Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# Bis(2-amino-3-carboxypyridinium) sulfate trihydrate

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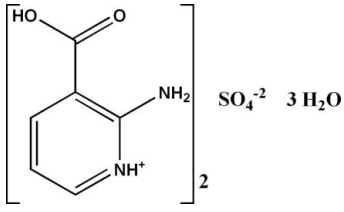
Received 9 March 2011; accepted 17 March 2011

Key indicators: single-crystal X-ray study; $T$ = 150 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.031; $wR$ factor = 0.079; data-to-parameter ratio = 15.4.

In the title compound, $2C_6H_7N_2O_2^+\cdot SO_4^{2-}\cdot 3H_2O$, there are two independent cations which are connected into N—H···O hydrogen-bonded dimers. In the crystal, O—H···O hydrogen-bonded sulfate–water sheets run parallel to (001) and are linked into a three-dimensional network *via* intermolecular N—H···O and O—H···O hydrogen bonds through the 2-aminonicotinium dimers. Further stabilization is provided by weak intermolecular C—H···O hydrogen bonds. $R_4^3(10)$ and $R_2^2(8)$ graph-set rings are observed. The crystal studied was an inversion twin with refined components of 0.45 (6) and 0.55 (6).

## Related literature

For related compounds, see: Athimoolam & Rajaram (2005); Berrah *et al.* (2005, 2011*a*,*b*); Dobson & Gerkin (1997); Giantsidis & Turnbull (2000); Pawlukojc *et al.* (2007). For hydrogen-bond motifs, see: Bernstein *et al.* (1995); Etter *et al.* (1990). For background to hydrogen bonding, see: Desiraju (2003).




## Experimental

### Crystal data

$2C_6H_7N_2O_2^+\cdot SO_4^{2-}\cdot 3H_2O$
$M_r$ = 428.39
Orthorhombic, $P2_12_12_1$
$a$ = 6.5372 (5) Å
$b$ = 12.3141 (10) Å
$c$ = 23.0274 (19) Å
$V$ = 1853.7 (3) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.24 mm$^{-1}$
$T$ = 150 K
0.58 × 0.13 × 0.04 mm

### Data collection

Bruker APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
$T_{min}$ = 0.845, $T_{max}$ = 0.970
23588 measured reflections
4229 independent reflections
3669 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.042

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.079
$S$ = 1.06
4229 reflections
274 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.27 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.28 e Å$^{-3}$
Absolute structure: Flack (1983), 1790 Friedel pairs
Flack parameter: 0.45 (6)

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1$A$—H1$A$···O3$W^{i}$ | 0.84 | 1.69 | 2.5152 (18) | 167 |
| O1$B$—H1$B$···O1$W$ | 0.84 | 1.69 | 2.5138 (18) | 168 |
| O1$W$—H1$W$···O2$W^{ii}$ | 0.82 (4) | 1.93 (3) | 2.754 (2) | 177 (4) |
| O3$W$—H5$W$···O2$W$ | 0.77 (3) | 1.98 (3) | 2.750 (2) | 176 (3) |
| O1$W$—H2$W$···O4 | 0.75 (4) | 2.03 (4) | 2.752 (2) | 164 (3) |
| O2$W$—H3$W$···O3$^{iii}$ | 0.80 (3) | 1.92 (3) | 2.7151 (19) | 169 (3) |
| O2$W$—H4$W$···O4 | 0.90 (3) | 1.87 (3) | 2.7675 (19) | 175 (3) |
| O3$W$—H6$W$···O2$^{iv}$ | 0.84 (2) | 1.88 (2) | 2.720 (2) | 171 (3) |
| N2$A$—H2$A$···O1 | 0.88 | 1.92 | 2.7681 (18) | 163 |
| N2$B$—H2$B$···O1$^{v}$ | 0.88 | 1.88 | 2.7419 (19) | 167 |
| N1$A$—H11$A$···O4 | 0.88 | 2.05 | 2.915 (2) | 166 |
| N1$B$—H11$B$···O2$^{v}$ | 0.88 | 1.94 | 2.817 (2) | 173 |
| N1$A$—H12$A$···O2$A$ | 0.88 | 2.09 | 2.726 (2) | 129 |
| N1$A$—H12$A$···O2$B$ | 0.88 | 2.27 | 2.979 (2) | 138 |
| N1$B$—H12$B$···O2$A$ | 0.88 | 2.25 | 2.963 (2) | 138 |
| N1$B$—H12$B$···O2$B$ | 0.88 | 2.10 | 2.733 (2) | 128 |
| C4$A$—H4$A$···O3$^{vi}$ | 0.95 | 2.46 | 3.143 (2) | 129 |
| C4$B$—H4$B$···O3$^{vii}$ | 0.95 | 2.31 | 3.169 (2) | 150 |

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

Data collection: *APEX2* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg & Berndt, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

We are grateful to the LCATM laboratory, Université Larbi Ben M'Hidi, Oum El Bouaghi, Algeria, for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5219).

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# supporting information

*Acta Cryst.* (2011). E**67**, o953–o954 [doi:10.1107/S1600536811010191]

## Bis(2-amino-3-carboxypyridinium) sulfate trihydrate

**Fadila Berrah, Amira Ouakkaf, Sofiane Bouacida and Thierry Roisnel**

### S1. Comment

Hydrogen bonds are the object of several studies, which aim to elucidate their influence on crystal construction and compounds propreties (Desiraju, 2003). Pyridine and its derivatives well known for their various chemical and biological activities, have proved their aptitude to built new edifices involving original hydrogen-bonding patterns due to their variety of potential hydrogen donors and acceptors (Athimoolam *et al.*, 2005; Dobson & Gerkin, 1997; Giantsidis & Turnbull, 2000). The title compound was obtained from 2-aminonicotinic acid and is a part of our search for new hybrid compounds based on protonated N-heterocyclic compounds and inorganic acids (Berrah *et al.*, 2005;2011*a*,*b*).

As shown in figure 1, the asymmetric unit includes two crystallographically independent 2-aminonicotinium cations (A and B), one sulfate anion and three water molecules. The cation geometry is similar to that reported for the structure of 2-aminonicotinic acid (Dobson & Gerkin, 1997; Pawlukojc *et al.*, 2007) except for C—O distances in the carboxylic group. In the 2-aminonicotinic acid structure, the two C—O distances are 1.234 (2) and 1.266 (2)Å since the carboxylic group transfers its proton to the hetero-ring nitrogen atom leading to a zwitterionic molecule.

The crystal packing of the title compound (Fig. 2) results from sulfate-water sheets extending parallel to (001) (Fig. 3) and linked together *via* 2-aminonicotinium dimers (Fig. 4). In one sheet, sulfate anions and $H_2O2W$ molecules alternate, leading to infinite chains running parallel to the *a* axis. These chains are further connected through $H_2O1W$ and $H_2O3W$ molecules in a way that $R^3_4(10)$ rings are formed (Fig. 3). The structure is stabilized *via* N—H···O, O—H···O and C—H···O Hydrogen bonds that link each dimer to its neighbors (Table 1, Fig. 4). $R^3_4$ (10) and $R^2_2(8)$ graph-set rings are observed (Fig. 4)(Etter *et al.*, 1990; Bernstein *et al.*, 1995).

### S2. Experimental

Colorless crystal of the title compound was obtained by slow evaporation of an aqueous solution of 2-amino-pyridine-3-carboxylic acid and sulfuric acid in 2:1 stoichiometric ratio.

### S3. Refinement

The H atoms of the water molecules were located in difference Fourier maps and were refined with $U_{iso}(H) = 1.5U_{eq}(O)$. The remaining H atoms were located in differnce Fourier maps but introduced in calculated positions and treated as riding on their parent atoms (C, N or O) with C—H = 0.95 Å, O—H = 0.84 Å and N—H = 0.88 Å with $U_{iso}(H) = 1.2$ $U_{eq}$(C or N) and $U_{iso}(H) = 1.5$ $U_{eq}(O)$.

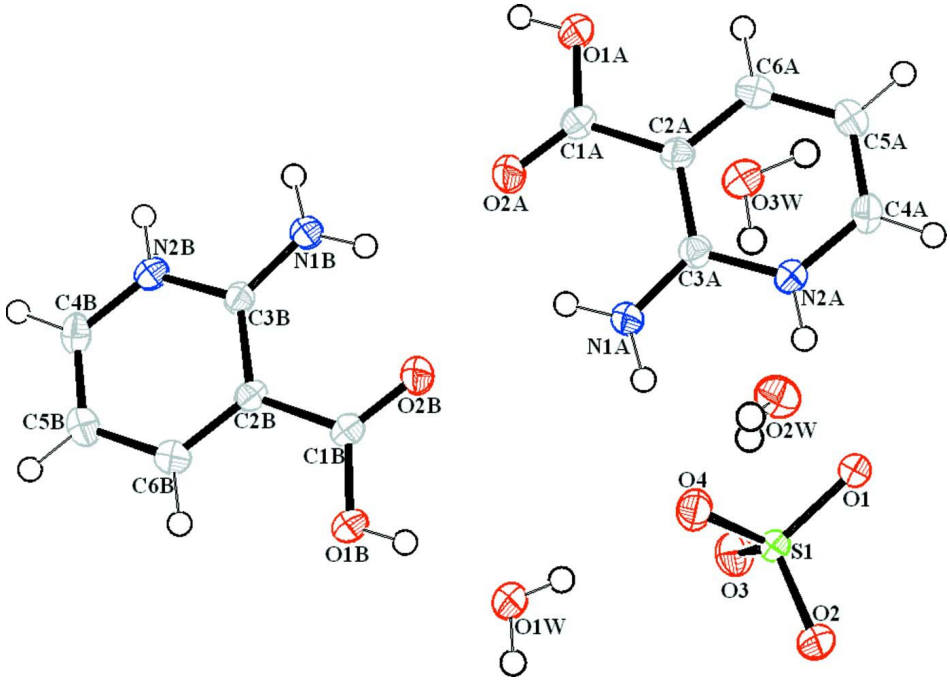


**Figure 1**

(Farrugia, 1997) The asymmetric unit of the title compound. Displacement are drawn at the 50% probability level.

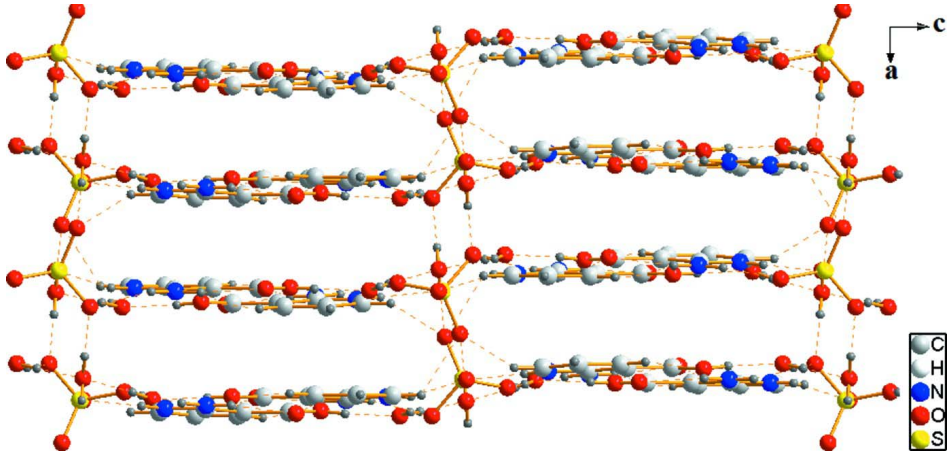


**Figure 2**

(Brandenburg & Berndt, 2001) A diagram of the three-dimentonal packing of (I) viewed along [010]. Hydrogen bonds are shown as dashed lines

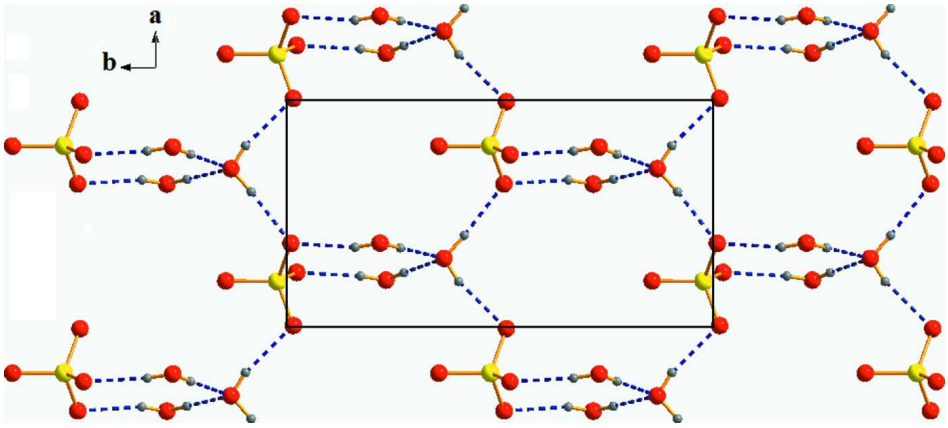


**Figure 3**

(Brandenburg & Berndt, 2001) A view of one sulfate-water sheet parallel to (001) and the $R^3_4(10)$ rings. Hydrogen bonds are shown as dashed lines.

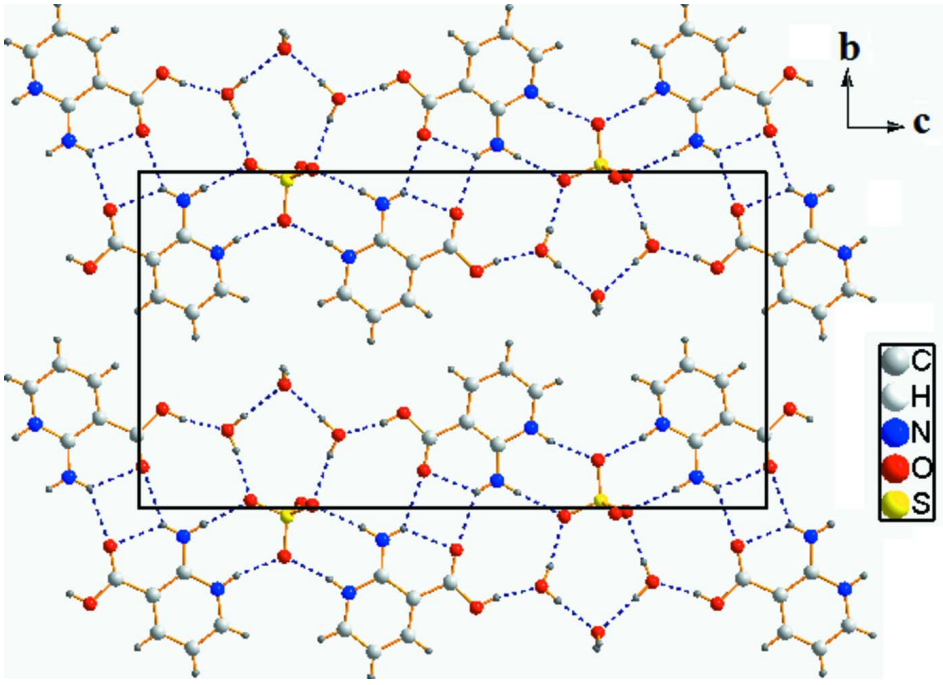


**Figure 4**

(Brandenburg & Berndt, 2001) Part of crystal packing showing cation dimers and $R^3_4(10)$ and $R^2_2(8)$ rings. Hydrogen bonds are shown as dashed lines.

### Bis(2-amino-3-carboxypyridinium) sulfate trihydrate

*Crystal data*

$2C_6H_7N_2O_2^+\cdot SO_4^{2-}\cdot 3H_2O$
$M_r$ = 428.39
Orthorhombic, $P2_12_12_1$
$a$ = 6.5372 (5) Å
$b$ = 12.3141 (10) Å
$c$ = 23.0274 (19) Å
$V$ = 1853.7 (3) Å$^3$
$Z$ = 4
$F(000)$ = 896
$D_x$ = 1.535 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 8735 reflections

$\theta$ = 2.4–27.2°
$\mu$ = 0.24 mm$^{-1}$
$T$ = 150 K

Needle, colourless
0.58 × 0.13 × 0.04 mm

*Data collection*

Bruker APEXII diffractometer
Graphite monochromator
CCD rotation images, thin slices scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
$T_{min}$ = 0.845, $T_{max}$ = 0.970
23588 measured reflections

4229 independent reflections
3669 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.042
$\theta_{max}$ = 27.5°, $\theta_{min}$ = 3.1°
$h$ = −8→5
$k$ = −15→15
$l$ = −29→29

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.079
$S$ = 1.06
4229 reflections
274 parameters
0 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
$w = 1/[\sigma^2(F_o^2) + (0.0369P)^2 + 0.4264P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.27 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.28 e Å$^{-3}$
Absolute structure: Flack (1983), 1790 Friedel pairs
Absolute structure parameter: 0.45 (6)

*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$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1A | 0.7166 (3) | 0.27959 (15) | 0.00318 (8) | 0.0216 (4) |
| C1B | 0.6471 (3) | 0.70977 (15) | 0.03679 (8) | 0.0200 (4) |
| C2A | 0.7181 (3) | 0.23143 (14) | 0.06245 (7) | 0.0207 (4) |
| C2B | 0.6478 (3) | 0.75822 (15) | −0.02254 (7) | 0.0190 (4) |
| C3A | 0.7116 (3) | 0.29935 (14) | 0.11251 (7) | 0.0201 (3) |
| C3B | 0.6631 (3) | 0.68958 (14) | −0.07242 (7) | 0.0190 (4) |
| C4A | 0.7238 (3) | 0.14018 (15) | 0.17195 (8) | 0.0263 (4) |
| H4A | 0.726 | 0.1102 | 0.21 | 0.032* |
| C4B | 0.6481 (3) | 0.84839 (16) | −0.13233 (8) | 0.0262 (4) |
| H4B | 0.6479 | 0.8782 | −0.1704 | 0.031* |
| C5A | 0.7264 (3) | 0.07309 (16) | 0.12519 (8) | 0.0312 (5) |
| H5A | 0.728 | −0.0036 | 0.1297 | 0.037* |

| | | | | |
|---|---|---|---|---|
| C5B | 0.6322 (3) | 0.91558 (16) | −0.08559 (8) | 0.0282 (4) |
| H5B | 0.6211 | 0.992 | −0.0904 | 0.034* |
| C6A | 0.7268 (3) | 0.12083 (16) | 0.07029 (9) | 0.0279 (4) |
| H6A | 0.7333 | 0.0752 | 0.0371 | 0.034* |
| C6B | 0.6326 (3) | 0.86880 (16) | −0.03039 (8) | 0.0247 (4) |
| H6B | 0.6222 | 0.9145 | 0.0027 | 0.03* |
| N1A | 0.7020 (3) | 0.40640 (12) | 0.11129 (7) | 0.0278 (3) |
| H11A | 0.7 | 0.4434 | 0.144 | 0.033* |
| H12A | 0.6976 | 0.4407 | 0.0778 | 0.033* |
| N1B | 0.6788 (3) | 0.58296 (12) | −0.07142 (7) | 0.0270 (4) |
| H11B | 0.6894 | 0.5465 | −0.1041 | 0.032* |
| H12B | 0.6785 | 0.5482 | −0.038 | 0.032* |
| N2A | 0.7181 (2) | 0.24906 (12) | 0.16507 (6) | 0.0215 (3) |
| H2A | 0.7187 | 0.2899 | 0.1964 | 0.026* |
| N2B | 0.6642 (2) | 0.73990 (13) | −0.12524 (6) | 0.0225 (3) |
| H2B | 0.6761 | 0.6992 | −0.1565 | 0.027* |
| O1 | 0.7971 (2) | 0.35697 (10) | 0.26811 (5) | 0.0259 (3) |
| O1A | 0.7192 (2) | 0.20503 (10) | −0.03781 (5) | 0.0294 (3) |
| H1A | 0.714 | 0.2352 | −0.0705 | 0.044* |
| O1B | 0.6533 (2) | 0.78383 (10) | 0.07796 (5) | 0.0277 (3) |
| H1B | 0.6398 | 0.7538 | 0.1105 | 0.042* |
| O2 | 0.7597 (2) | 0.52317 (11) | 0.32163 (5) | 0.0311 (3) |
| O1W | 0.6295 (3) | 0.71875 (14) | 0.18121 (6) | 0.0467 (5) |
| H1W | 0.652 (5) | 0.765 (3) | 0.2061 (14) | 0.07* |
| H2W | 0.653 (5) | 0.664 (3) | 0.1933 (14) | 0.07* |
| O2A | 0.7137 (2) | 0.37665 (11) | −0.00595 (5) | 0.0296 (3) |
| O2B | 0.6414 (2) | 0.61242 (10) | 0.04572 (5) | 0.0266 (3) |
| O3 | 0.9930 (2) | 0.51502 (12) | 0.24034 (6) | 0.0301 (3) |
| O2W | 0.3026 (2) | 0.36878 (11) | 0.23220 (6) | 0.0270 (3) |
| H3W | 0.201 (4) | 0.405 (2) | 0.2347 (11) | 0.04* |
| H4W | 0.405 (4) | 0.417 (2) | 0.2307 (11) | 0.04* |
| O4 | 0.6310 (2) | 0.50965 (11) | 0.22342 (5) | 0.0259 (3) |
| O3W | 0.2063 (3) | 0.23235 (12) | 0.14171 (6) | 0.0325 (3) |
| H5W | 0.239 (4) | 0.271 (2) | 0.1664 (11) | 0.049* |
| H6W | 0.227 (4) | 0.170 (2) | 0.1557 (11) | 0.049* |
| S1 | 0.79804 (7) | 0.47766 (4) | 0.263808 (18) | 0.01992 (10) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1A | 0.0196 (8) | 0.0255 (10) | 0.0197 (8) | −0.0003 (8) | −0.0009 (7) | −0.0008 (7) |
| C1B | 0.0188 (9) | 0.0236 (10) | 0.0176 (8) | 0.0009 (7) | −0.0004 (7) | −0.0013 (7) |
| C2A | 0.0205 (9) | 0.0210 (9) | 0.0207 (8) | −0.0023 (7) | −0.0018 (7) | −0.0009 (7) |
| C2B | 0.0192 (9) | 0.0212 (9) | 0.0165 (8) | −0.0012 (7) | −0.0016 (7) | −0.0003 (7) |
| C3A | 0.0203 (8) | 0.0203 (8) | 0.0196 (8) | −0.0009 (8) | −0.0001 (8) | 0.0007 (7) |
| C3B | 0.0205 (9) | 0.0199 (9) | 0.0167 (8) | 0.0008 (7) | −0.0006 (7) | 0.0007 (7) |
| C4A | 0.0318 (10) | 0.0239 (9) | 0.0232 (9) | 0.0002 (8) | −0.0036 (8) | 0.0062 (8) |
| C4B | 0.0300 (11) | 0.0261 (10) | 0.0225 (9) | 0.0020 (8) | −0.0008 (8) | 0.0081 (8) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C5A | 0.0451 (12) | 0.0192 (9) | 0.0293 (10) | −0.0003 (9) | −0.0034 (9) | 0.0025 (8) |
| C5B | 0.0336 (11) | 0.0214 (10) | 0.0294 (10) | 0.0018 (8) | −0.0012 (8) | 0.0047 (8) |
| C6A | 0.0354 (11) | 0.0218 (9) | 0.0266 (10) | 0.0000 (8) | −0.0017 (9) | −0.0036 (8) |
| C6B | 0.0278 (10) | 0.0221 (9) | 0.0241 (9) | 0.0003 (8) | −0.0007 (8) | −0.0021 (8) |
| N1A | 0.0465 (9) | 0.0181 (8) | 0.0188 (7) | 0.0007 (8) | −0.0003 (8) | −0.0004 (6) |
| N1B | 0.0436 (10) | 0.0204 (8) | 0.0171 (7) | 0.0013 (8) | −0.0001 (7) | −0.0006 (6) |
| N2A | 0.0256 (8) | 0.0214 (7) | 0.0175 (7) | 0.0004 (7) | −0.0014 (6) | 0.0000 (6) |
| N2B | 0.0270 (8) | 0.0243 (8) | 0.0162 (7) | 0.0004 (6) | 0.0004 (6) | −0.0011 (6) |
| O1 | 0.0404 (7) | 0.0191 (6) | 0.0181 (6) | −0.0016 (6) | −0.0021 (6) | 0.0004 (5) |
| O1A | 0.0454 (8) | 0.0252 (7) | 0.0176 (6) | 0.0011 (7) | −0.0006 (6) | −0.0015 (5) |
| O1B | 0.0414 (8) | 0.0250 (7) | 0.0166 (6) | 0.0008 (6) | −0.0005 (6) | −0.0018 (5) |
| O2 | 0.0508 (9) | 0.0240 (7) | 0.0184 (6) | 0.0046 (6) | 0.0021 (6) | −0.0021 (6) |
| O1W | 0.0970 (15) | 0.0245 (8) | 0.0185 (7) | 0.0102 (9) | −0.0078 (8) | −0.0008 (6) |
| O2A | 0.0453 (8) | 0.0226 (7) | 0.0208 (6) | 0.0020 (6) | 0.0017 (6) | 0.0026 (5) |
| O2B | 0.0363 (8) | 0.0224 (7) | 0.0212 (7) | 0.0017 (6) | 0.0004 (6) | 0.0031 (6) |
| O3 | 0.0274 (7) | 0.0295 (8) | 0.0332 (8) | −0.0038 (6) | 0.0025 (6) | 0.0054 (7) |
| O2W | 0.0264 (7) | 0.0248 (7) | 0.0297 (7) | −0.0016 (6) | 0.0013 (7) | −0.0017 (6) |
| O4 | 0.0284 (7) | 0.0260 (7) | 0.0234 (7) | −0.0015 (6) | −0.0034 (5) | 0.0041 (6) |
| O3W | 0.0538 (9) | 0.0244 (8) | 0.0193 (7) | −0.0026 (7) | −0.0042 (7) | −0.0014 (6) |
| S1 | 0.0259 (2) | 0.0184 (2) | 0.01552 (19) | −0.00133 (19) | −0.00044 (18) | 0.00021 (17) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1A—O2A | 1.214 (2) | C5B—C6B | 1.395 (3) |
| C1A—O1A | 1.317 (2) | C5B—H5B | 0.95 |
| C1A—C2A | 1.488 (2) | C6A—H6A | 0.95 |
| C1B—O2B | 1.217 (2) | C6B—H6B | 0.95 |
| C1B—O1B | 1.316 (2) | N1A—H11A | 0.88 |
| C1B—C2B | 1.491 (2) | N1A—H12A | 0.88 |
| C2A—C6A | 1.375 (3) | N1B—H11B | 0.88 |
| C2A—C3A | 1.425 (2) | N1B—H12B | 0.88 |
| C2B—C6B | 1.377 (3) | N2A—H2A | 0.88 |
| C2B—C3B | 1.430 (2) | N2B—H2B | 0.88 |
| C3A—N1A | 1.320 (2) | O1—S1 | 1.4895 (13) |
| C3A—N2A | 1.360 (2) | O1A—H1A | 0.84 |
| C3B—N1B | 1.317 (2) | O1B—H1B | 0.84 |
| C3B—N2B | 1.365 (2) | O2—S1 | 1.4662 (13) |
| C4A—N2A | 1.351 (2) | O1W—H1W | 0.82 (3) |
| C4A—C5A | 1.357 (3) | O1W—H2W | 0.75 (3) |
| C4A—H4A | 0.95 | O3—S1 | 1.4591 (14) |
| C4B—N2B | 1.350 (2) | O2W—H3W | 0.80 (3) |
| C4B—C5B | 1.362 (3) | O2W—H4W | 0.89 (3) |
| C4B—H4B | 0.95 | O4—S1 | 1.4877 (13) |
| C5A—C6A | 1.394 (3) | O3W—H5W | 0.77 (3) |
| C5A—H5A | 0.95 | O3W—H6W | 0.85 (3) |
| | | | |
| O2A—C1A—O1A | 124.23 (16) | C2A—C6A—C5A | 122.46 (18) |
| O2A—C1A—C2A | 123.47 (16) | C2A—C6A—H6A | 118.8 |

| | | | |
|---|---|---|---|
| O1A—C1A—C2A | 112.30 (15) | C5A—C6A—H6A | 118.8 |
| O2B—C1B—O1B | 124.18 (16) | C2B—C6B—C5B | 121.86 (18) |
| O2B—C1B—C2B | 123.32 (16) | C2B—C6B—H6B | 119.1 |
| O1B—C1B—C2B | 112.51 (15) | C5B—C6B—H6B | 119.1 |
| C6A—C2A—C3A | 118.44 (16) | C3A—N1A—H11A | 120 |
| C6A—C2A—C1A | 121.03 (16) | C3A—N1A—H12A | 120 |
| C3A—C2A—C1A | 120.52 (15) | H11A—N1A—H12A | 120 |
| C6B—C2B—C3B | 118.95 (16) | C3B—N1B—H11B | 120 |
| C6B—C2B—C1B | 121.05 (16) | C3B—N1B—H12B | 120 |
| C3B—C2B—C1B | 120.00 (15) | H11B—N1B—H12B | 120 |
| N1A—C3A—N2A | 118.38 (15) | C4A—N2A—C3A | 123.86 (15) |
| N1A—C3A—C2A | 124.77 (15) | C4A—N2A—H2A | 118.1 |
| N2A—C3A—C2A | 116.85 (15) | C3A—N2A—H2A | 118.1 |
| N1B—C3B—N2B | 117.89 (16) | C4B—N2B—C3B | 123.82 (16) |
| N1B—C3B—C2B | 125.49 (15) | C4B—N2B—H2B | 118.1 |
| N2B—C3B—C2B | 116.61 (15) | C3B—N2B—H2B | 118.1 |
| N2A—C4A—C5A | 120.77 (17) | C1A—O1A—H1A | 109.5 |
| N2A—C4A—H4A | 119.6 | C1B—O1B—H1B | 109.5 |
| C5A—C4A—H4A | 119.6 | H1W—O1W—H2W | 109 (3) |
| N2B—C4B—C5B | 120.77 (17) | H3W—O2W—H4W | 105 (2) |
| N2B—C4B—H4B | 119.6 | H5W—O3W—H6W | 104 (3) |
| C5B—C4B—H4B | 119.6 | O3—S1—O2 | 111.42 (9) |
| C4A—C5A—C6A | 117.56 (18) | O3—S1—O4 | 109.05 (8) |
| C4A—C5A—H5A | 121.2 | O2—S1—O4 | 109.93 (8) |
| C6A—C5A—H5A | 121.2 | O3—S1—O1 | 110.06 (9) |
| C4B—C5B—C6B | 117.98 (18) | O2—S1—O1 | 108.68 (7) |
| C4B—C5B—H5B | 121 | O4—S1—O1 | 107.62 (8) |
| C6B—C5B—H5B | 121 | | |

| | | | |
|---|---|---|---|
| O2A—C1A—C2A—C6A | −178.3 (2) | C1B—C2B—C3B—N2B | −179.57 (16) |
| O1A—C1A—C2A—C6A | 1.6 (3) | N2A—C4A—C5A—C6A | 1.1 (3) |
| O2A—C1A—C2A—C3A | 1.3 (3) | N2B—C4B—C5B—C6B | −0.1 (3) |
| O1A—C1A—C2A—C3A | −178.75 (18) | C3A—C2A—C6A—C5A | 1.0 (3) |
| O2B—C1B—C2B—C6B | 173.11 (18) | C1A—C2A—C6A—C5A | −179.38 (18) |
| O1B—C1B—C2B—C6B | −6.9 (2) | C4A—C5A—C6A—C2A | −2.1 (3) |
| O2B—C1B—C2B—C3B | −6.5 (3) | C3B—C2B—C6B—C5B | −0.1 (3) |
| O1B—C1B—C2B—C3B | 173.45 (16) | C1B—C2B—C6B—C5B | −179.72 (17) |
| C6A—C2A—C3A—N1A | −179.65 (19) | C4B—C5B—C6B—C2B | −0.2 (3) |
| C1A—C2A—C3A—N1A | 0.7 (3) | C5A—C4A—N2A—C3A | 1.0 (3) |
| C6A—C2A—C3A—N2A | 1.1 (3) | N1A—C3A—N2A—C4A | 178.57 (18) |
| C1A—C2A—C3A—N2A | −178.53 (16) | C2A—C3A—N2A—C4A | −2.1 (3) |
| C6B—C2B—C3B—N1B | 179.90 (18) | C5B—C4B—N2B—C3B | 0.9 (3) |
| C1B—C2B—C3B—N1B | −0.5 (3) | N1B—C3B—N2B—C4B | 179.60 (18) |
| C6B—C2B—C3B—N2B | 0.8 (3) | C2B—C3B—N2B—C4B | −1.2 (3) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1*A*—H1*A*···O3*W*$^{i}$ | 0.84 | 1.69 | 2.5152 (18) | 167 |
| O1*B*—H1*B*···O1*W* | 0.84 | 1.69 | 2.5138 (18) | 168 |
| O1*W*—H1*W*···O2*W*$^{ii}$ | 0.82 (4) | 1.93 (3) | 2.754 (2) | 177 (4) |
| O3*W*—H5*W*···O2*W* | 0.77 (3) | 1.98 (3) | 2.750 (2) | 176 (3) |
| O1*W*—H2*W*···O4 | 0.75 (4) | 2.03 (4) | 2.752 (2) | 164 (3) |
| O2*W*—H3*W*···O3$^{iii}$ | 0.80 (3) | 1.92 (3) | 2.7151 (19) | 169 (3) |
| O2*W*—H4*W*···O4 | 0.90 (3) | 1.87 (3) | 2.7675 (19) | 175 (3) |
| O3*W*—H6*W*···O2$^{iv}$ | 0.84 (2) | 1.88 (2) | 2.720 (2) | 171 (3) |
| N2*A*—H2*A*···O1 | 0.88 | 1.92 | 2.7681 (18) | 163 |
| N2*B*—H2*B*···O1$^{v}$ | 0.88 | 1.88 | 2.7419 (19) | 167 |
| N1*A*—H11*A*···O4 | 0.88 | 2.05 | 2.915 (2) | 166 |
| N1*B*—H11*B*···O2$^{v}$ | 0.88 | 1.94 | 2.817 (2) | 173 |
| N1*A*—H12*A*···O2*A* | 0.88 | 2.09 | 2.726 (2) | 129 |
| N1*A*—H12*A*···O2*B* | 0.88 | 2.27 | 2.979 (2) | 138 |
| N1*B*—H12*B*···O2*A* | 0.88 | 2.25 | 2.963 (2) | 138 |
| N1*B*—H12*B*···O2*B* | 0.88 | 2.10 | 2.733 (2) | 128 |
| C4*A*—H4*A*···O3$^{vi}$ | 0.95 | 2.46 | 3.143 (2) | 129 |
| C4*B*—H4*B*···O3$^{vii}$ | 0.95 | 2.31 | 3.169 (2) | 150 |
| C6*A*—H6*A*···O1*A* | 0.95 | 2.35 | 2.697 (2) | 101 |
| C6*B*—H6*B*···O1*B* | 0.95 | 2.37 | 2.709 (2) | 100 |

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