8—H8	0.9300
C1—C3 ⁱ	1.390 (4)	C9—H9	0.9300
O2—S1—O1	112.24 (15)	C1 ⁱ —C3—C4	119.7 (3)
O2—S1—O4	113.33 (16)	N1—C4—C3	112.3 (2)
O1—S1—O4	113.05 (14)	N1—C4—H4A	109.1
O2—S1—O3	107.05 (17)	C3—C4—H4A	109.1
O1—S1—O3	107.22 (14)	N1—C4—H4B	109.1
O4—S1—O3	103.15 (13)	C3—C4—H4B	109.1
S1—O3—H3	109 (3)	H4A—C4—H4B	107.9
H11—O1W—H12	101 (5)	N1—C5—N2	121.3 (2)
C5—N1—C4	125.7 (2)	N1—C5—C6	121.2 (3)
C5—N1—H1	117 (2)	N2—C5—C6	117.5 (2)
C4—N1—H1	115 (2)	C7—C6—C5	119.6 (3)
C5—N2—C9	122.4 (2)	C7—C6—H6	120.2
C5—N2—H2	118 (2)	C5—C6—H6	120.2
C9—N2—H2	120 (2)	C6—C7—C8	121.0 (3)
C2—C1—C3 ⁱ	120.5 (3)	C6—C7—H7	119.5
C2—C1—H1A	119.7	C8—C7—H7	119.5
C3 ⁱ —C1—H1A	119.7	C9—C8—C7	118.4 (3)
C1—C2—C3	120.9 (3)	C9—C8—H8	120.8
C1—C2—H2A	119.6	C7—C8—H8	120.8
C3—C2—H2A	119.6	C8—C9—N2	121.2 (3)
C2—C3—C1 ⁱ	118.6 (3)	C8—C9—H9	119.4
C2—C3—C4	121.7 (3)	N2—C9—H9	119.4
C3 ⁱ —C1—C2—C3	0.3 (5)	C9—N2—C5—N1	179.5 (3)
C1—C2—C3—C1 ⁱ	-0.3 (4)	C9—N2—C5—C6	0.2 (4)
C1—C2—C3—C4	179.0 (2)	N1—C5—C6—C7	-179.0 (3)
C5—N1—C4—C3	80.0 (3)	N2—C5—C6—C7	0.3 (4)
C2—C3—C4—N1	-115.8 (3)	C5—C6—C7—C8	-0.5 (4)
C1 ⁱ —C3—C4—N1	63.5 (3)	C6—C7—C8—C9	0.2 (5)
C4—N1—C5—N2	8.5 (4)	C7—C8—C9—N2	0.3 (5)
C4—N1—C5—C6	-172.2 (3)	C5—N2—C9—C8	-0.5 (4)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
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O3—H3···O1w ⁱⁱ	0.84 (1)	1.75 (1)	2.592 (4)	178 (5)
O1w—H11···O2	0.84 (1)	1.93 (2)	2.749 (3)	164 (5)
O1w—H12···O4 ⁱⁱⁱ	0.84 (1)	1.98 (1)	2.813 (3)	174 (5)
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N1—H1···O4 ^{iv}	0.88 (1)	2.03 (1)	2.903 (3)	170 (3)

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

Fig. 1

