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2-[3-(Pyridin-1-ium-2-yl)-1*H*-pyrazol-1-yl]-6-[3-(pyridin-2-yl)-1*H*-pyrazol-1-yl]-pyridinium sulfate methanol monosolvate

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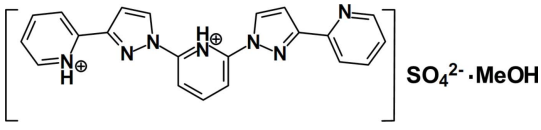
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; disorder in solvent or counterion; R factor = 0.053; wR factor = 0.163; data-to-parameter ratio = 12.6.

The title solvated salt, $C_{21}H_{17}N_7^{2+}\cdot SO_4^{2-}\cdot CH_3OH$, was obtained when we attempted to prepare the complex of ferrous sulfate and 2,6-bis[3-(pyridin-2-yl)-1*H*-pyrazol-1-yl]-pyridine in methanol. The dihedral angles between adjacent pyridine and pyrazole rings range from 3.8 (1) to 13.4 (1)°. An intramolecular N—H···N hydrogen bond occurs. In the crystal, N—H···O and O—H···N hydrogen bonds between solvent methanol molecules and the cations generate zigzag chains along [110].

Related literature

For general background to the chemistry of oligapyridine ligands, see: Constable *et al.* (1988, 1992, 1997); Fu, Li *et al.* (1996); Fu, Sun *et al.* (1996). For the synthesis of the ligand, see: Jameson & Goldsby (1990).



Experimental

Crystal data

$C_{21}H_{17}N_7^{2+}\cdot SO_4^{2-}\cdot CH_4O$
M_r = 495.52
Triclinic, $P\overline{1}$
a = 9.2575 (5) Å
b = 12.1707 (7) Å
c = 12.1991 (7) Å
α = 112.786 (6)°
β = 100.997 (5)°
γ = 106.363 (5)°
V = 1143.90 (11) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.19 mm^{-1}
T = 293 K
0.26 × 0.23 × 0.20 mm

Data collection

Bruker APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.952, T_{max} = 0.963
7326 measured reflections
4192 independent reflections
2629 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.163
S = 1.01
4192 reflections
334 parameters
21 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N7—H7···N6	0.86 (1)	2.35 (1)	2.713 (10)	106 (1)
O5—H5···N1	0.86 (3)	1.97 (3)	2.79 (3)	159 (4)
N7—H7···O5^{i}	0.86 (1)	1.88 (1)	2.690 (10)	156 (1)

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); 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: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KJ2223).

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2-[3-(Pyridin-1-ium-2-yl)-1*H*-pyrazol-1-yl]-6-[3-(pyridin-2-yl)-1*H*-pyrazol-1-yl]pyridinium sulfate methanol monosolvate

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S1. Comment

Helicates can be obtained by the self assembly of oligopyridine ligands with transition metal ions (Constable, 1992). 2,6′:2′,6":2",6‴:2‴,6""-Quinquepyridine reacts with Ag^{I} ions to give a mononuclear single-stranded helical complex (Constable *et al.* 1988). Mn^{II} single-stranded helicates bridged by Cl^{-} (Fu, Li *et al.* 1996) and Ag^{I} dinuclear double-stranded helicates (Fu, Sun *et al.* 1996) were obtained from the quinquepyridine when methyl groups were introduced at the 6 and 6"" positions. The presence of alkyl groups bound to the 4 and 4′ positions of quaterpyridine leads to the complete formation of the head-to-head conformer over the head-to-tail conformer (Constable *et al.* 1997). This encouraged us to investigate the coordination chemistry of transition metal ions with a new ligand containing a N_5 donor set. In this work, 2,6-di[3-(2-pyridyl)-1*H*-pyrazol-1-yl]-pyridine (Jameson & Goldsby, 1990) was used to react with ferrous sulfate in methanol, and the title compoud was obtained as yellow crystals.

In the structure, dihedral angles between the pyrazole and the pyridine rings (the rings are defined by the nitrogen atoms) are as follows: N1/N2N3 = 3.8 (1), N2N3/N4 = 4.3 (1), N4/N5N6 = 13.4 (1), N5N6/N7 =4.3 (1) °. Intramolecular N—H···N hydrogen bond and intermolecular N—H···O, and O—H···N hydrogen bonds were observed in the crystal. The intermolecular N—H···O and O—H···N hydrogen bonds between solvent methanol molecules and the organic molecules generate zigzag hydrogen bond chains running in the [110] direction.

S2. Experimental

2,6-Di[3-(2-pyridyl)-1*H*-pyrazol-1-yl]-pyridine was prepared using methods described in the literature (Jameson & Goldsby, 1990). A solution of 2-(1*H*-pyrazol-3-yl)-pyridine (11.76 g, 81 mmol) in 100 ml of anhydrous 2-methoxyethyl ether was stirred with potassium (6.0 g, 153 mmol) at 70 ° C under argon until the metal dissolved. To this solution was aadded 2,6-dibromopyridine (5.90 g, 24.8 mmol) in one portion. The mixture was stirred at 110 ° C for 4 days. The crude product was washed with hot water twice, and recrystallized from dichloromethane-hexane, 2,6-di[3- (2-pyridyl)-1*H*-pyrazol-1-yl]-pyridine was obtained as light yellow powder (yield 60%).

2,6-Di[3-(2-pyridyl)-1*H*-pyrazol-1-yl]-pyridine (18.3 mg, 0.05 mmol) and $FeSO_4.4H_2O$ (14 mg, 0.05 mmol) were mixed in methanol (3 ml) in a vial, the vial was covered and heated to 60 ° C for 48 h. After cooling, the title compound was obtained as yellow crystals suitable for X-ray structure analysis.

S3. Refinement

H atoms bonded to O atoms were located in a difference map. Other H atoms were positioned geometrically and refined using a riding model with N—H = 0.86 (aromatic), C—H = 0.93 (aromatic) and C—H = 0.96 (CH_3). All H atoms were refined with U_{iso}(H) = 1.2 times (1.5 for methyl groups) U_{eq}(C). The four oxygen atoms in sulfate anion are disordered over two positions. The site occupancy factors of these disordered oxygen atoms were refined by free variable to

0.782 (10) for O1, O2, O3 and O4, and 0.218 (10) for O1′, O2′, O3'and O4′, respectively, with distances restraints of S—O = 1.44 (1) Å and angles restraints of O—S—O = 109.5°. Only the major component O atoms were refined with anisotropic displacement parameters.

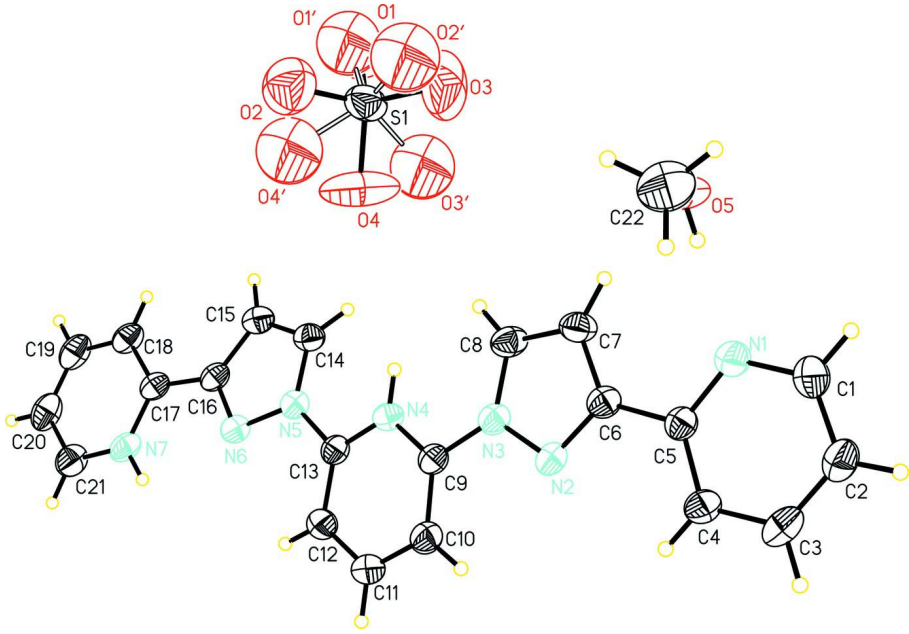

Figure 1

The molecular structure of the title complex with atom labels and 30% probability displacement ellipsoids for non-H atoms.

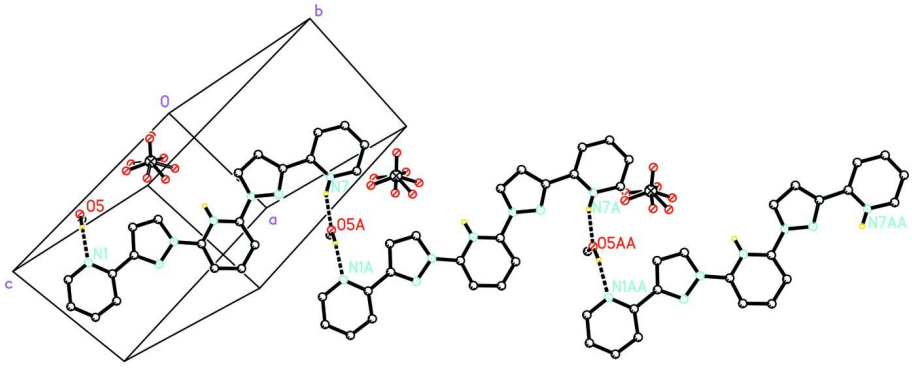

Figure 2

The chain formed by the lintermolecular N—H···O, and O—H···N hydrogen bonds (dashed lines) in the crystal. H atoms not involved in hydrogen bonding have been omitted for clarity.

2-[3-(Pyridin-1-ium-2-yl)-1*H*-pyrazol-1-yl]-6-[3-(pyridin-2-yl)-1*H*-pyrazol-1-yl]pyridinium sulfate methanol monosolvate

Crystal data

$C_{21}H_{17}N_7^{2+}\cdot SO_4^{2-}\cdot CH_4O$
M_r = 495.52
Triclinic, $P\overline{1}$
Hall symbol: -P 1

a = 9.2575 (5) Å
b = 12.1707 (7) Å
c = 12.1991 (7) Å
α = 112.786 (6)°

β = 100.997 (5)°
γ = 106.363 (5)°
V = 1143.90 (11) Å^3
Z = 2
F(000) = 516
D_x = 1.439 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å

Cell parameters from 2589 reflections
θ = 3.3–29.3°
μ = 0.19 mm^{-1}
T = 293 K
Block, yellow
0.26 × 0.23 × 0.20 mm

Data collection

Bruker APEX CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 10.3592 pixels mm^{-1}
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.952, T_{max} = 0.963

7326 measured reflections
4192 independent reflections
2629 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 25.4°, θ_{min} = 3.3°
h = −11→11
k = −12→14
l = −14→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.163
S = 1.01
4192 reflections
334 parameters
21 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
$w = 1/[\sigma^2(F_o^2) + (0.092P)^2 + 0.0074P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

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 $F^2 > \sigma(F^2)$ 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}	Occ. (<1)
S1	0.08891 (9)	0.24309 (9)	0.39262 (8)	0.0688 (3)	
O1	−0.0316 (7)	0.2731 (8)	0.3422 (6)	0.143 (2)	0.782 (10)
O2	0.1501 (6)	0.1801 (6)	0.2961 (4)	0.123 (2)	0.782 (10)
O3	0.0335 (7)	0.1588 (5)	0.4409 (6)	0.146 (2)	0.782 (10)
O4	0.2181 (6)	0.3518 (4)	0.4819 (6)	0.145 (3)	0.782 (10)
O1′	−0.034 (3)	0.262 (3)	0.320 (3)	0.177 (7)*	0.218 (10)
O2′	0.033 (3)	0.1150 (12)	0.373 (2)	0.177 (7)*	0.218 (10)
O3′	0.127 (3)	0.3358 (19)	0.5232 (11)	0.177 (7)*	0.218 (10)

O4′	0.231 (2)	0.281 (3)	0.366 (3)	0.177 (7)*	0.218 (10)
O5	−0.0119 (3)	0.2807 (3)	0.8003 (2)	0.0970 (9)	
H5	0.042 (5)	0.344 (3)	0.875 (2)	0.146*	
N1	0.2107 (3)	0.4485 (2)	1.0422 (2)	0.0633 (7)	
N2	0.4816 (3)	0.7105 (2)	1.01850 (19)	0.0505 (6)	
N3	0.4380 (3)	0.7522 (2)	0.9335 (2)	0.0510 (6)	
N4	0.4932 (3)	0.8909 (2)	0.84709 (19)	0.0498 (6)	
H4A	0.3947	0.8512	0.7984	0.060*	
N5	0.5238 (3)	1.0240 (2)	0.7534 (2)	0.0501 (6)	
N6	0.6192 (3)	1.1068 (2)	0.7231 (2)	0.0510 (6)	
N7	0.7420 (3)	1.2708 (2)	0.6334 (2)	0.0594 (6)	
H7	0.7990	1.2619	0.6913	0.071*	
C1	0.2076 (4)	0.3868 (3)	1.1128 (3)	0.0732 (9)	
H1	0.1124	0.3195	1.0930	0.088*	
C2	0.3357 (4)	0.4170 (3)	1.2119 (3)	0.0681 (9)	
H2	0.3274	0.3722	1.2587	0.082*	
C3	0.4761 (4)	0.5147 (3)	1.2404 (3)	0.0653 (9)	
H3	0.5660	0.5361	1.3062	0.078*	
C4	0.4840 (3)	0.5811 (3)	1.1715 (2)	0.0552 (7)	
H4	0.5789	0.6482	1.1902	0.066*	
C5	0.3484 (3)	0.5469 (3)	1.0735 (2)	0.0481 (7)	
C6	0.3476 (3)	0.6161 (3)	0.9981 (2)	0.0506 (7)	
C7	0.2185 (3)	0.5979 (3)	0.9010 (3)	0.0622 (8)	
H7A	0.1134	0.5383	0.8700	0.075*	
C8	0.2800 (4)	0.6859 (3)	0.8621 (3)	0.0611 (8)	
H8	0.2247	0.6984	0.7988	0.073*	
C9	0.5506 (3)	0.8563 (3)	0.9304 (2)	0.0477 (6)	
C10	0.7073 (3)	0.9165 (3)	1.0114 (3)	0.0572 (7)	
H10	0.7430	0.8894	1.0690	0.069*	
C11	0.8084 (4)	1.0183 (3)	1.0032 (3)	0.0636 (8)	
H11	0.9147	1.0614	1.0560	0.076*	
C12	0.7519 (3)	1.0566 (3)	0.9164 (3)	0.0581 (7)	
H12	0.8182	1.1247	0.9090	0.070*	
C13	0.5926 (3)	0.9889 (3)	0.8413 (2)	0.0477 (6)	
C14	0.3652 (3)	0.9869 (3)	0.6920 (3)	0.0565 (7)	
H14	0.2790	0.9308	0.6982	0.068*	
C15	0.3582 (3)	1.0485 (3)	0.6199 (3)	0.0584 (7)	
H15	0.2669	1.0431	0.5669	0.070*	
C16	0.5178 (3)	1.1216 (3)	0.6422 (2)	0.0507 (7)	
C17	0.5826 (3)	1.2052 (3)	0.5893 (2)	0.0515 (7)	
C18	0.4928 (4)	1.2218 (3)	0.4983 (3)	0.0623 (8)	
H18	0.3822	1.1775	0.4658	0.075*	
C19	0.5648 (5)	1.3030 (4)	0.4550 (3)	0.0745 (10)	
H19	0.5028	1.3145	0.3941	0.089*	
C20	0.7278 (5)	1.3675 (3)	0.5008 (3)	0.0786 (10)	
H20	0.7773	1.4223	0.4711	0.094*	
C21	0.8167 (4)	1.3495 (3)	0.5917 (3)	0.0729 (9)	
H21	0.9276	1.3917	0.6238	0.087*	

C22	0.0440 (5)	0.1814 (5)	0.7471 (4)	0.1141 (14)
H22A	0.0433	0.1681	0.6641	0.171*
H22B	−0.0246	0.1024	0.7417	0.171*
H22C	0.1511	0.2066	0.7997	0.171*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0483 (5)	0.0784 (6)	0.0764 (6)	0.0165 (4)	0.0085 (4)	0.0448 (5)
O1	0.090 (3)	0.216 (6)	0.144 (4)	0.085 (3)	0.009 (3)	0.102 (4)
O2	0.119 (4)	0.146 (5)	0.108 (3)	0.061 (4)	0.046 (3)	0.053 (3)
O3	0.193 (5)	0.137 (4)	0.151 (5)	0.051 (4)	0.087 (4)	0.105 (4)
O4	0.112 (3)	0.080 (3)	0.146 (4)	0.014 (2)	−0.060 (3)	0.025 (3)
O5	0.0841 (17)	0.0708 (18)	0.0880 (18)	0.0114 (15)	−0.0245 (14)	0.0295 (15)
N1	0.0612 (16)	0.0629 (17)	0.0612 (15)	0.0157 (14)	0.0120 (13)	0.0350 (14)
N2	0.0603 (15)	0.0498 (14)	0.0427 (12)	0.0229 (13)	0.0153 (11)	0.0231 (11)
N3	0.0574 (14)	0.0456 (14)	0.0464 (12)	0.0191 (12)	0.0135 (11)	0.0208 (11)
N4	0.0498 (13)	0.0459 (14)	0.0433 (12)	0.0162 (12)	0.0099 (10)	0.0156 (11)
N5	0.0551 (14)	0.0462 (14)	0.0478 (13)	0.0199 (12)	0.0161 (11)	0.0217 (12)
N6	0.0549 (13)	0.0464 (14)	0.0482 (13)	0.0182 (12)	0.0130 (11)	0.0220 (11)
N7	0.0757 (18)	0.0522 (15)	0.0476 (13)	0.0229 (14)	0.0098 (12)	0.0276 (12)
C1	0.075 (2)	0.071 (2)	0.079 (2)	0.0189 (18)	0.0226 (18)	0.048 (2)
C2	0.079 (2)	0.078 (2)	0.0627 (19)	0.035 (2)	0.0237 (18)	0.0445 (19)
C3	0.082 (2)	0.076 (2)	0.0429 (16)	0.044 (2)	0.0162 (16)	0.0251 (17)
C4	0.0577 (17)	0.0513 (18)	0.0465 (15)	0.0196 (15)	0.0112 (14)	0.0177 (14)
C5	0.0535 (16)	0.0457 (17)	0.0437 (14)	0.0205 (14)	0.0167 (13)	0.0187 (13)
C6	0.0558 (17)	0.0440 (16)	0.0458 (15)	0.0196 (14)	0.0134 (13)	0.0170 (13)
C7	0.0514 (17)	0.0538 (19)	0.0665 (18)	0.0087 (15)	0.0031 (15)	0.0301 (16)
C8	0.0600 (19)	0.0566 (19)	0.0597 (18)	0.0196 (16)	0.0044 (15)	0.0303 (16)
C9	0.0535 (16)	0.0453 (16)	0.0424 (14)	0.0215 (14)	0.0165 (13)	0.0173 (13)
C10	0.0591 (18)	0.063 (2)	0.0544 (17)	0.0257 (16)	0.0172 (15)	0.0314 (16)
C11	0.0526 (17)	0.073 (2)	0.0581 (18)	0.0192 (17)	0.0113 (14)	0.0305 (17)
C12	0.0539 (17)	0.0571 (19)	0.0592 (17)	0.0154 (15)	0.0172 (15)	0.0287 (16)
C13	0.0545 (16)	0.0451 (17)	0.0427 (14)	0.0208 (14)	0.0166 (13)	0.0188 (13)
C14	0.0522 (17)	0.0539 (18)	0.0522 (16)	0.0184 (15)	0.0122 (14)	0.0185 (15)
C15	0.0560 (18)	0.0578 (19)	0.0530 (16)	0.0247 (16)	0.0103 (14)	0.0202 (15)
C16	0.0635 (18)	0.0450 (17)	0.0409 (14)	0.0263 (15)	0.0137 (13)	0.0160 (13)
C17	0.0630 (19)	0.0444 (16)	0.0431 (15)	0.0258 (15)	0.0129 (14)	0.0157 (13)
C18	0.076 (2)	0.068 (2)	0.0525 (16)	0.0421 (18)	0.0160 (15)	0.0295 (17)
C19	0.108 (3)	0.080 (2)	0.0595 (19)	0.057 (2)	0.028 (2)	0.0413 (19)
C20	0.119 (3)	0.068 (2)	0.066 (2)	0.042 (2)	0.036 (2)	0.041 (2)
C21	0.085 (2)	0.060 (2)	0.0634 (19)	0.0145 (19)	0.0183 (18)	0.0320 (18)
C22	0.105 (3)	0.122 (4)	0.106 (3)	0.047 (3)	0.019 (3)	0.051 (3)

Geometric parameters (Å, º)

S1—O4	1.365 (3)	C3—H3	0.9300
S1—O1	1.378 (3)	C4—C5	1.387 (4)

S1—O3	1.396 (3)	C4—H4	0.9300
S1—O2′	1.400 (9)	C5—C6	1.469 (4)
S1—O4′	1.403 (9)	C6—C7	1.411 (4)
S1—O1′	1.432 (9)	C7—C8	1.359 (4)
S1—O2	1.448 (4)	C7—H7A	0.9300
S1—O3′	1.451 (9)	C8—H8	0.9300
O5—C22	1.422 (5)	C9—C10	1.382 (4)
O5—H5	0.863 (11)	C10—C11	1.378 (4)
N1—C1	1.342 (4)	C10—H10	0.9300
N1—C5	1.344 (3)	C11—C12	1.385 (4)
N2—C6	1.334 (3)	C11—H11	0.9300
N2—N3	1.363 (3)	C12—C13	1.381 (4)
N3—C8	1.362 (4)	C12—H12	0.9300
N3—C9	1.415 (3)	C14—C15	1.362 (4)
N4—C9	1.321 (3)	C14—H14	0.9300
N4—C13	1.321 (3)	C15—C16	1.402 (4)
N4—H4A	0.8600	C15—H15	0.9300
N5—N6	1.357 (3)	C16—C17	1.458 (4)
N5—C14	1.366 (3)	C17—C18	1.372 (4)
N5—C13	1.410 (3)	C18—C19	1.366 (5)
N6—C16	1.329 (3)	C18—H18	0.9300
N7—C21	1.339 (4)	C19—C20	1.370 (5)
N7—C17	1.343 (4)	C19—H19	0.9300
N7—H7	0.8600	C20—C21	1.377 (4)
C1—C2	1.367 (4)	C20—H20	0.9300
C1—H1	0.9300	C21—H21	0.9300
C2—C3	1.364 (4)	C22—H22A	0.9600
C2—H2	0.9300	C22—H22B	0.9600
C3—C4	1.372 (4)	C22—H22C	0.9600

O4—S1—O1	111.7 (4)	N1—C5—C6	116.3 (2)
O4—S1—O3	111.2 (3)	C4—C5—C6	121.8 (3)
O1—S1—O3	111.2 (4)	N2—C6—C7	111.2 (2)
O4—S1—O2′	132.2 (10)	N2—C6—C5	120.1 (2)
O1—S1—O2′	112.3 (12)	C7—C6—C5	128.6 (3)
O3—S1—O2′	33.1 (10)	C8—C7—C6	105.5 (3)
O4—S1—O4′	60.1 (10)	C8—C7—H7A	127.2
O1—S1—O4′	116.2 (10)	C6—C7—H7A	127.2
O3—S1—O4′	131.3 (9)	C7—C8—N3	106.9 (2)
O2′—S1—O4′	113.6 (11)	C7—C8—H8	126.6
O4—S1—O1′	116.8 (13)	N3—C8—H8	126.6
O1—S1—O1′	9.8 (16)	N4—C9—C10	124.0 (3)
O3—S1—O1′	114.6 (14)	N4—C9—N3	114.9 (2)
O2′—S1—O1′	109.6 (12)	C10—C9—N3	121.0 (2)
O4′—S1—O1′	110.6 (13)	C11—C10—C9	117.2 (3)
O4—S1—O2	104.5 (3)	C11—C10—H10	121.4
O1—S1—O2	110.1 (3)	C9—C10—H10	121.4
O3—S1—O2	107.8 (3)	C10—C11—C12	120.2 (3)

O2′—S1—O2	77.0 (10)	C10—C11—H11	119.9
O4′—S1—O2	45.5 (11)	C12—C11—H11	119.9
O1′—S1—O2	100.4 (13)	C13—C12—C11	116.9 (3)
O4—S1—O3′	44.6 (9)	C13—C12—H12	121.5
O1—S1—O3′	96.3 (11)	C11—C12—H12	121.5
O3—S1—O3′	79.9 (9)	N4—C13—C12	124.2 (2)
O2′—S1—O3′	112.3 (11)	N4—C13—N5	115.0 (2)
O4′—S1—O3′	104.6 (11)	C12—C13—N5	120.7 (3)
O1′—S1—O3′	105.8 (12)	C15—C14—N5	106.4 (3)
O2—S1—O3′	146.4 (10)	C15—C14—H14	126.8
C22—O5—H5	120 (3)	N5—C14—H14	126.8
C1—N1—C5	117.1 (3)	C14—C15—C16	105.5 (2)
C6—N2—N3	104.5 (2)	C14—C15—H15	127.2
C8—N3—N2	111.9 (2)	C16—C15—H15	127.2
C8—N3—C9	127.6 (2)	N6—C16—C15	111.6 (2)
N2—N3—C9	120.4 (2)	N6—C16—C17	118.6 (3)
C9—N4—C13	117.5 (2)	C15—C16—C17	129.8 (2)
C9—N4—H4A	121.3	N7—C17—C18	117.8 (3)
C13—N4—H4A	121.3	N7—C17—C16	117.4 (2)
N6—N5—C14	112.0 (2)	C18—C17—C16	124.8 (3)
N6—N5—C13	119.9 (2)	C19—C18—C17	120.4 (3)
C14—N5—C13	128.1 (2)	C19—C18—H18	119.8
C16—N6—N5	104.4 (2)	C17—C18—H18	119.8
C21—N7—C17	123.3 (3)	C18—C19—C20	120.4 (3)
C21—N7—H7	118.3	C18—C19—H19	119.8
C17—N7—H7	118.3	C20—C19—H19	119.8
N1—C1—C2	124.0 (3)	C19—C20—C21	118.7 (3)
N1—C1—H1	118.0	C19—C20—H20	120.7
C2—C1—H1	118.0	C21—C20—H20	120.7
C3—C2—C1	118.3 (3)	N7—C21—C20	119.4 (3)
C3—C2—H2	120.9	N7—C21—H21	120.3
C1—C2—H2	120.9	C20—C21—H21	120.3
C2—C3—C4	119.6 (3)	O5—C22—H22A	109.5
C2—C3—H3	120.2	O5—C22—H22B	109.5
C4—C3—H3	120.2	H22A—C22—H22B	109.5
C3—C4—C5	119.0 (3)	O5—C22—H22C	109.5
C3—C4—H4	120.5	H22A—C22—H22C	109.5
C5—C4—H4	120.5	H22B—C22—H22C	109.5
N1—C5—C4	121.9 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N7—H7···N6	0.86 (1)	2.35 (1)	2.713 (10)	106 (1)
O5—H5···N1	0.86 (3)	1.97 (3)	2.79 (3)	159 (4)
N7—H7···O5^{i}	0.86 (1)	1.88 (1)	2.690 (10)	156 (1)

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