

Bis(2,6-diaminopyridin-1-ium) hexaaqua-cobalt(II) disulfate dihydrate

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Received 30 June 2010; accepted 6 July 2010

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.001$ Å; R factor = 0.022; wR factor = 0.064; data-to-parameter ratio = 28.3.

In the title compound, $(\text{C}_5\text{H}_8\text{N}_3)_2[\text{Co}(\text{H}_2\text{O})_6](\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$, the complete complex cation is generated by crystallographic inversion symmetry, such that the Co^{II} cation is octahedrally coordinated by six water molecules. The organic cation is essentially planar, with a maximum deviation of 0.013 (1) Å. In the crystal structure, the ions and molecules are linked into a pseudo-layered three-dimensional supramolecular network via $\text{O}-\text{H} \cdots \text{O}$ and $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds. Weak intermolecular $\pi-\pi$ interactions further stabilize the crystal structure [centroid-centroid distance = 3.5231 (4) Å].

Related literature

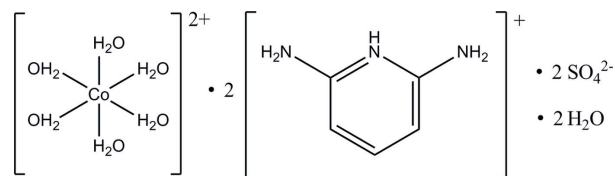
For general background to and applications of 1,6-diaminopyridinium ions, see: Abu Zuhri & Cox (1989); Inuzuka & Fujimoto (1990); Ma & Huang (2003); Patani & LaVoie (1996). For closely related hexaaquacobalt(II) structures, see: Li *et al.* (2004); Pan *et al.* (2003). For closely related pyridinium structures, see: Al-Dajani, Abdallah *et al.* (2009, 2010); Al-Dajani, Salhin *et al.* (2009). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).

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[¶] Thomson Reuters ResearcherID: C-7576-2009.

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Experimental

Crystal data

$(\text{C}_5\text{H}_8\text{N}_3)_2[\text{Co}(\text{H}_2\text{O})_6](\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$
 $M_r = 615.47$
Orthorhombic, *Pbca*
 $a = 6.6219$ (1) Å
 $b = 14.4347$ (2) Å
 $c = 24.7590$ (3) Å

$V = 2366.59$ (6) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.99$ mm⁻¹
 $T = 100$ K
 $0.35 \times 0.31 \times 0.21$ mm

Data collection

Bruker SMART APEXII CCD
diffractometer
Absorption correction: multi-scan
(*SADABS*; Bruker, 2009)
 $T_{\text{min}} = 0.725$, $T_{\text{max}} = 0.821$

86569 measured reflections
6333 independent reflections
5758 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.064$
 $S = 1.08$
6333 reflections

224 parameters
All H-atom parameters refined
 $\Delta\rho_{\text{max}} = 0.60$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.38$ e Å⁻³

Table 1

Selected bond lengths (Å).

Co1—O1W	2.0801 (5)	Co1—O3W	2.1064 (5)
Co1—O2W	2.0985 (5)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
O1W—H1W1 \cdots O1 ⁱ	0.848 (14)	1.863 (15)	2.7088 (7)	175.4 (13)
O1W—H2W1 \cdots O4W ⁱⁱ	0.840 (13)	1.948 (13)	2.7853 (8)	174.2 (13)
O2W—H1W2 \cdots O2	0.800 (14)	1.923 (14)	2.7217 (8)	176.3 (14)
O2W—H2W2 \cdots O3 ⁱⁱⁱ	0.815 (14)	2.025 (13)	2.8352 (8)	172.7 (15)
O3W—H1W3 \cdots O4W ⁱ	0.836 (15)	1.898 (15)	2.7318 (8)	175.1 (13)
O3W—H2W3 \cdots O3 ^{iv}	0.805 (15)	1.991 (15)	2.7928 (8)	173.6 (14)
O4W—H1W4 \cdots O2	0.863 (17)	1.910 (17)	2.7643 (8)	169.9 (16)
O4W—H2W4 \cdots O3 ⁱ	0.784 (15)	1.994 (15)	2.7157 (7)	152.8 (18)
N1—H1N1 \cdots O1	0.883 (13)	2.005 (12)	2.8412 (7)	157.6 (12)
N2—H2N2 \cdots O2 ^v	0.810 (15)	2.424 (15)	3.1769 (9)	155.1 (13)
N3—H1N3 \cdots O1	0.851 (13)	2.347 (13)	3.0660 (7)	142.6 (11)
N2—H1N2 \cdots O4	0.776 (15)	2.162 (15)	2.8977 (9)	158.5 (14)
N3—H2N3 \cdots O4 ^{vi}	0.844 (14)	2.079 (14)	2.9155 (8)	171.0 (12)

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINTE* (Bruker, 2009); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *PLATON* (Spek, 2009).

NH gratefully acknowledges funding from Universiti Sains Malaysia (USM) under the University Research Grant (No. 1001/PFARMASI/815025). HKF and JHG thank USM for the Research University Golden Goose Grant (No. 1001/PFIZIK/811012). JHG also thanks USM for the award of a USM Fellowship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5536).

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supplementary materials

Acta Cryst. (2010). E66, m917-m918 [doi:10.1107/S1600536810026693]

Bis(2,6-diaminopyridin-1-ium) hexaaquacobalt(II) disulfate dihydrate

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Comment

Generally 1,6-diaminopyridinium has an important role in the preparation of aromatic azo dyes, the subject of many polarographic investigations (Abu Zuhri & Cox, 1989). It also exhibits amino-imino tautomerization property (Inuzuka & Fujimoto, 1990). Molecules containing pyridyl moiety exhibit biological activity and low toxicity (Patani & LaVoie, 1996; Ma & Huang, 2003).

The asymmetric unit of the title complex comprises of half of hexaaquacobalt(II) cation, a protonated 2,6-diaminopyridin-1-ium cation, a sulphate anion and a water molecule of crystallization. The complete complex (Fig. 1) is generated by the crystallographic inversion center [symmetry code of atoms labelled with suffix A: $-x+1, -y+1, -z+1$]. Within the metal complex cation $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, the Co^{II} ion is coordinated by six water molecules at the vertices of the almost ideal octahedron. The Co—O bond lengths range from 2.0801 (5) to 2.1064 (5) Å and the O—Co—O angles span the ranges of 87.50 (2)–92.50 (2)° and 179.999 (1)–180.00 (3)°. The 2,6-diaminopyridinium organic cation (C1–C5/N1–N3) is essentially planar, with a maximum deviation of -0.013 (1) Å at atom C5. Comparing to the unprotonated structure (Al-Dajani, Salhin *et al.*, 2009), protonation at atom N1 has led to a slight increase in the C1—N1—C5 angle to 123.55 (5)°. The geometric parameters are consistent to those observed in closely related hexaaquacobalt(II) (Pan *et al.*, 2003; Li *et al.*, 2004) and 1,6-diaminopyridinium (Al-Dajani, Abdallah *et al.*, 2009,2010; Al-Dajani, Salhin *et al.*, 2009) structures.

The crystal structure is mainly stabilized by a network of O—H \cdots O and N—H \cdots O hydrogen bonds (Table 2). In this network, the water molecule O atoms and organic N atoms act as donors whereas the sulphate O atoms provide the most extensive part as acceptors. A three-dimensional supramolecular structure (Fig. 2) is built up in such an arrangement that the 2,6-diaminopyridinium organic layers are sandwiched between layers formed through the remaining ions and water molecules. The crystal structure is further stabilized by weak intermolecular $\text{Cg1}\cdots\text{Cg1}$ interactions [$\text{Cg1}\cdots\text{Cg1} = 3.5231$ (4) Å; symmetry codes: $x-1/2, y, -z+3/2$ and $x+1/2, y, -z+3/2$] where Cg1 is the centroid of C1–C5/N1 pyridine ring.

Experimental

In a round bottom flask was added with stirring 1,4-dioxane (25 ml), 2,6-diaminopyridine (0.02 mol, 2.2 g) and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (0.01 mol, 2.8 g) dissolved in water. The concoction was refluxed for 24 h and a red solution was then formed. Red blocks of (I) were formed overnight at room temperature. The filtrate was washed with 1,4-dioxane and dried at 333 K.

Refinement

All H-atoms were located from difference Fourier map and allowed to refine freely [ranges of C—H = 0.938 (13)–0.980 (13) Å, N—H = 0.776 (15)–0.884 (13) Å and O—H = 0.784 (16)–0.863 (17) Å].

Figures

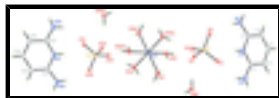


Fig. 1. The molecular structure of (I), showing 50% probability displacement ellipsoids for non-H atoms. The suffix A corresponds to the symmetry code $[-x+1, -y+1, -z+1]$.

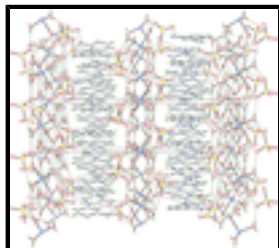


Fig. 2. The crystal structure of (I), viewed along the b axis, showing the three-dimensional supramolecular structure. Intermolecular interactions have been shown as dashed lines.

Bis(2,6-diaminopyridin-1-ium) hexaaquacobalt(II) disulfate dihydrate

Crystal data

$(C_5H_8N_3)_2[Co(H_2O)_6](SO_4)_2 \cdot 2H_2O$

$M_r = 615.47$

Orthorhombic, $Pbca$

Hall symbol: $-P\ 2ac\ 2ab$

$a = 6.6219\ (1)\ \text{\AA}$

$b = 14.4347\ (2)\ \text{\AA}$

$c = 24.7590\ (3)\ \text{\AA}$

$V = 2366.59\ (6)\ \text{\AA}^3$

$Z = 4$

$F(000) = 1284$

$D_x = 1.727\ \text{Mg m}^{-3}$

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

Cell parameters from 9901 reflections

$\theta = 3.5\text{--}37.6^\circ$

$\mu = 0.99\ \text{mm}^{-1}$

$T = 100\ \text{K}$

Block, red

$0.35 \times 0.31 \times 0.21\ \text{mm}$

Data collection

Bruker SMART APEXII CCD diffractometer

Radiation source: fine-focus sealed tube graphite

φ and ω scans

Absorption correction: multi-scan (*SADABS*; Bruker, 2009)

$T_{\min} = 0.725$, $T_{\max} = 0.821$

86569 measured reflections

6333 independent reflections

5758 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$

$\theta_{\max} = 37.7^\circ$, $\theta_{\min} = 1.6^\circ$

$h = -11 \rightarrow 11$

$k = -24 \rightarrow 24$

$l = -42 \rightarrow 42$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.022$

$wR(F^2) = 0.064$

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

All H-atom parameters refined

$S = 1.08$	$w = 1/[\sigma^2(F_o^2) + (0.0322P)^2 + 0.6554P]$
6333 reflections	where $P = (F_o^2 + 2F_c^2)/3$
224 parameters	$(\Delta/\sigma)_{\max} = 0.001$
0 restraints	$\Delta\rho_{\max} = 0.60 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\min} = -0.38 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1)K.

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 $F^2 > 2\text{sigma}(F^2)$ 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	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.5000	0.5000	0.5000	0.00813 (3)
O1W	0.60030 (8)	0.62537 (4)	0.46843 (2)	0.01288 (8)
O2W	0.37213 (8)	0.57254 (4)	0.56500 (2)	0.01253 (8)
O3W	0.23481 (8)	0.51148 (4)	0.45350 (2)	0.01281 (9)
O4W	0.50958 (8)	0.83091 (4)	0.53640 (2)	0.01281 (9)
S1	0.86829 (2)	0.696844 (10)	0.616698 (6)	0.00760 (3)
O1	0.93408 (8)	0.79469 (3)	0.62001 (2)	0.01200 (8)
O2	0.64851 (8)	0.69401 (4)	0.60506 (2)	0.01254 (8)
O3	0.97898 (8)	0.64929 (4)	0.57237 (2)	0.01158 (8)
O4	0.90760 (9)	0.65018 (4)	0.66828 (2)	0.01417 (9)
N1	0.89603 (9)	0.85415 (4)	0.72893 (2)	0.00943 (8)
N2	0.97396 (10)	0.72061 (4)	0.77643 (3)	0.01420 (10)
N3	0.82794 (10)	0.97979 (4)	0.67371 (2)	0.01328 (10)
C1	0.91746 (10)	0.81030 (4)	0.77745 (2)	0.00979 (9)
C2	0.88017 (10)	0.86024 (5)	0.82461 (3)	0.01229 (10)
C3	0.82632 (11)	0.95288 (5)	0.82032 (3)	0.01297 (10)
C4	0.80547 (11)	0.99626 (5)	0.77070 (3)	0.01179 (10)
C5	0.84005 (9)	0.94478 (4)	0.72390 (2)	0.00965 (9)
H1W1	0.542 (2)	0.6492 (10)	0.4413 (6)	0.030 (4)*
H2W1	0.724 (2)	0.6368 (10)	0.4648 (6)	0.028 (3)*
H1W2	0.451 (2)	0.6080 (10)	0.5781 (6)	0.025 (3)*
H2W2	0.264 (2)	0.5990 (10)	0.5680 (6)	0.030 (4)*
H1W3	0.160 (2)	0.5580 (11)	0.4558 (6)	0.029 (4)*
H2W3	0.165 (2)	0.4675 (11)	0.4463 (6)	0.028 (3)*

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H1W4	0.559 (3)	0.7850 (12)	0.5544 (6)	0.036 (4)*
H2W4	0.514 (2)	0.8192 (13)	0.5055 (6)	0.032 (4)*
H1N1	0.923 (2)	0.8224 (9)	0.6993 (5)	0.021 (3)*
H2N2	1.014 (2)	0.6963 (10)	0.8039 (6)	0.023 (3)*
H1N3	0.836 (2)	0.9442 (9)	0.6464 (5)	0.021 (3)*
H1N2	0.983 (2)	0.6940 (10)	0.7493 (6)	0.023 (3)*
H2N3	0.769 (2)	1.0311 (10)	0.6695 (5)	0.022 (3)*
H2	0.888 (2)	0.8281 (9)	0.8575 (5)	0.024 (3)*
H3	0.794 (2)	0.9854 (9)	0.8525 (5)	0.017 (3)*
H4	0.768 (2)	1.0617 (9)	0.7676 (5)	0.021 (3)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.00772 (5)	0.00786 (5)	0.00880 (5)	-0.00035 (4)	-0.00063 (4)	0.00026 (3)
O1W	0.01163 (19)	0.0125 (2)	0.0145 (2)	-0.00216 (16)	-0.00227 (17)	0.00427 (15)
O2W	0.01003 (19)	0.0139 (2)	0.01366 (19)	-0.00017 (16)	-0.00004 (16)	-0.00345 (16)
O3W	0.01056 (19)	0.01071 (19)	0.0172 (2)	0.00053 (16)	-0.00386 (17)	-0.00187 (15)
O4W	0.0138 (2)	0.0137 (2)	0.01087 (19)	0.00064 (16)	-0.00068 (16)	-0.00023 (16)
S1	0.00845 (6)	0.00744 (6)	0.00691 (5)	-0.00042 (4)	0.00023 (4)	-0.00030 (4)
O1	0.0154 (2)	0.00811 (18)	0.01252 (19)	-0.00296 (16)	0.00154 (17)	-0.00110 (14)
O2	0.00834 (18)	0.0135 (2)	0.0158 (2)	-0.00022 (15)	-0.00093 (16)	-0.00211 (16)
O3	0.01201 (19)	0.01219 (19)	0.01052 (18)	0.00079 (15)	0.00229 (15)	-0.00298 (15)
O4	0.0201 (2)	0.0137 (2)	0.00873 (17)	-0.00068 (18)	-0.00182 (17)	0.00294 (15)
N1	0.0103 (2)	0.0097 (2)	0.00826 (19)	0.00011 (16)	-0.00031 (16)	-0.00037 (15)
N2	0.0180 (3)	0.0110 (2)	0.0136 (2)	0.00237 (19)	-0.0038 (2)	0.00052 (18)
N3	0.0147 (2)	0.0138 (2)	0.0113 (2)	0.00146 (19)	-0.00063 (19)	0.00307 (17)
C1	0.0089 (2)	0.0109 (2)	0.0096 (2)	-0.00068 (18)	-0.00122 (18)	0.00055 (17)
C2	0.0127 (2)	0.0153 (3)	0.0089 (2)	0.0001 (2)	-0.00031 (19)	-0.00021 (18)
C3	0.0119 (2)	0.0157 (3)	0.0113 (2)	0.0000 (2)	0.0004 (2)	-0.00380 (19)
C4	0.0112 (2)	0.0108 (2)	0.0134 (2)	0.00028 (19)	0.0003 (2)	-0.00217 (18)
C5	0.0080 (2)	0.0101 (2)	0.0109 (2)	-0.00041 (18)	-0.00031 (18)	0.00074 (17)

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

Co1—O1W ⁱ	2.0801 (5)	S1—O3	1.4875 (5)
Co1—O1W	2.0801 (5)	N1—C1	1.3652 (8)
Co1—O2W ⁱ	2.0985 (5)	N1—C5	1.3654 (8)
Co1—O2W	2.0985 (5)	N1—H1N1	0.884 (13)
Co1—O3W ⁱ	2.1064 (5)	N2—C1	1.3478 (9)
Co1—O3W	2.1064 (5)	N2—H2N2	0.810 (14)
O1W—H1W1	0.848 (16)	N2—H1N2	0.776 (15)
O1W—H2W1	0.841 (16)	N3—C5	1.3438 (8)
O2W—H1W2	0.799 (15)	N3—H1N3	0.851 (14)
O2W—H2W2	0.817 (16)	N3—H2N3	0.843 (15)
O3W—H1W3	0.836 (16)	C1—C2	1.3942 (9)
O3W—H2W3	0.806 (16)	C2—C3	1.3881 (10)
O4W—H1W4	0.863 (17)	C2—H2	0.938 (13)

O4W—H2W4	0.784 (16)	C3—C4	1.3859 (10)
S1—O4	1.4672 (5)	C3—H3	0.949 (13)
S1—O1	1.4803 (5)	C4—C5	1.3953 (9)
S1—O2	1.4842 (5)	C4—H4	0.980 (13)
O1W ⁱ —Co1—O1W	180.0	O4—S1—O3	110.06 (3)
O1W ⁱ —Co1—O2W ⁱ	89.02 (2)	O1—S1—O3	109.64 (3)
O1W—Co1—O2W ⁱ	90.98 (2)	O2—S1—O3	109.10 (3)
O1W ⁱ —Co1—O2W	90.98 (2)	C1—N1—C5	123.55 (5)
O1W—Co1—O2W	89.02 (2)	C1—N1—H1N1	117.9 (9)
O2W ⁱ —Co1—O2W	180.0	C5—N1—H1N1	118.5 (9)
O1W ⁱ —Co1—O3W ⁱ	89.56 (2)	C1—N2—H2N2	119.5 (10)
O1W—Co1—O3W ⁱ	90.44 (2)	C1—N2—H1N2	120.9 (11)
O2W ⁱ —Co1—O3W ⁱ	92.50 (2)	H2N2—N2—H1N2	119.0 (15)
O2W—Co1—O3W ⁱ	87.50 (2)	C5—N3—H1N3	120.2 (9)
O1W ⁱ —Co1—O3W	90.44 (2)	C5—N3—H2N3	118.2 (9)
O1W—Co1—O3W	89.56 (2)	H1N3—N3—H2N3	117.5 (13)
O2W ⁱ —Co1—O3W	87.50 (2)	N2—C1—N1	117.24 (6)
O2W—Co1—O3W	92.50 (2)	N2—C1—C2	124.16 (6)
O3W ⁱ —Co1—O3W	180.0	N1—C1—C2	118.60 (6)
Co1—O1W—H1W1	120.3 (10)	C3—C2—C1	118.66 (6)
Co1—O1W—H2W1	121.4 (10)	C3—C2—H2	123.9 (8)
H1W1—O1W—H2W1	106.3 (14)	C1—C2—H2	117.4 (8)
Co1—O2W—H1W2	111.5 (11)	C4—C3—C2	121.91 (6)
Co1—O2W—H2W2	131.1 (10)	C4—C3—H3	120.0 (8)
H1W2—O2W—H2W2	103.8 (14)	C2—C3—H3	118.0 (8)
Co1—O3W—H1W3	121.3 (10)	C3—C4—C5	118.63 (6)
Co1—O3W—H2W3	122.5 (11)	C3—C4—H4	122.0 (8)
H1W3—O3W—H2W3	108.0 (16)	C5—C4—H4	119.4 (8)
H1W4—O4W—H2W4	109.0 (17)	N3—C5—N1	117.44 (6)
O4—S1—O1	109.73 (3)	N3—C5—C4	123.90 (6)
O4—S1—O2	109.29 (3)	N1—C5—C4	118.63 (6)
O1—S1—O2	109.01 (3)		
C5—N1—C1—N2	-179.89 (6)	C2—C3—C4—C5	-0.05 (11)
C5—N1—C1—C2	0.09 (10)	C1—N1—C5—N3	178.90 (6)
N2—C1—C2—C3	178.85 (7)	C1—N1—C5—C4	0.99 (10)
N1—C1—C2—C3	-1.13 (10)	C3—C4—C5—N3	-178.76 (7)
C1—C2—C3—C4	1.12 (11)	C3—C4—C5—N1	-0.99 (10)

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

Hydrogen-bond geometry (Å, °)

<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>
O1W—H1W1 \cdots O1 ⁱⁱ	0.848 (14)	1.863 (15)	2.7088 (7)	175.4 (13)
O1W—H2W1 \cdots O4W ⁱⁱⁱ	0.840 (13)	1.948 (13)	2.7853 (8)	174.2 (13)
O2W—H1W2 \cdots O2	0.800 (14)	1.923 (14)	2.7217 (8)	176.3 (14)
O2W—H2W2 \cdots O3 ^{iv}	0.815 (14)	2.025 (13)	2.8352 (8)	172.7 (15)

supplementary materials

O3W—H1W3...O4W ⁱⁱ	0.836 (15)	1.898 (15)	2.7318 (8)	175.1 (13)
O3W—H2W3...O3 ⁱ	0.805 (15)	1.991 (15)	2.7928 (8)	173.6 (14)
O4W—H1W4...O2	0.863 (17)	1.910 (17)	2.7643 (8)	169.9 (16)
O4W—H2W4...O3 ⁱⁱ	0.784 (15)	1.994 (15)	2.7157 (7)	152.8 (18)
N1—H1N1...O1	0.883 (13)	2.005 (12)	2.8412 (7)	157.6 (12)
N2—H2N2...O2 ^v	0.810 (15)	2.424 (15)	3.1769 (9)	155.1 (13)
N3—H1N3...O1	0.851 (13)	2.347 (13)	3.0660 (7)	142.6 (11)
N2—H1N2...O4	0.776 (15)	2.162 (15)	2.8977 (9)	158.5 (14)
N3—H2N3...O4 ^{vi}	0.844 (14)	2.079 (14)	2.9155 (8)	171.0 (12)

Symmetry codes: (ii) $x-1/2, -y+3/2, -z+1$; (iii) $x+1/2, -y+3/2, -z+1$; (iv) $x-1, y, z$; (i) $-x+1, -y+1, -z+1$; (v) $x+1/2, y, -z+3/2$; (vi) $-x+3/2, y+1/2, z$.

Fig. 1

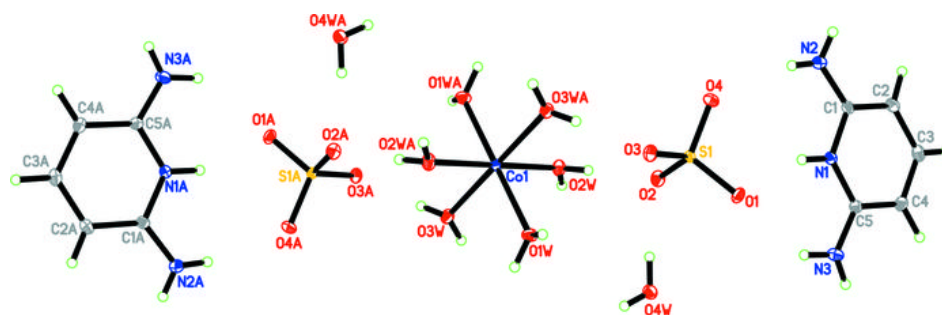


Fig. 2

