

Bis(2-aminopyridinium) 5,5'-disulfane-diylbis(1,3,4-thiadiazole-2-thiolate) monohydrate

Pusu Zhao,^{a*} Zhiyan Guo^a and Hailian Xiao^b

^aNew Materials & Function Coordination Chemistry Laboratory, Qingdao University of Science and Technology, Qingdao Shandong 266042, People's Republic of China, and ^bCollege of Materials Science and Engineering, Qingdao University of Science & Technology, Qingdao 266042, People's Republic of China
Correspondence e-mail: zhaopusu@163.com

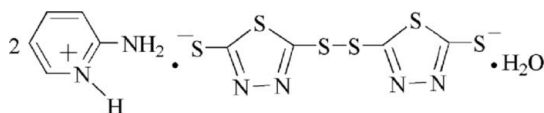
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Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.048; wR factor = 0.086; data-to-parameter ratio = 18.2.

In the crystal of the title compound, $2\text{C}_5\text{H}_7\text{N}_2^+ \cdot \text{C}_4\text{N}_4\text{S}_6^{2-} \cdot \text{H}_2\text{O}$, intermolecular $\text{N}-\text{H} \cdots \text{S}$ and $\text{N}-\text{H} \cdots \text{N}$ hydrogen bonds link four cations and two dianions into a centrosymmetric cluster. The crystal packing is further consolidated by $\pi-\pi$ interactions between the five- and six-membered rings of neighbouring clusters [centroid-centroid distances = 3.692 (3), 3.718 (3), 3.660 (3) and 3.696 (3) Å] and *via* $\text{O}-\text{H} \cdots \text{N}$, $\text{O}-\text{H} \cdots \text{S}$ and $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds involving the uncoordinated water molecules.

Related literature

For general background to supramolecular compounds, see: Rowsell & Yaghi (2005); Neville *et al.* (2008); Huang *et al.* (2007); Burchell *et al.* (2006). For related structures, see: Jebas *et al.* (2006); Jian *et al.* (2006); Banerjee *et al.* (2006); Moers *et al.* (2000).



Experimental

Crystal data

$2\text{C}_5\text{H}_7\text{N}_2^+ \cdot \text{C}_4\text{N}_4\text{S}_6^{2-} \cdot \text{H}_2\text{O}$
 $M_r = 504.71$
Monoclinic, $P2_1/c$
 $a = 7.3109$ (15) Å
 $b = 14.112$ (3) Å
 $c = 20.930$ (4) Å
 $\beta = 98.13$ (3)°

$V = 2137.8$ (7) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.67$ mm⁻¹
 $T = 295$ K
 $0.24 \times 0.22 \times 0.20$ mm

Data collection

Enraf-Nonius CAD-4 diffractometer

9377 measured reflections
4911 independent reflections

3931 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

3 standard reflections every 100 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.086$
 $S = 1.17$
4911 reflections
270 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.55$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.26$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|--|----------|--------------|--------------|----------------|
| $\text{N1}-\text{H1A} \cdots \text{S6}$ | 0.86 | 2.63 | 3.488 (3) | 177 |
| $\text{N2}-\text{H2A} \cdots \text{N8}$ | 0.86 | 1.87 | 2.726 (3) | 171 |
| $\text{N3}-\text{H3A} \cdots \text{S1}$ | 0.86 | 2.43 | 3.273 (3) | 166 |
| $\text{N4}-\text{H4A} \cdots \text{N5}$ | 0.86 | 1.97 | 2.826 (3) | 179 |
| $\text{O1W}-\text{H2W1} \cdots \text{N6}$ | 0.80 (4) | 2.07 (4) | 2.860 (3) | 169 (4) |
| $\text{N1}-\text{H1B} \cdots \text{O1W}^i$ | 0.86 | 2.07 | 2.898 (3) | 162 |
| $\text{O1W}-\text{H1W1} \cdots \text{S6}^{ii}$ | 0.83 (4) | 2.47 (4) | 3.294 (3) | 175 (3) |
| $\text{N3}-\text{H3B} \cdots \text{S6}^{iii}$ | 0.86 | 2.49 | 3.338 (2) | 171 |

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

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *NRCVAX* (Gabe *et al.*, 1989); 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: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV5028).

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Bis(2-aminopyridinium) 5,5'-disulfanediylbis(1,3,4-thiadiazole-2-thiolate) monohydrate

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Comment

Research on supramolecular compounds has become popular because of their potential applications in areas such as gas storage (Rowse *et al.*, 2005), magnetism (Neville *et al.*, 2008) and optics (Huang *et al.*, 2007). Among many strategies for achieving supramolecular compounds with predefined structures, the choice and design of organic molecules as hydrogen-bond acceptors or donors are undoubtedly a key part of the construction of intriguing frameworks driven by hydrogen-bonding interactions (Burchell *et al.*, 2006).

However, in these hydrogen-bond supramolecular compounds, 2-amino-pyridine often only forms co-crystals with another organic acid, such as 3-aminobenzoic acid, naphthalene-1,5-disulfonic acid and nicotinic acid (Jebas *et al.*, 2006). It is less studied that the co-crystals are aggregated by 2-amino-pyridine with a non-acid compound. For example, non-acids compounds of saccharinate (Banerjee *et al.*, 2006) and bis(methanesulfonyl)amide (Moers *et al.*, 2000) have been used to form co-crystals with 2-aminopyridinium and their crystal structures have been reported.

Herein, we will give another report about the synthesis and characterization of a 2:1 proton-transfer salt formed by 2-aminopyridinium with a non-acid compound of di(2-mercapto-1,3,4-thiadiazyl) disulfide and a water molecule.

Scheme I

The asymmetric unit contains one deprotonated di(2-mercapto-1,3,4-thiadiazyl) disulfide molecule, two protonated 2-amino-pyridine molecules and one water molecule. In the deprotonated di(2-mercapto-1,3,4-thiadiazyl) disulfide, two 2-mercapto-1,3,4-thiadiazyl groups are located at *cis*-position of the S3—S4 bond. In addition, these two 2-mercapto-1,3,4-thiadiazyl groups are in an opposite position with the dihedral angle between them being 6.84 (2)°. This geometry looks like that there is a C₂ symmetric axis passing through the mid-point of the S3—S4 bond. The S3—S4 bond length is 2.06438 (11) Å, which is longer than that in dibenzothiazyl-disulfide [(2.027 (2) Å)] (Jian *et al.*, 2006). All of the other bond lengths and bond angles in the two pyridyl rings and two thiazolyl rings are in the normal range.

In the crystal lattice, there are eight kinds of hydrogen bonds (Table 2), five of which link two 2-mercapto-1,3,4-thiadiazyl disulfide and four 2-amino-pyridinium ions together to form a macrocycle unit and three of which related to the water molecule help to connect all of the macrocycles to build a three dimensional network of the molecules.

As shown in Fig. 2, after accepting a proton from 2-mercapto-1,3,4-thiadiazyl disulfide, 2-amino-pyridinium ion has become a complete hydrogen bond donor. For example, each of the 2-amino-pyridinium ion containing N4 atom provides its three hydrogen bond donor sites such as N4—H4A, N3—H3A and N3—H3B to participate in building hydrogen bonds with two deprotonated 2-mercapto-1,3,4-thiadiazyl disulfide molecules, and finally to form three hydrogen bonds of N4—H4A...N5, N3—H3A...S1 and N3—H3B...S6. Each of the 2-amino-pyridinium ion containing N2 atom provides two hydrogen bond donor sites of N1—H1A and N2—H2A to construct hydrogen bonds with one deprotonated 2-mercapto-1,3,4-thiadiazyl disulfide molecule, and ultimately to form two hydrogen bonds of N1—H1A...S6 and N2—H2A...N8. Through above hydrogen bond connections, four 2-amino-pyridinium ions and two deprotonated 2-mercapto-1,3,4-thi-

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adiazyl disulfide molecules are joined together to give a macrocycle unit. Then, each three macrocycle units are linked together by a water molecule through three hydrogen bonds of N1—H1B···O1W, O1W—H1W1···S6 and O1W—H2W1···N6. Namely, the water molecule acts as two hydrogen bond donor as well as one hydrogen bond acceptor to join three macrocycle units together. Additionally, since the existence of two S3—S4 bonds, each macrocycle is bended to two layers and in each macrocycle unit, there are six hydrogen bond sites to link with six water molecules. Thus, all macrocycles are connected by water molecules to construct a three-dimensional architecture. On the other hand, among the pyridyl and thiadiazyl rings, there are $\pi\cdots\pi$ stacking interactions (Table 2) which further stabilize the crystal packing.

Experimental

Compound (I) was synthesized by heating together, for 20 min under reflux, 2-amino-pyridine (0.94 g, 10 mmol) and di(2-mercapto-1,3,4-thiadiazyl) disulfide (1.49 g, 5 mmol) in distilled water (30 ml). The colourless crystals were obtained after slow evaporation of the water solvent at room temperature.

Refinement

The water H atoms were found in a difference Fourier map, and refined isotropically. All other H atoms were fixed geometrically (C—H 0.93 Å, N—H 0.86 Å), and treated as riding, with $U_{\text{iso}} = 1.2 U_{\text{eq}}$ of the parent atom.

Figures

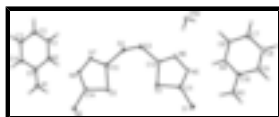


Fig. 1. The structure of the title compound showing 30% probability displacement ellipsoids and the atom-numbering scheme.

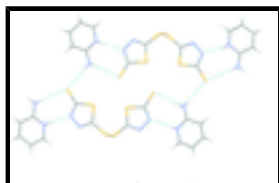
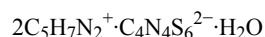


Fig. 2. A hydrogen-bonded (dashed lines) centrosymmetric cluster in (I).

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Crystal data



$$M_r = 504.71$$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$$a = 7.3109 (15) \text{ \AA}$$

$$b = 14.112 (3) \text{ \AA}$$

$$c = 20.930 (4) \text{ \AA}$$

$$\beta = 98.13 (3)^\circ$$

$$V = 2137.8 (7) \text{ \AA}^3$$

$$Z = 4$$

$$F(000) = 1040$$

$$D_x = 1.568 \text{ Mg m}^{-3}$$

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

Cell parameters from 25 reflections

$$\theta = 4\text{--}14^\circ$$

$$\mu = 0.67 \text{ mm}^{-1}$$

$$T = 295 \text{ K}$$

Block, colourless

$$0.24 \times 0.22 \times 0.20 \text{ mm}$$

Data collection

| | |
|--|--|
| Enraf–Nonius CAD-4 diffractometer | $R_{\text{int}} = 0.023$ |
| Radiation source: fine-focus sealed tube | $\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 1.8^\circ$ |
| graphite | $h = -9 \rightarrow 9$ |
| ω scans | $k = -18 \rightarrow 17$ |
| 9377 measured reflections | $l = -27 \rightarrow 27$ |
| 4911 independent reflections | 3 standard reflections every 100 reflections |
| 3931 reflections with $I > 2\sigma(I)$ | intensity decay: none |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.048$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.086$ | H atoms treated by a mixture of independent and constrained refinement |
| $S = 1.17$ | $w = 1/[\sigma^2(F_o^2) + (0.0278P)^2 + 0.2825P]$ |
| 4911 reflections | where $P = (F_o^2 + 2F_c^2)/3$ |
| 270 parameters | $(\Delta/\sigma)_{\text{max}} = 0.001$ |
| 0 restraints | $\Delta\rho_{\text{max}} = 0.55 \text{ e } \text{\AA}^{-3}$ |
| | $\Delta\rho_{\text{min}} = -0.26 \text{ e } \text{\AA}^{-3}$ |

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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|----|--------------|--------------|--------------|----------------------------------|
| S1 | 0.40901 (12) | 0.94077 (5) | 0.59925 (3) | 0.0364 (2) |
| S2 | 0.26262 (10) | 0.84201 (4) | 0.47444 (3) | 0.02842 (17) |
| S3 | 0.18855 (10) | 0.64715 (4) | 0.40985 (3) | 0.02446 (15) |
| S4 | 0.37606 (10) | 0.66357 (4) | 0.34565 (3) | 0.02432 (15) |
| S5 | 0.29173 (9) | 0.86996 (4) | 0.30034 (3) | 0.02237 (15) |
| S6 | 0.12212 (10) | 0.98806 (4) | 0.18451 (3) | 0.02636 (16) |
| N1 | -0.1312 (3) | 0.89557 (15) | 0.04470 (11) | 0.0380 (6) |

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|------|-------------|--------------|---------------|-------------|
| H1A | -0.0716 | 0.9175 | 0.0800 | 0.046* |
| H1B | -0.1810 | 0.9339 | 0.0153 | 0.046* |
| N2 | -0.0676 (3) | 0.74324 (14) | 0.08195 (10) | 0.0251 (5) |
| H2A | -0.0060 | 0.7670 | 0.1163 | 0.030* |
| N3 | 0.6664 (4) | 0.84178 (15) | 0.72187 (11) | 0.0387 (6) |
| H3A | 0.6044 | 0.8593 | 0.6858 | 0.046* |
| H3B | 0.7133 | 0.8835 | 0.7493 | 0.046* |
| N4 | 0.6138 (3) | 0.68622 (14) | 0.69089 (10) | 0.0237 (5) |
| H4A | 0.5520 | 0.7064 | 0.6555 | 0.028* |
| N5 | 0.4136 (3) | 0.75310 (14) | 0.57420 (9) | 0.0231 (5) |
| N6 | 0.3619 (3) | 0.68528 (14) | 0.52826 (9) | 0.0231 (5) |
| N7 | 0.1864 (3) | 0.72209 (14) | 0.23431 (10) | 0.0254 (5) |
| N8 | 0.1316 (3) | 0.79840 (14) | 0.19588 (9) | 0.0247 (5) |
| C1 | -0.0815 (4) | 0.64796 (18) | 0.07686 (13) | 0.0314 (6) |
| H1C | -0.0260 | 0.6098 | 0.1104 | 0.038* |
| C2 | -0.1754 (4) | 0.60765 (19) | 0.02344 (14) | 0.0349 (7) |
| H2B | -0.1856 | 0.5421 | 0.0198 | 0.042* |
| C3 | -0.2571 (4) | 0.66701 (19) | -0.02635 (13) | 0.0322 (6) |
| H3C | -0.3223 | 0.6405 | -0.0634 | 0.039* |
| C4 | -0.2419 (4) | 0.76228 (18) | -0.02103 (12) | 0.0260 (6) |
| H4B | -0.2945 | 0.8010 | -0.0546 | 0.031* |
| C5 | -0.1462 (4) | 0.80276 (17) | 0.03563 (12) | 0.0247 (6) |
| C6 | 0.6319 (4) | 0.59150 (17) | 0.70022 (12) | 0.0249 (6) |
| H6B | 0.5793 | 0.5503 | 0.6681 | 0.030* |
| C7 | 0.7250 (4) | 0.55568 (18) | 0.75551 (12) | 0.0274 (6) |
| H7B | 0.7364 | 0.4906 | 0.7620 | 0.033* |
| C8 | 0.8036 (4) | 0.62005 (19) | 0.80266 (12) | 0.0282 (6) |
| H8B | 0.8678 | 0.5972 | 0.8411 | 0.034* |
| C9 | 0.7875 (4) | 0.71541 (18) | 0.79316 (12) | 0.0266 (6) |
| H9A | 0.8410 | 0.7571 | 0.8248 | 0.032* |
| C10 | 0.6895 (4) | 0.75046 (18) | 0.73512 (12) | 0.0250 (6) |
| C11 | 0.3711 (4) | 0.84127 (17) | 0.55446 (12) | 0.0247 (5) |
| C12 | 0.2803 (4) | 0.72031 (16) | 0.47427 (11) | 0.0216 (5) |
| C13 | 0.2721 (3) | 0.74813 (16) | 0.29047 (11) | 0.0205 (5) |
| C14 | 0.1749 (3) | 0.88218 (17) | 0.22216 (11) | 0.0197 (5) |
| O1W | 0.3564 (3) | 0.48901 (14) | 0.56202 (10) | 0.0342 (5) |
| H2W1 | 0.371 (5) | 0.542 (3) | 0.5504 (17) | 0.058 (12)* |
| H1W1 | 0.293 (5) | 0.498 (2) | 0.5915 (18) | 0.055 (12)* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|------------|------------|------------|-------------|-------------|-------------|
| S1 | 0.0584 (6) | 0.0233 (3) | 0.0242 (4) | 0.0096 (3) | -0.0051 (3) | -0.0068 (3) |
| S2 | 0.0413 (4) | 0.0220 (3) | 0.0193 (3) | 0.0082 (3) | -0.0047 (3) | -0.0003 (2) |
| S3 | 0.0300 (4) | 0.0230 (3) | 0.0191 (3) | -0.0054 (3) | -0.0009 (3) | -0.0009 (2) |
| S4 | 0.0292 (4) | 0.0247 (3) | 0.0178 (3) | 0.0056 (3) | -0.0008 (3) | 0.0005 (2) |
| S5 | 0.0259 (4) | 0.0225 (3) | 0.0169 (3) | -0.0031 (3) | -0.0033 (3) | -0.0015 (2) |
| S6 | 0.0318 (4) | 0.0221 (3) | 0.0233 (3) | -0.0021 (3) | -0.0025 (3) | 0.0033 (2) |

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| N1 | 0.0514 (17) | 0.0233 (11) | 0.0325 (13) | -0.0013 (11) | -0.0176 (12) | 0.0000 (9) |
| N2 | 0.0286 (13) | 0.0262 (11) | 0.0180 (11) | -0.0024 (9) | -0.0053 (9) | -0.0025 (8) |
| N3 | 0.0507 (17) | 0.0279 (12) | 0.0316 (13) | -0.0065 (11) | -0.0146 (12) | -0.0018 (9) |
| N4 | 0.0251 (13) | 0.0281 (11) | 0.0159 (10) | -0.0007 (9) | -0.0035 (9) | -0.0007 (8) |
| N5 | 0.0300 (13) | 0.0223 (10) | 0.0157 (10) | 0.0003 (9) | -0.0011 (9) | -0.0004 (8) |
| N6 | 0.0275 (13) | 0.0221 (10) | 0.0187 (11) | -0.0015 (9) | -0.0004 (9) | 0.0005 (8) |
| N7 | 0.0345 (14) | 0.0214 (11) | 0.0184 (10) | 0.0005 (9) | -0.0030 (10) | -0.0006 (8) |
| N8 | 0.0325 (14) | 0.0220 (10) | 0.0170 (11) | -0.0012 (9) | -0.0052 (9) | -0.0003 (8) |
| C1 | 0.0382 (18) | 0.0242 (14) | 0.0312 (15) | 0.0003 (12) | 0.0024 (13) | 0.0047 (11) |
| C2 | 0.0412 (19) | 0.0233 (13) | 0.0400 (17) | -0.0050 (12) | 0.0053 (14) | -0.0069 (11) |
| C3 | 0.0278 (16) | 0.0399 (16) | 0.0282 (14) | -0.0052 (12) | 0.0010 (12) | -0.0121 (11) |
| C4 | 0.0232 (15) | 0.0342 (14) | 0.0191 (13) | 0.0012 (11) | -0.0023 (11) | -0.0019 (10) |
| C5 | 0.0228 (15) | 0.0274 (13) | 0.0227 (13) | -0.0019 (11) | -0.0012 (11) | -0.0026 (10) |
| C6 | 0.0241 (15) | 0.0272 (13) | 0.0235 (13) | -0.0001 (11) | 0.0032 (11) | -0.0044 (10) |
| C7 | 0.0249 (15) | 0.0290 (13) | 0.0286 (14) | 0.0047 (11) | 0.0050 (12) | 0.0023 (11) |
| C8 | 0.0204 (14) | 0.0443 (16) | 0.0200 (13) | 0.0036 (12) | 0.0031 (11) | 0.0049 (11) |
| C9 | 0.0226 (15) | 0.0355 (15) | 0.0203 (13) | -0.0033 (11) | -0.0021 (11) | -0.0044 (10) |
| C10 | 0.0232 (15) | 0.0266 (13) | 0.0248 (13) | -0.0041 (11) | 0.0017 (11) | -0.0042 (10) |
| C11 | 0.0288 (15) | 0.0274 (13) | 0.0174 (12) | 0.0038 (11) | 0.0016 (11) | -0.0008 (10) |
| C12 | 0.0247 (14) | 0.0212 (12) | 0.0180 (12) | -0.0013 (10) | 0.0002 (10) | -0.0030 (9) |
| C13 | 0.0222 (14) | 0.0215 (12) | 0.0174 (12) | 0.0018 (10) | 0.0009 (10) | 0.0008 (9) |
| C14 | 0.0189 (13) | 0.0248 (12) | 0.0152 (12) | -0.0007 (10) | 0.0013 (10) | 0.0005 (9) |
| O1W | 0.0491 (15) | 0.0229 (11) | 0.0295 (12) | -0.0011 (9) | 0.0022 (10) | 0.0002 (8) |

Geometric parameters (Å, °)

| | | | |
|--------|-------------|----------|-----------|
| S1—C11 | 1.689 (3) | N6—C12 | 1.299 (3) |
| S2—C12 | 1.722 (2) | N7—C13 | 1.304 (3) |
| S2—C11 | 1.749 (3) | N7—N8 | 1.370 (3) |
| S3—C12 | 1.754 (2) | N8—C14 | 1.324 (3) |
| S3—S4 | 2.0638 (11) | C1—C2 | 1.352 (4) |
| S4—C13 | 1.757 (2) | C1—H1C | 0.9300 |
| S5—C13 | 1.735 (2) | C2—C3 | 1.403 (4) |
| S5—C14 | 1.744 (2) | C2—H2B | 0.9300 |
| S6—C14 | 1.708 (2) | C3—C4 | 1.352 (4) |
| N1—C5 | 1.326 (3) | C3—H3C | 0.9300 |
| N1—H1A | 0.8600 | C4—C5 | 1.410 (3) |
| N1—H1B | 0.8600 | C4—H4B | 0.9300 |
| N2—C5 | 1.348 (3) | C6—C7 | 1.355 (4) |
| N2—C1 | 1.351 (3) | C6—H6B | 0.9300 |
| N2—H2A | 0.8600 | C7—C8 | 1.403 (4) |
| N3—C10 | 1.324 (3) | C7—H7B | 0.9300 |
| N3—H3A | 0.8600 | C8—C9 | 1.363 (4) |
| N3—H3B | 0.8600 | C8—H8B | 0.9300 |
| N4—C6 | 1.355 (3) | C9—C10 | 1.410 (4) |
| N4—C10 | 1.356 (3) | C9—H9A | 0.9300 |
| N4—H4A | 0.8600 | O1W—H2W1 | 0.80 (4) |
| N5—C11 | 1.334 (3) | O1W—H1W1 | 0.83 (4) |
| N5—N6 | 1.371 (3) | | |

supplementary materials

| | | | |
|-------------------------|-------------|--------------------------|--------------|
| Cg1...Cg3 ⁱ | 3.692 (3) | Cg2...Cg4 ⁱⁱⁱ | 3.660 (3) |
| Cg1...Cg3 ⁱⁱ | 3.718 (3) | Cg2...Cg4 ^{iv} | 3.696 (3) |
| C12—S2—C11 | 88.39 (12) | N1—C5—N2 | 119.6 (2) |
| C12—S3—S4 | 102.56 (9) | N1—C5—C4 | 122.8 (2) |
| C13—S4—S3 | 103.82 (9) | N2—C5—C4 | 117.6 (2) |
| C13—S5—C14 | 88.00 (11) | N4—C6—C7 | 121.2 (2) |
| C5—N1—H1A | 120.0 | N4—C6—H6B | 119.4 |
| C5—N1—H1B | 120.0 | C7—C6—H6B | 119.4 |
| H1A—N1—H1B | 120.0 | C6—C7—C8 | 117.7 (2) |
| C5—N2—C1 | 122.9 (2) | C6—C7—H7B | 121.1 |
| C5—N2—H2A | 118.5 | C8—C7—H7B | 121.1 |
| C1—N2—H2A | 118.5 | C9—C8—C7 | 121.2 (2) |
| C10—N3—H3A | 120.0 | C9—C8—H8B | 119.4 |
| C10—N3—H3B | 120.0 | C7—C8—H8B | 119.4 |
| H3A—N3—H3B | 120.0 | C8—C9—C10 | 119.7 (2) |
| C6—N4—C10 | 122.6 (2) | C8—C9—H9A | 120.2 |
| C6—N4—H4A | 118.7 | C10—C9—H9A | 120.2 |
| C10—N4—H4A | 118.7 | N3—C10—N4 | 118.7 (2) |
| C11—N5—N6 | 113.89 (19) | N3—C10—C9 | 123.8 (2) |
| C12—N6—N5 | 113.05 (19) | N4—C10—C9 | 117.5 (2) |
| C13—N7—N8 | 111.79 (19) | N5—C11—S1 | 126.22 (19) |
| C14—N8—N7 | 115.17 (19) | N5—C11—S2 | 110.88 (18) |
| N2—C1—C2 | 120.5 (3) | S1—C11—S2 | 122.88 (15) |
| N2—C1—H1C | 119.8 | N6—C12—S2 | 113.78 (18) |
| C2—C1—H1C | 119.8 | N6—C12—S3 | 121.56 (18) |
| C1—C2—C3 | 118.4 (2) | S2—C12—S3 | 124.59 (14) |
| C1—C2—H2B | 120.8 | N7—C13—S5 | 114.06 (17) |
| C3—C2—H2B | 120.8 | N7—C13—S4 | 120.60 (18) |
| C4—C3—C2 | 120.7 (3) | S5—C13—S4 | 125.02 (14) |
| C4—C3—H3C | 119.6 | N8—C14—S6 | 124.38 (18) |
| C2—C3—H3C | 119.6 | N8—C14—S5 | 110.99 (17) |
| C3—C4—C5 | 119.8 (2) | S6—C14—S5 | 124.63 (14) |
| C3—C4—H4B | 120.1 | H2W1—O1W—H1W1 | 102 (3) |
| C5—C4—H4B | 120.1 | | |
| C12—S3—S4—C13 | -98.27 (12) | N6—N5—C11—S2 | -0.5 (3) |
| C11—N5—N6—C12 | -0.4 (3) | C12—S2—C11—N5 | 0.9 (2) |
| C13—N7—N8—C14 | 0.1 (3) | C12—S2—C11—S1 | -177.71 (19) |
| C5—N2—C1—C2 | 0.7 (4) | N5—N6—C12—S2 | 1.1 (3) |
| N2—C1—C2—C3 | 0.2 (4) | N5—N6—C12—S3 | -175.97 (18) |
| C1—C2—C3—C4 | 0.1 (5) | C11—S2—C12—N6 | -1.1 (2) |
| C2—C3—C4—C5 | -1.2 (4) | C11—S2—C12—S3 | 175.82 (19) |
| C1—N2—C5—N1 | 178.1 (3) | S4—S3—C12—N6 | -106.0 (2) |
| C1—N2—C5—C4 | -1.9 (4) | S4—S3—C12—S2 | 77.26 (17) |
| C3—C4—C5—N1 | -177.9 (3) | N8—N7—C13—S5 | 0.1 (3) |
| C3—C4—C5—N2 | 2.1 (4) | N8—N7—C13—S4 | -173.73 (18) |
| C10—N4—C6—C7 | 1.2 (4) | C14—S5—C13—N7 | -0.1 (2) |
| N4—C6—C7—C8 | -0.5 (4) | C14—S5—C13—S4 | 173.34 (18) |
| C6—C7—C8—C9 | -0.2 (4) | S3—S4—C13—N7 | -100.7 (2) |

| | | | |
|--------------|-----------|---------------|--------------|
| C7—C8—C9—C10 | 0.3 (4) | S3—S4—C13—S5 | 86.25 (17) |
| C6—N4—C10—N3 | 179.5 (2) | N7—N8—C14—S6 | -179.89 (19) |
| C6—N4—C10—C9 | -1.1 (4) | N7—N8—C14—S5 | -0.2 (3) |
| C8—C9—C10—N3 | 179.7 (3) | C13—S5—C14—N8 | 0.2 (2) |
| C8—C9—C10—N4 | 0.3 (4) | C13—S5—C14—S6 | 179.88 (18) |
| N6—N5—C11—S1 | 178.1 (2) | | |

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

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> |
|-----------------------------|-------------|---------------|-----------------------|-------------------------|
| N1—H1A...S6 | 0.86 | 2.63 | 3.488 (3) | 177 |
| N2—H2A...N8 | 0.86 | 1.87 | 2.726 (3) | 171 |
| N3—H3A...S1 | 0.86 | 2.43 | 3.273 (3) | 166 |
| N4—H4A...N5 | 0.86 | 1.97 | 2.826 (3) | 179 |
| O1W—H2W1...N6 | 0.80 (4) | 2.07 (4) | 2.860 (3) | 169 (4) |
| N1—H1B...O1W ^v | 0.86 | 2.07 | 2.898 (3) | 162 |
| O1W—H1W1...S6 ^{iv} | 0.83 (4) | 2.47 (4) | 3.294 (3) | 175 (3) |
| N3—H3B...S6 ^{vi} | 0.86 | 2.49 | 3.338 (2) | 171 |

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

Fig. 1

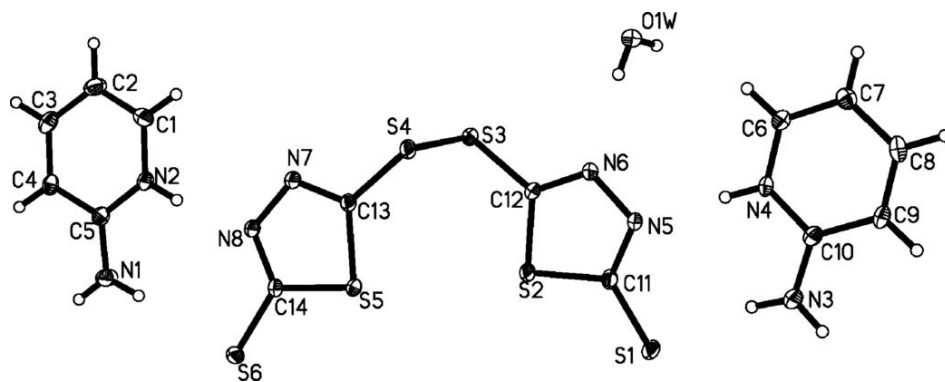


Fig. 2

