# organic compounds

## Piperazine-1,4-diium bis(piperazin-1-ium) bis(3-carboxylato-4-hydroxy-benzenesulfonate) dihydrate

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The asymmetric unit of the title compound, $C_4H_{12}N_2^{2+} \cdot 2C_4H_{11}N_2^+ \cdot 2C_7H_4O_6S^{2-} \cdot 2H_2O$, consists of one-half of a piperazine-1,4-diium cation situated around an inversion centre, one piperazin-1-ium cation, one 3-carboxylato-4-hydroxybenzenesulfonate dianion and a water molecule. Extensive intermolecular O—H···O, N—H···O and N—H···N hydrogen bonds link these structural components into a three-dimensional network.
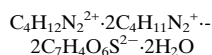
## Related literature

For the role of water molecules in self-assembly processes, see: Smith *et al.* (2007).
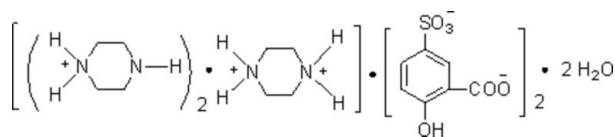


## Experimental

### Crystal data

$C_4H_{12}N_2^{2+} \cdot 2C_4H_{11}N_2^+ \cdot 2C_7H_4O_6S^{2-} \cdot 2H_2O$
$M_r = 730.80$
Monoclinic, $P2_1/n$
$a = 7.724$ (3) Å
$b = 12.010$ (4) Å
$c = 17.699$ (6) Å
$\beta = 99.416$ (5)°
$V = 1619.8$ (10) Å$^3$
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.24$ mm$^{-1}$
$T = 294$ (2) K
$0.20 \times 0.20 \times 0.14$ mm

### Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.944$, $T_{max} = 0.958$
8198 measured reflections
2853 independent reflections
2452 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.105$
$S = 1.09$
2853 reflections
247 parameters
10 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.28$ e Å$^{-3}$
$\Delta\rho_{min} = -0.40$ e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1A···O6[i] | 0.899 (10) | 2.282 (19) | 2.978 (2) | 134 (2) |
| N1—H1A···O7[ii] | 0.899 (10) | 2.501 (18) | 3.199 (3) | 134.9 (19) |
| N2—H2A···O1[iii] | 0.901 (9) | 2.216 (14) | 3.055 (3) | 155 (2) |
| N2—H2A···O3[iii] | 0.901 (9) | 2.468 (17) | 3.240 (3) | 144 (2) |
| N2—H2B···O5[iv] | 0.909 (9) | 1.744 (10) | 2.653 (2) | 178 (3) |
| N2—H2B···O4[iv] | 0.909 (9) | 2.65 (2) | 3.227 (2) | 122.5 (19) |
| N3—H3A···O2[v] | 0.904 (10) | 2.214 (11) | 3.087 (2) | 162 (2) |
| N3—H3A···O1[v] | 0.904 (10) | 2.55 (2) | 3.216 (3) | 131 (2) |
| N3—H3B···N1[v] | 0.911 (10) | 1.869 (12) | 2.772 (2) | 171 (4) |
| O7—H7A···O4[vi] | 0.846 (10) | 1.918 (12) | 2.752 (2) | 168 (3) |
| O7—H7B···O2[vii] | 0.856 (10) | 2.124 (10) | 2.963 (2) | 166 (3) |

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2001); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2119).

## References

Bruker (2000). *SMART* (Version 5.051) and *SAINT* (Version 5.A06). *SADABS* (Version 2.03). Bruker AXS Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.

Sheldrick, G. M. (2001). *SHELXTL*. Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.

Smith, G., Wermuth, U. D., Young, D. J. & White, J. M. (2007). *Polyhedron*, **26**, 3645–3652.

**supplementary materials**

# Piperazine-1,4-diium bis(piperazin-1-ium) bis(3-carboxylato-4-hydroxybenzenesulfonate) dihydrate

## K.-M. Su and Z.-H. Li

## Comment

5-Sulfosalicylic acid (SSA) has three potential donor sites, the sulfonic, carboxylic and phenolic groups, and thus can form mono-, di- and trianionic species through deprotonation. The presence of a number of oxygen atoms in the three substituent groups of SSA usually results in a deficit of hydrogen- bond donor sites and therefore in the self-assembly process of crystallization water molecules are often incorporated into the crystal structures (Smith *et al.*, 2007)

Here we report the synthesis and crystal structure of piperazine-1,4-diium bispiperazine-1-ium bis(3-carboxy-4-hydroxy-benzenesulfonate) dihydrate (Fig. 1) which was obtained from a solution of 2-hydroxy-5-sulfobenzoic acid and piperazine. The asymmetric unit of the title compound comprises one half of a piperazine-1,4-diium cation, which lies about an inversion centre, a piperazine-1-ium cation, a 3-carboxy-4-hydroxybenzenesulfonate anion and a water molecule. In the crystal structure the component molecules are connected by hydrogen bonds into a three-dimensional hydrogen-bonded framework structure. (Table 1, Fig. 2). The water molecules function as a bridge between two anions and a monocation. The hydroxyl group of the 5-sulfosalicylate anion forms an intramolecular O5–H⋯O6 hydrogen bond and is not involved as donor in intermolecular hydrogen bonds.

## Experimental

2-Hydroxy-5-sulfobenzoic acid (2.18 g, 10 mmol) and piperazine (1.72 g, 20 mmol) were dissolved in warm $H_2O$ (20 ml). Crystals of the title compound were obtained by slow evaporation of this solution.

## Refinement

H atoms of the water molecule and those from the N–H groups were located in Fourier difference maps. In the refinement process the O—H and N—H distances were restrained to 0.85 and 0.90 Å with the s.u. value of 0.01 Å. Their $U_{iso}$ values were set to $1.2U_{eq}(N)$ and $1.5U_{eq}(O)$. All other H atoms were positioned geometrically and refined using a riding model approximation with C—H = 0.93 Å for aromatic H atoms, and 0.97 Å for methylene H atoms; $U_{iso}$ values were set to $1.2U_{eq}(C)$.
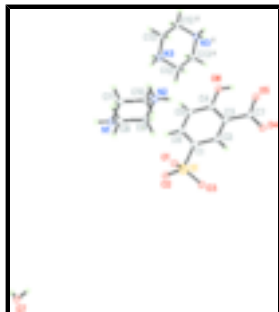
# supplementary materials

**Figures**

Fig. 1. The molecular structure of the title compound with 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitary radii. [Symmetry codes: (i) $-x$, $2 - y$, $-z$.]
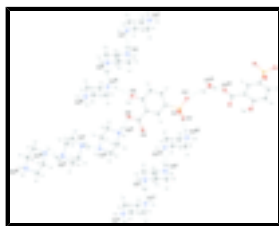
Fig. 2. Fragment of hydrogen-bond framework structure (O—H···O, N—H···O and N–H···N hydrogen bonds are shown as dotted lines). [Symmetry codes: (i) $1/2 - x$, $1/2 + y$, $1/2 - z$, (ii) $-x$, $2 - y$, $-z$, (iii) $x - 1/2$, $3/2 - y$, $z - 1/2$, (iv) $1 - x$, $1 - y$, $-z$, (v) $1/2 + x$, $3/2 - y$, $z - 1/2$, (vi) $1/2 - x$, $y - 1/2$, $-1/2 - z$, (vii) $x$, $y$, $z - 1$, (viii) $3/2 - x$, $y - 1/2$, $1/2 - z$, (ix) $1 + x$, $y - 1$, $z$, (x) $1 - x$, $1 - y$, $-z$, (xi) $1/2 + x$, $1/2 - y$, $z - 1/2$, (xii) $x - 1/2$, $1/2 - y$, $z - 1/2$, (xiii) $x - 1/2$, $1/2 - y$, $1/2 + z$.]

## Piperazine-1,4-diium bis(piperazin-1-ium) bis(3-carboxylato-4-hydroxybenzenesulfonate) dihydrate

*Crystal data*

| | |
|---|---|
| $C_4H_{12}N_2^{2+}\cdot2C_4H_{11}N_2^+\cdot2C_7H_4O_6S^{2-}\cdot2H_2O$ | $F_{000} = 776$ |
| $M_r = 730.80$ | $D_x = 1.498$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation<br>$\lambda = 0.71073$ Å |
| Hall symbol: -P 2yn | Cell parameters from 4798 reflections |
| $a = 7.724$ (3) Å | $\theta = 2.3–26.4°$ |
| $b = 12.010$ (4) Å | $\mu = 0.24$ mm$^{-1}$ |
| $c = 17.699$ (6) Å | $T = 294$ (2) K |
| $\beta = 99.416$ (5)° | Block, colourless |
| $V = 1619.8$ (10) Å$^3$ | $0.20 \times 0.20 \times 0.14$ mm |
| $Z = 2$ | |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 2853 independent reflections |
| Radiation source: fine-focus sealed tube | 2452 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int} = 0.037$ |
| $T = 294(2)$ K | $\theta_{max} = 25.0°$ |
| $\varphi$ and $\omega$ scans | $\theta_{min} = 2.1°$ |
| Absorption correction: multi-scan (SADABS; Bruker, 2000) | $h = -9{\rightarrow}8$ |
| $T_{min} = 0.944$, $T_{max} = 0.958$ | $k = -14{\rightarrow}11$ |
| 8198 measured reflections | $l = -17{\rightarrow}21$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.039$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.105$ | $w = 1/[\sigma^2(F_o^2) + (0.0528P)^2 + 0.6089P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.09$ | $(\Delta/\sigma)_{max} = 0.004$ |
| 2853 reflections | $\Delta\rho_{max} = 0.28$ e Å$^{-3}$ |
| 247 parameters | $\Delta\rho_{min} = -0.40$ e Å$^{-3}$ |
| 10 restraints | Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$ |
| Primary atom site location: structure-invariant direct methods | Extinction coefficient: 0.230 (8) |

*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 $F^2 > 2\text{sigma}(F^2)$ 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 ($Å^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}*/U_{eq}$ |
|---|---|---|---|---|
| S1 | 0.33584 (6) | 0.33623 (4) | 0.23951 (2) | 0.0306 (2) |
| O1 | 0.5201 (2) | 0.35108 (16) | 0.27055 (9) | 0.0593 (5) |
| O2 | 0.2267 (2) | 0.37177 (13) | 0.29422 (8) | 0.0484 (4) |
| O3 | 0.3016 (2) | 0.22447 (11) | 0.21122 (9) | 0.0535 (4) |
| O4 | 0.3169 (2) | 0.31539 (13) | −0.06257 (8) | 0.0499 (4) |
| O5 | 0.2461 (2) | 0.48385 (12) | −0.10870 (7) | 0.0472 (4) |
| O6 | 0.1735 (2) | 0.63756 (12) | −0.02424 (8) | 0.0519 (4) |
| H6 | 0.1892 | 0.6064 | −0.0638 | 0.078* |
| N1 | 0.7258 (2) | 0.65358 (13) | 0.39164 (9) | 0.0326 (4) |
| N2 | 0.8061 (2) | 0.62463 (15) | 0.24103 (9) | 0.0370 (4) |
| N3 | 0.0209 (2) | 0.99737 (15) | 0.08123 (9) | 0.0410 (4) |
| C1 | 0.2855 (2) | 0.42488 (14) | 0.15965 (9) | 0.0261 (4) |
| C2 | 0.3024 (2) | 0.38773 (15) | 0.08759 (10) | 0.0288 (4) |
| H2 | 0.3382 | 0.3149 | 0.0811 | 0.035* |
| C3 | 0.2668 (2) | 0.45750 (14) | 0.02448 (10) | 0.0288 (4) |

| | | | | |
|---|---|---|---|---|
| C4 | 0.2127 (3) | 0.56680 (15) | 0.03522 (10) | 0.0339 (4) |
| C5 | 0.1953 (3) | 0.60341 (15) | 0.10785 (11) | 0.0388 (5) |
| H5 | 0.1585 | 0.6759 | 0.1148 | 0.047* |
| C6 | 0.2320 (3) | 0.53326 (14) | 0.16965 (10) | 0.0321 (4) |
| H6A | 0.2210 | 0.5585 | 0.2183 | 0.039* |
| C7 | 0.2801 (3) | 0.41366 (16) | −0.05363 (10) | 0.0341 (4) |
| C8 | 0.8899 (2) | 0.59941 (18) | 0.37924 (11) | 0.0382 (5) |
| H8A | 0.9252 | 0.5450 | 0.4193 | 0.046* |
| H8B | 0.9822 | 0.6547 | 0.3818 | 0.046* |
| C9 | 0.8657 (3) | 0.54291 (17) | 0.30255 (11) | 0.0395 (5) |
| H9A | 0.9757 | 0.5099 | 0.2944 | 0.047* |
| H9B | 0.7795 | 0.4839 | 0.3012 | 0.047* |
| C10 | 0.6410 (3) | 0.67931 (19) | 0.25350 (11) | 0.0432 (5) |
| H10A | 0.5482 | 0.6242 | 0.2506 | 0.052* |
| H10B | 0.6063 | 0.7343 | 0.2137 | 0.052* |
| C11 | 0.6661 (3) | 0.73499 (17) | 0.33071 (11) | 0.0390 (5) |
| H11A | 0.7521 | 0.7941 | 0.3322 | 0.047* |
| H11B | 0.5561 | 0.7679 | 0.3392 | 0.047* |
| C12 | −0.0561 (3) | 0.90188 (17) | 0.03482 (12) | 0.0438 (5) |
| H12A | −0.1402 | 0.8642 | 0.0611 | 0.053* |
| H12B | 0.0356 | 0.8492 | 0.0284 | 0.053* |
| C13 | 0.1453 (3) | 1.05918 (18) | 0.04175 (13) | 0.0436 (5) |
| H13A | 0.2431 | 1.0113 | 0.0355 | 0.052* |
| H13B | 0.1911 | 1.1227 | 0.0725 | 0.052* |
| O7 | 0.5718 (3) | 0.15577 (14) | 0.93556 (11) | 0.0578 (5) |
| H1A | 0.743 (3) | 0.6892 (18) | 0.4369 (8) | 0.051 (7)* |
| H2A | 0.888 (3) | 0.6784 (16) | 0.2422 (12) | 0.056 (7)* |
| H2B | 0.791 (3) | 0.5867 (18) | 0.1959 (9) | 0.063 (7)* |
| H3A | 0.082 (3) | 0.969 (2) | 0.1249 (10) | 0.073 (8)* |
| H3B | −0.068 (3) | 1.042 (3) | 0.0910 (16) | 0.116 (13)* |
| H7A | 0.500 (3) | 0.2061 (18) | 0.9427 (15) | 0.074 (9)* |
| H7B | 0.611 (4) | 0.159 (2) | 0.8932 (11) | 0.085 (11)* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.0391 (3) | 0.0295 (3) | 0.0232 (3) | 0.00406 (18) | 0.00550 (19) | 0.00462 (17) |
| O1 | 0.0418 (9) | 0.0830 (13) | 0.0480 (9) | 0.0019 (8) | −0.0077 (7) | 0.0194 (9) |
| O2 | 0.0637 (10) | 0.0530 (9) | 0.0330 (8) | 0.0146 (7) | 0.0217 (7) | 0.0104 (7) |
| O3 | 0.0968 (13) | 0.0265 (8) | 0.0383 (8) | 0.0016 (7) | 0.0141 (8) | 0.0069 (6) |
| O4 | 0.0739 (11) | 0.0404 (9) | 0.0371 (8) | 0.0104 (7) | 0.0138 (7) | −0.0099 (6) |
| O5 | 0.0766 (11) | 0.0421 (8) | 0.0224 (7) | −0.0043 (7) | 0.0064 (7) | −0.0005 (6) |
| O6 | 0.0973 (13) | 0.0290 (8) | 0.0283 (7) | 0.0066 (8) | 0.0072 (8) | 0.0079 (6) |
| N1 | 0.0375 (9) | 0.0364 (9) | 0.0249 (8) | −0.0023 (7) | 0.0084 (7) | −0.0043 (7) |
| N2 | 0.0472 (10) | 0.0387 (10) | 0.0264 (8) | −0.0080 (8) | 0.0099 (7) | −0.0069 (7) |
| N3 | 0.0516 (11) | 0.0431 (10) | 0.0284 (8) | 0.0132 (8) | 0.0068 (8) | 0.0035 (7) |
| C1 | 0.0304 (9) | 0.0238 (9) | 0.0237 (9) | −0.0020 (7) | 0.0026 (7) | 0.0013 (7) |
| C2 | 0.0364 (10) | 0.0233 (9) | 0.0267 (9) | 0.0023 (7) | 0.0050 (7) | −0.0012 (7) |

| | | | | | |
|---|---|---|---|---|---|
| C3 | 0.0358 (10) | 0.0262 (9) | 0.0243 (9) | −0.0035 (7) | 0.0043 (7) | −0.0016 (7) |
| C4 | 0.0495 (11) | 0.0241 (9) | 0.0273 (9) | −0.0017 (8) | 0.0037 (8) | 0.0036 (7) |
| C5 | 0.0626 (13) | 0.0211 (9) | 0.0334 (10) | 0.0065 (8) | 0.0097 (9) | −0.0019 (8) |
| C6 | 0.0459 (11) | 0.0267 (9) | 0.0246 (9) | −0.0004 (8) | 0.0083 (8) | −0.0035 (7) |
| C7 | 0.0414 (11) | 0.0339 (11) | 0.0268 (9) | −0.0032 (8) | 0.0052 (8) | −0.0041 (8) |
| C8 | 0.0326 (10) | 0.0506 (12) | 0.0305 (10) | −0.0001 (9) | 0.0029 (8) | 0.0036 (9) |
| C9 | 0.0415 (11) | 0.0407 (11) | 0.0385 (11) | 0.0053 (9) | 0.0130 (9) | −0.0018 (9) |
| C10 | 0.0498 (12) | 0.0472 (12) | 0.0300 (10) | 0.0077 (9) | −0.0009 (9) | −0.0009 (9) |
| C11 | 0.0464 (12) | 0.0353 (11) | 0.0357 (11) | 0.0051 (9) | 0.0081 (9) | −0.0021 (8) |
| C12 | 0.0529 (13) | 0.0308 (10) | 0.0533 (13) | −0.0001 (9) | 0.0252 (10) | 0.0053 (9) |
| C13 | 0.0308 (10) | 0.0437 (12) | 0.0552 (13) | −0.0011 (8) | 0.0035 (9) | −0.0156 (10) |
| O7 | 0.0689 (12) | 0.0518 (10) | 0.0547 (11) | 0.0163 (9) | 0.0164 (9) | 0.0113 (8) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| S1—O3 | 1.4420 (16) | C3—C7 | 1.499 (2) |
| S1—O2 | 1.4481 (15) | C4—C5 | 1.386 (3) |
| S1—O1 | 1.4505 (17) | C5—C6 | 1.373 (3) |
| S1—C1 | 1.7615 (17) | C5—H5 | 0.9300 |
| O4—C7 | 1.230 (2) | C6—H6A | 0.9300 |
| O5—C7 | 1.283 (2) | C8—C9 | 1.502 (3) |
| O6—C4 | 1.348 (2) | C8—H8A | 0.9700 |
| O6—H6 | 0.8200 | C8—H8B | 0.9700 |
| N1—C11 | 1.473 (3) | C9—H9A | 0.9700 |
| N1—C8 | 1.473 (3) | C9—H9B | 0.9700 |
| N1—H1A | 0.899 (10) | C10—C11 | 1.505 (3) |
| N2—C9 | 1.482 (3) | C10—H10A | 0.9700 |
| N2—C10 | 1.483 (3) | C10—H10B | 0.9700 |
| N2—H2A | 0.901 (9) | C11—H11A | 0.9700 |
| N2—H2B | 0.909 (9) | C11—H11B | 0.9700 |
| N3—C13 | 1.478 (3) | C12—C13$^i$ | 1.491 (3) |
| N3—C12 | 1.478 (3) | C12—H12A | 0.9700 |
| N3—H3A | 0.904 (10) | C12—H12B | 0.9700 |
| N3—H3B | 0.911 (10) | C13—C12$^i$ | 1.491 (3) |
| C1—C2 | 1.378 (2) | C13—H13A | 0.9700 |
| C1—C6 | 1.386 (3) | C13—H13B | 0.9700 |
| C2—C3 | 1.387 (2) | O7—H7A | 0.846 (10) |
| C2—H2 | 0.9300 | O7—H7B | 0.856 (10) |
| C3—C4 | 1.400 (3) | | |
| O3—S1—O2 | 114.38 (10) | O4—C7—O5 | 123.75 (17) |
| O3—S1—O1 | 111.03 (11) | O4—C7—C3 | 120.52 (17) |
| O2—S1—O1 | 110.67 (11) | O5—C7—C3 | 115.70 (16) |
| O3—S1—C1 | 106.26 (9) | N1—C8—C9 | 110.56 (15) |
| O2—S1—C1 | 106.39 (9) | N1—C8—H8A | 109.5 |
| O1—S1—C1 | 107.68 (9) | C9—C8—H8A | 109.5 |
| C4—O6—H6 | 109.5 | N1—C8—H8B | 109.5 |
| C11—N1—C8 | 111.01 (15) | C9—C8—H8B | 109.5 |
| C11—N1—H1A | 108.6 (16) | H8A—C8—H8B | 108.1 |

| | | | |
|---|---|---|---|
| C8—N1—H1A | 110.0 (15) | N2—C9—C8 | 110.04 (17) |
| C9—N2—C10 | 110.81 (15) | N2—C9—H9A | 109.7 |
| C9—N2—H2A | 108.9 (16) | C8—C9—H9A | 109.7 |
| C10—N2—H2A | 107.3 (16) | N2—C9—H9B | 109.7 |
| C9—N2—H2B | 107.1 (16) | C8—C9—H9B | 109.7 |
| C10—N2—H2B | 111.2 (16) | H9A—C9—H9B | 108.2 |
| H2A—N2—H2B | 111.6 (14) | N2—C10—C11 | 110.24 (17) |
| C13—N3—C12 | 111.15 (15) | N2—C10—H10A | 109.6 |
| C13—N3—H3A | 108.0 (18) | C11—C10—H10A | 109.6 |
| C12—N3—H3A | 106.5 (18) | N2—C10—H10B | 109.6 |
| C13—N3—H3B | 111 (2) | C11—C10—H10B | 109.6 |
| C12—N3—H3B | 109 (2) | H10A—C10—H10B | 108.1 |
| H3A—N3—H3B | 111.4 (15) | N1—C11—C10 | 110.37 (16) |
| C2—C1—C6 | 119.86 (16) | N1—C11—H11A | 109.6 |
| C2—C1—S1 | 120.35 (14) | C10—C11—H11A | 109.6 |
| C6—C1—S1 | 119.77 (13) | N1—C11—H11B | 109.6 |
| C1—C2—C3 | 120.89 (16) | C10—C11—H11B | 109.6 |
| C1—C2—H2 | 119.6 | H11A—C11—H11B | 108.1 |
| C3—C2—H2 | 119.6 | N3—C12—C13$^i$ | 110.23 (16) |
| C2—C3—C4 | 118.77 (16) | N3—C12—H12A | 109.6 |
| C2—C3—C7 | 119.73 (16) | C13$^i$—C12—H12A | 109.6 |
| C4—C3—C7 | 121.46 (16) | N3—C12—H12B | 109.6 |
| O6—C4—C5 | 118.72 (17) | C13$^i$—C12—H12B | 109.6 |
| O6—C4—C3 | 121.27 (17) | H12A—C12—H12B | 108.1 |
| C5—C4—C3 | 120.00 (17) | N3—C13—C12$^i$ | 110.34 (16) |
| C6—C5—C4 | 120.35 (17) | N3—C13—H13A | 109.6 |
| C6—C5—H5 | 119.8 | C12$^i$—C13—H13A | 109.6 |
| C4—C5—H5 | 119.8 | N3—C13—H13B | 109.6 |
| C5—C6—C1 | 120.11 (17) | C12$^i$—C13—H13B | 109.6 |
| C5—C6—H6A | 119.9 | H13A—C13—H13B | 108.1 |
| C1—C6—H6A | 119.9 | H7A—O7—H7B | 115.7 (17) |
| O3—S1—C1—C2 | −28.96 (17) | C4—C5—C6—C1 | −0.5 (3) |
| O2—S1—C1—C2 | −151.24 (15) | C2—C1—C6—C5 | 0.3 (3) |
| O1—S1—C1—C2 | 90.08 (17) | S1—C1—C6—C5 | 178.95 (15) |
| O3—S1—C1—C6 | 152.35 (15) | C2—C3—C7—O4 | 2.4 (3) |
| O2—S1—C1—C6 | 30.07 (17) | C4—C3—C7—O4 | −175.29 (19) |
| O1—S1—C1—C6 | −88.61 (17) | C2—C3—C7—O5 | −179.54 (17) |
| C6—C1—C2—C3 | 0.1 (3) | C4—C3—C7—O5 | 2.8 (3) |
| S1—C1—C2—C3 | −178.61 (14) | C11—N1—C8—C9 | −57.8 (2) |
| C1—C2—C3—C4 | −0.1 (3) | C10—N2—C9—C8 | −57.4 (2) |
| C1—C2—C3—C7 | −177.83 (16) | N1—C8—C9—N2 | 57.3 (2) |
| C2—C3—C4—O6 | −178.85 (18) | C9—N2—C10—C11 | 57.3 (2) |
| C7—C3—C4—O6 | −1.2 (3) | C8—N1—C11—C10 | 57.5 (2) |
| C2—C3—C4—C5 | −0.2 (3) | N2—C10—C11—N1 | −56.9 (2) |
| C7—C3—C4—C5 | 177.50 (18) | C13—N3—C12—C13$^i$ | −57.3 (2) |
| O6—C4—C5—C6 | 179.22 (19) | C12—N3—C13—C12$^i$ | 57.4 (2) |
| C3—C4—C5—C6 | 0.5 (3) | | |

Symmetry codes: (i) −*x*, −*y*+2, −*z.*

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1A···O6[ii] | 0.899 (10) | 2.282 (19) | 2.978 (2) | 134 (2) |
| N1—H1A···O7[iii] | 0.899 (10) | 2.501 (18) | 3.199 (3) | 134.9 (19) |
| N2—H2A···O1[iv] | 0.901 (9) | 2.216 (14) | 3.055 (3) | 155 (2) |
| N2—H2A···O3[iv] | 0.901 (9) | 2.468 (17) | 3.240 (3) | 144 (2) |
| N2—H2B···O5[v] | 0.909 (9) | 1.744 (10) | 2.653 (2) | 178 (3) |
| N2—H2B···O4[v] | 0.909 (9) | 2.65 (2) | 3.227 (2) | 122.5 (19) |
| N3—H3A···O2[vi] | 0.904 (10) | 2.214 (11) | 3.087 (2) | 162 (2) |
| N3—H3A···O1[vi] | 0.904 (10) | 2.55 (2) | 3.216 (3) | 131 (2) |
| N3—H3B···N1[vi] | 0.911 (10) | 1.869 (12) | 2.772 (2) | 171 (4) |
| O7—H7A···O4[vii] | 0.846 (10) | 1.918 (12) | 2.752 (2) | 168 (3) |
| O7—H7B···O2[viii] | 0.856 (10) | 2.124 (10) | 2.963 (2) | 166 (3) |

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

**Fig. 1**

**Fig. 2**