



# Crystal structure of bis(piperazin-1-ium- $\kappa N^4$ )-bis(thiosulfato- $\kappa S$ )zinc(II) dihydrate

Avijit Kumar Paul\*

Department of Chemistry, National Institute of Technology Kurukshetra, Haryana 136 119, India. \*Correspondence e-mail: apaul@nitkkr.ac.in

Received 27 October 2017

Accepted 9 January 2018

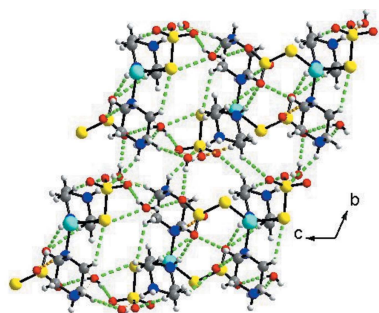
Edited by A. M. Chippindale, University of Reading, England

**Keywords:** crystal structure; zinc thiosulfate; piperazine; hydrogen bonding.**CCDC reference:** 1571150**Supporting information:** this article has supporting information at journals.iucr.org/e

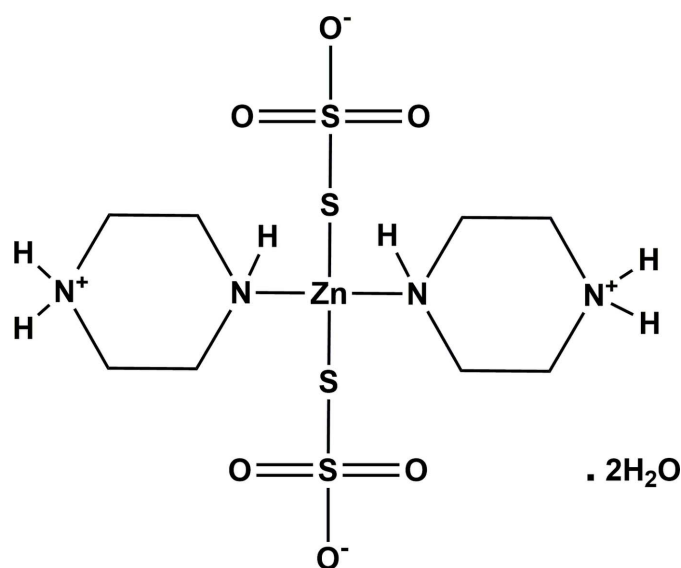
In the title compound,  $[\text{Zn}(\text{C}_4\text{H}_{11}\text{N}_2)_2(\text{S}_2\text{O}_3)_2]\cdot 2\text{H}_2\text{O}$ , two thiosulfate ions coordinate to the zinc(II) atom through the terminal S atoms. The tetrahedral coordination around the  $\text{Zn}^{\text{II}}$  ion is completed by ligating to two N atoms of two piperazinium ions. The remaining two N atoms of the piperazinium ions are diprotonated and do not coordinate to the metal centre. In the crystal, however, they are involved in  $\text{N}-\text{H}\cdots\text{O}_{\text{water}}$  and  $\text{N}-\text{H}\cdots\text{O}_{\text{sulfato}}$  hydrogen bonds. Together, a series of  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds, involving the O atoms of the thiosulfate ions and the water molecules as acceptors and the hydrogen atoms of the piperazinium ions and the water molecules as donors, form a three-dimensional supramolecular structure. Within this framework there are a number of intra- and intermolecular  $\text{C}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\text{S}$  contacts present.

## 1. Chemical context

Over the last few decades, a large number of amine-templated metal complexes and compounds with extended structures have been synthesized in the presence of a number of inorganic anions (Férey, 2008). One series of anions, namely the sulfur-containing oxoanions, and in particular sulfates and sulfites, are widely used in the synthesis of higher dimensional inorganic compounds because of their multidentate coordination capacity towards metal ions (Rao *et al.*, 2006). In these examples, the anions bind to the metal cations through the oxygen atoms. The thiosulfate ion is a new example of an sulfur oxoanion used in amine-templated synthesis, although the reactivity of this ligand is less than that of the sulfate and sulfite ions. In this heteroatomic ligand, the terminal S atom, as well as the O atoms, can bind to a range of metal ions. However, the long S—S bond is unstable under acidic conditions or at high temperature. Hence, the thiosulfate anion has not, to date, been explored extensively as a network-building unit for higher dimensional structures (Paul *et al.*, 2011). Despite these stability complications, Baggio and co-workers have synthesized a few molecular and one-dimensional structures containing thiosulfate anions that are connected to the metal through oxygen as well as sulfur atoms (Baggio *et al.*, 1996, 1997; Freire *et al.*, 2001; Harvey *et al.*, 2004). Our continuing synthetic efforts using the thiosulfate anion have resulted in the synthesis of some new three-dimensional structures in the family of cadmium–thiosulfate hybrid compounds formed in the presence of organic linkers (Paul *et al.*, 2009*a,b*, 2010). It is noteworthy that all of the reported metal–thiosulfate compounds are synthesized in the presence of nitrogen-containing aromatic organic linkers. Aromatic

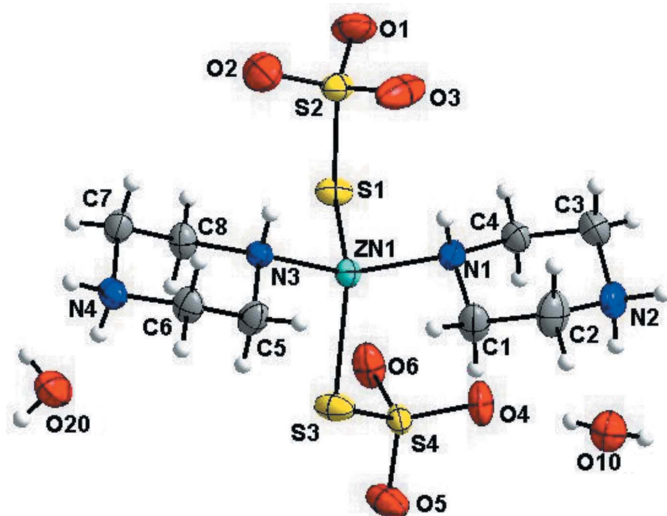


ligands play a dual role in metal–thiosulfate formation as they increase the dimensionality of the local structure and increase structure stabilization *via* secondary interactions, such as hydrogen bonds. Recently, Natarajan and co-workers (Karthik & Natarajan, 2016) have reported on some three-dimensional zinc–thiosulfate hybrid structures with aromatic N-donor organic linkers. Metal–thiosulfate compounds prepared in the presence of aliphatic amines are, however, rare (Paul, 2016) and require investigation. The title compound, is the first example of an aliphatic-amine-templated zinc thiosulfate compound. Its synthesis and crystal structure are reported on herein.



## 2. Structural commentary

The molecular structure of the title compound is illustrated in Fig. 1. In the complex, the  $\text{Zn}^{2+}$  ion is coordinated by two sulfur atoms of the thiosulfate ligands (S1 and S3) and two



**Figure 1**  
The asymmetric unit of the title compound, with atom labelling and showing 50% probability displacement ellipsoids.

**Table 1**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1\cdots O2^i$	0.83 (2)	2.25 (2)	3.041 (2)	160 (2)
$N2-H2AN\cdots O6^{ii}$	0.95 (3)	1.80 (3)	2.730 (2)	166 (2)
$N2-H2BN\cdots O10$	0.93 (2)	1.89 (2)	2.811 (3)	170 (2)
$N3-H3\cdots O3^i$	0.84 (2)	2.03 (2)	2.853 (2)	166 (2)
$N4-H4AN\cdots O20$	0.87 (2)	2.09 (2)	2.892 (2)	154 (2)
$N4-H4BN\cdots O5^{iii}$	0.94 (2)	1.84 (2)	2.763 (2)	169 (2)
$O10-H10A\cdots O4$	0.85 (3)	1.94 (4)	2.780 (2)	175 (3)
$O10-H10B\cdots O1^{iv}$	0.76 (3)	2.02 (3)	2.777 (2)	176 (4)
$O20-H20A\cdots O1^v$	0.82 (3)	2.02 (3)	2.804 (2)	163 (3)
$O20-H20B\cdots O5^{vi}$	0.74 (3)	2.17 (3)	2.866 (2)	158 (3)
$C3-H3A\cdots O6^{iv}$	0.97	2.45	3.221 (2)	136
$C4-H4A\cdots O3$	0.97	2.49	3.175 (3)	128
$C4-H4B\cdots O4$	0.97	2.54	3.463 (2)	159
$C5-H5B\cdots S3$	0.97	2.86	3.453 (2)	120
$C8-H8B\cdots O2$	0.97	2.50	3.318 (2)	142

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

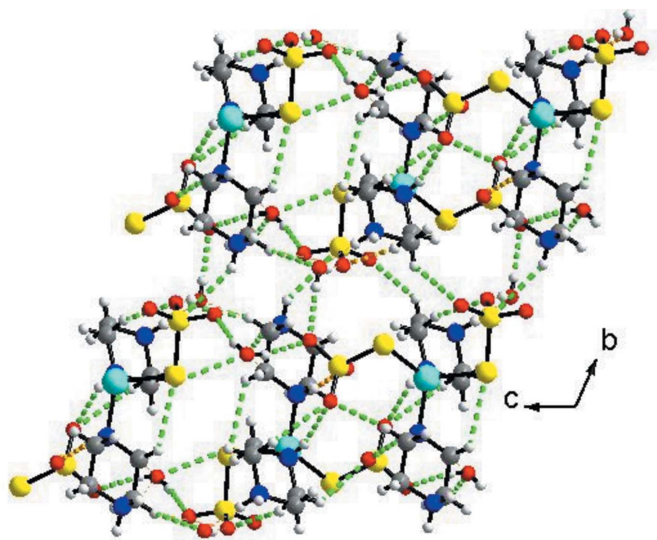
nitrogen atoms from the piperazinium ions (N1 and N3), in an approximately tetrahedral geometry ( $\text{ZnS}_2\text{N}_2$ , CN = 4). The Zn–S bond lengths are 2.2927 (4)  $\text{\AA}$  for Zn1–S1 and 2.3324 (4)  $\text{\AA}$  for Zn1–S3. The Zn–N bond lengths are 2.0879 (13)  $\text{\AA}$  for Zn1–N1 and 2.0727 (12)  $\text{\AA}$  for Zn1–N3. The N/S–Zn1–S/N bond angles lie in the range 101.24 (4) to 116.79 (2)°, confirming the tetrahedral nature of the zinc ions. Within the two thiosulfate ligands, the S–S bond lengths are 2.0511 (5)  $\text{\AA}$  for S1–S2 and 2.0332 (5)  $\text{\AA}$  for S3–S4. The S–O bond lengths vary from 1.4437 (14) to 1.4623 (13)  $\text{\AA}$ , while the O–S–O angles vary from 104.53 (5) to 112.85 (10)°, which is indicative of a fairly regular tetrahedral arrangement. In the molecular unit, the two thiosulfate units are bonded to the zinc(II) ion only through the terminal S atoms, and the oxygen atoms are uncoordinated. In addition, only one nitrogen atom of each piperazinium ion is bonded to the zinc(II) ion, the second being diprotonated in each case.

## 3. Supramolecular features

The supramolecular architecture (Fig. 2) arises from a three-dimensional network of  $\text{N-H}\cdots\text{O}$  and  $\text{O-H}\cdots\text{O}$  hydrogen bonds involving the uncoordinated oxygen atoms of the thiosulfate ligands, the protonated piperazine units and the lattice water molecules (Table 1). These intermolecular interactions lead to the formation of a supramolecular framework. Within this framework there are a number of intra- and intermolecular  $\text{C-H}\cdots\text{O}$  and  $\text{C-H}\cdots\text{S}$  contacts present (Table 1).

## 4. Database survey

A search of the Cambridge Structural Database (CSD, Version 35.9, last update May 2017; Groom *et al.*, 2016) for zinc–thiosulfato complexes gave 12 hits, all involving aromatic amines and/or thioureas. Díaz de Vivar *et al.* (2006) have described a molecular zinc–thiosulfate complex prepared in the presence of a tridentate aromatic ligand, *viz.* aqua(thio-



**Figure 2**  
A view along the  $a$  axis of the crystal packing of the title compound. The hydrogen bonds are shown as dashed lines (see Table 1).

sulfato- $\kappa O,S$ ][2,4,6-tris(2-pyridyl)-1,3,5-triazine- $N,N',N''$ ]-zinc(II) hemihydrate (CSD refcode: WEHTOT). The thiosulfate ligand is coordinated to the zinc ions through S and O atoms, forming octahedral zinc centres. In addition, a zinc–thiosulfate complex containing both one-dimensional cationic and anionic chains has been reported by the same authors, *viz.* *catena*-[ $(\mu^2$ -4,4'-bipyridine- $\kappa N,N'$ )tetraaquazinc(II) bis( $\mu^2$ -4,4'-bipyridine- $\kappa N,N'$ )( $\mu^2$ -thiosulfato- $\kappa O,S$ )bis(thiosulfato- $\kappa S$ )dizinc(II) dihydrate] [PEYLEL; Díaz de Vivar *et al.*, 2007]. Both types of chain contain 4,4'-bipyridine ligands as linkers.

Karthik & Natarajan (2016) have recently reported four higher-dimensional zinc–thiosulfate compounds synthesized in the presence of various aromatic ligands, *viz.* *catena*-[bis( $\mu$ -4,4'-bipyridine)bis( $\mu$ -thiosulfato)dizinc] (IJUWER), *catena*-[( $\mu$ -4,4'-propane-1,3-diyl)dipyridine)( $\mu$ -thiosulfato)zinc] (IJUWIV), and *catena*-[bis( $\mu$ -4,4'-ethene-1,2-diyl)dipyridine)bis( $\mu$ -thiosulfato)dizinc dihydrate] (IJUWOB) and *catena*-[bis( $\mu$ -4,4'-ethane-1,2-diyl)dipyridine)bis( $\mu$ -thiosulfato)dizinc ( $\mu$ -4,4'-ethane-1,2-diyl)dipyridine)( $\mu$ -thiosulfato)zinc trihydrate] (IJUWUH).

A number of molecular cadmium–thiosulfate and manganese–thiosulfate structures have been reported by Baggio and co-workers (Baggio *et al.*, 1996, 1997; Freire *et al.*, 2001; Harvey *et al.*, 2004). They were synthesized in the presence of 2,2'-bipyridine or 1,10-phenanthroline.

There are a few examples in which zero-dimensional cadmium–thiosulfate compounds form simple dinuclear complexes, in which the thiosulfate unit is bound to the metal through both the sulfur and the oxygen atoms. As expected, the structures are stabilized through C–H $\cdots$ O hydrogen-bonding interactions and  $\pi$ – $\pi$  interactions. One cadmium thiosulfate compound, bis(propane-1,3-diamine)(thiosulfato)-cadmium (CSD refcode: ORUJOC), which was reported recently, was isolated in the presence of the aliphatic amine 1,3-diaminopropane (Paul, 2016). One molecular piper-

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	[Zn(C <sub>4</sub> H <sub>11</sub> N <sub>2</sub> ) <sub>2</sub> (S <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> ] $\cdot$ 2H <sub>2</sub> O
$M_r$	499.94
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	293
$a, b, c$ (Å)	8.7631 (1), 10.5623 (2), 11.6072 (2)
$\alpha, \beta, \gamma$ (°)	113.736 (1), 98.761 (1), 91.472 (1)
$V$ (Å <sup>3</sup> )	967.49 (3)
$Z$	2
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	1.74
Crystal size (mm)	0.22 $\times$ 0.18 $\times$ 0.16
Data collection	
Diffractometer	Bruker SMART APEX CCD area detector
Absorption correction	Multi-scan (SADABS; Bruker, 2000)
$T_{\min}, T_{\max}$	0.700, 0.768
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	19938, 7607, 5927
$R_{\text{int}}$	0.027
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.782
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.032, 0.079, 1.01
No. of reflections	7607
No. of parameters	266
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.47, -0.36

Computer programs: SMART and SAINT (Bruker, 2000), SHELXS97 (Sheldrick, 2008), SHELXL2016/6 (Sheldrick, 2015), ORTEP-3 for Windows (Farrugia, 2012), PLATON (Spek, 2009) and publCIF (Westrip, 2010).

azinium thiosulfate monohydrate structure has been reported, (piperazinediium thiosulfate monohydrate; CSD refcode: AROWUA; Srinivasan *et al.*, 2011), in which the protonated aliphatic amine and thiosulfate units are linked together through extensive hydrogen bonds. It is noteworthy that there are no previous examples in the literature of zinc–thiosulfate structures that crystallize in the presence of aliphatic amines.

## 5. Synthesis and crystallization

Zn(NO<sub>3</sub>)<sub>2</sub> $\cdot$ 6H<sub>2</sub>O (0.297 g, 1 mmol) was dissolved in 5 ml distilled water. Then (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.296 g, 2 mmol) was added to the solution, which was stirred for 15 min. Piperazine (0.172 g, 2 mmol) was dissolved separately in distilled water (5 ml) and the solution poured into the initial reaction mixture until the pH was 8. The resulting solution was left undisturbed and after 1 week, colourless block-shaped crystals were obtained. The product was filtered and washed with cold water. The yield was approximately 85% based on Zn metal. Elemental analysis calculated for C<sub>8</sub>H<sub>26</sub>N<sub>4</sub>O<sub>8</sub>S<sub>4</sub>Zn: C 19.20, H 5.24, N 11.20%; found: C 19.27, H 5.29, N 11.16%.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The NH, NH<sub>2</sub> and water H atoms

were located in difference-Fourier maps and freely refined. The C-bound H atoms were included in calculated positions and refined as riding: C–H = 0.97 Å with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

### Acknowledgements

The author thanks Professor S. Natarajan for providing facilities.

### Funding information

The author thanks the SERB and DST, India, for research grants.

### References

- Baggio, R., Baggio, S., Pardo, M. I. & Garland, M. T. (1996). *Acta Cryst.* **C52**, 1939–1942.
- Baggio, S., Pardo, M. I., Baggio, R. & Garland, M. T. (1997). *Acta Cryst.* **C53**, 727–729.
- Bruker (2000). *SMART, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Díaz de Vivar, M. E., Baggio, S. & Baggio, R. (2006). *Acta Cryst.* **C62**, m192–m194.
- Díaz de Vivar, M. E., Baggio, S., Garland, M. T. & Baggio, R. (2007). *Acta Cryst.* **C63**, m123–m125.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Férey, G. (2008). *Chem. Soc. Rev.* **37**, 191–214.
- Freire, E., Baggio, S., Baggio, R. & Mombrú, A. (2001). *Acta Cryst.* **C57**, 14–17.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Harvey, M., Baggio, S., Pardo, H. & Baggio, R. (2004). *Acta Cryst.* **C60**, m79–m81.
- Karthik, R. & Natarajan, S. (2016). *Cryst. Growth Des.* **16**, 2239–2248.
- Paul, A. K. (2016). *J. Mol. Struct.* **1125**, 696–704.
- Paul, A. K., Karthik, R. & Natarajan, S. (2011). *Cryst. Growth Des.* **11**, 5741–5749.
- Paul, A. K., Madras, G. & Natarajan, S. (2009a). *CrystEngComm*, **11**, 55–57.
- Paul, A. K., Madras, G. & Natarajan, S. (2009b). *Phys. Chem. Chem. Phys.* **11**, 11285–11296.
- Paul, A. K., Madras, G. & Natarajan, S. (2010). *Dalton Trans.* **39**, 2263–2279.
- Rao, C. N. R., Behera, J. N. & Dan, M. (2006). *Chem. Soc. Rev.* **35**, 375–387.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Srinivasan, B. R., Naik, A. R., Dhuri, S. N., Näther, C. & Bensch, W. (2011). *J. Chem. Sci.* **123**, 55–61.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

## supporting information

*Acta Cryst.* (2018). E74, 176-179 [https://doi.org/10.1107/S2056989018000555]

## Crystal structure of bis(piperazin-1-ium- $\kappa$ N<sup>4</sup>)bis(thiosulfato- $\kappa$ S)zinc(II) dihydrate

Avijit Kumar Paul

### Computing details

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2016/6* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXL2016/6* (Sheldrick, 2015), *PLATON* (Spek, 2009) and *pubCIF* (Westrip, 2010).

### Bis(piperazin-1-ium- $\kappa$ N<sup>4</sup>)bis(thiosulfato- $\kappa$ S)zinc(II) dihydrate

#### Crystal data

[Zn(C<sub>4</sub>H<sub>11</sub>N<sub>2</sub>)<sub>2</sub>(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub>]:2H<sub>2</sub>O

$M_r = 499.94$

Triclinic,  $P\bar{1}$

$a = 8.7631$  (1) Å

$b = 10.5623$  (2) Å

$c = 11.6072$  (2) Å

$\alpha = 113.736$  (1)°

$\beta = 98.761$  (1)°

$\gamma = 91.472$  (1)°

$V = 967.49$  (3) Å<sup>3</sup>

$Z = 2$

$F(000) = 520$

$D_x = 1.716$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 3790 reflections

$\theta = 2.0$ – $26.0$ °

$\mu = 1.74$  mm<sup>-1</sup>

$T = 293$  K

Block, colorless

$0.22 \times 0.18 \times 0.16$  mm

#### Data collection

Bruker SMART APEX CCD area detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(SADABS; Bruker, 2000)

$T_{\min} = 0.700$ ,  $T_{\max} = 0.768$

19938 measured reflections

7607 independent reflections

5927 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\max} = 33.7$ °,  $\theta_{\min} = 2.0$ °

$h = -13 \rightarrow 13$

$k = -16 \rightarrow 9$

$l = -18 \rightarrow 17$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.079$

$S = 1.01$

7607 reflections

266 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.040P)^2]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.47 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.36 \text{ e } \text{\AA}^{-3}$$

### Special details

**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.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.36403 (2)	0.36678 (2)	0.17364 (2)	0.02307 (5)
S1	0.19769 (4)	0.23705 (4)	-0.01347 (4)	0.02921 (8)
S2	0.28149 (4)	0.31755 (4)	-0.12806 (4)	0.02866 (8)
S3	0.31486 (6)	0.34577 (4)	0.35739 (4)	0.03543 (10)
S4	0.27051 (4)	0.13632 (4)	0.29154 (4)	0.02567 (8)
O1	0.22237 (19)	0.21735 (14)	-0.25891 (12)	0.0508 (4)
O2	0.22392 (19)	0.45077 (14)	-0.10572 (15)	0.0541 (4)
O3	0.44978 (15)	0.32601 (19)	-0.09909 (15)	0.0612 (4)
O4	0.40860 (15)	0.06807 (14)	0.25701 (14)	0.0486 (3)
O5	0.2234 (2)	0.11500 (13)	0.39847 (14)	0.0544 (4)
O6	0.14635 (14)	0.09045 (13)	0.18082 (13)	0.0435 (3)
N1	0.59630 (14)	0.33597 (13)	0.16071 (13)	0.0261 (2)
H1	0.627 (2)	0.3885 (19)	0.1297 (18)	0.033 (5)*
N2	0.86568 (17)	0.19550 (17)	0.20334 (16)	0.0381 (3)
H2AN	0.968 (3)	0.172 (2)	0.194 (2)	0.053 (6)*
H2BN	0.831 (3)	0.149 (2)	0.249 (2)	0.058 (7)*
N3	0.34859 (14)	0.57724 (12)	0.22385 (12)	0.0225 (2)
H3	0.396 (2)	0.5979 (17)	0.1754 (17)	0.024 (4)*
N4	0.24360 (17)	0.84404 (13)	0.37115 (13)	0.0298 (3)
H4AN	0.186 (2)	0.8219 (19)	0.4161 (19)	0.037 (5)*
H4BN	0.229 (2)	0.937 (2)	0.3879 (19)	0.043 (5)*
C1	0.69716 (19)	0.37986 (18)	0.28807 (16)	0.0381 (4)
H1A	0.654430	0.334114	0.335305	0.046*
H1B	0.696156	0.479233	0.335289	0.046*
C2	0.8636 (2)	0.34663 (19)	0.2805 (2)	0.0454 (5)
H2A	0.911324	0.399270	0.241316	0.055*
H2B	0.922320	0.372326	0.365901	0.055*
C3	0.7752 (2)	0.1542 (2)	0.07222 (18)	0.0421 (4)
H3A	0.777441	0.055408	0.022780	0.051*
H3B	0.821264	0.203770	0.029594	0.051*
C4	0.60942 (19)	0.18742 (16)	0.07979 (15)	0.0315 (3)
H4A	0.552976	0.164170	-0.005869	0.038*
H4B	0.561198	0.129930	0.114233	0.038*
C5	0.4203 (2)	0.66344 (15)	0.35818 (15)	0.0327 (3)
H5A	0.528902	0.647499	0.370824	0.039*
H5B	0.370312	0.634514	0.413833	0.039*

C6	0.40821 (19)	0.81761 (15)	0.39612 (16)	0.0330 (3)
H6A	0.450934	0.868622	0.486215	0.040*
H6B	0.467790	0.849836	0.347563	0.040*
C7	0.17408 (19)	0.76190 (16)	0.23399 (16)	0.0333 (3)
H7A	0.227849	0.791358	0.180529	0.040*
H7B	0.065948	0.778454	0.219288	0.040*
C8	0.18624 (17)	0.60873 (15)	0.19857 (16)	0.0308 (3)
H8A	0.124751	0.578258	0.247102	0.037*
H8B	0.143694	0.557112	0.108512	0.037*
O10	0.72416 (18)	0.05969 (17)	0.32966 (15)	0.0460 (3)
H10A	0.629 (4)	0.060 (3)	0.303 (3)	0.098 (11)*
H10B	0.742 (3)	-0.015 (3)	0.313 (3)	0.074 (10)*
O20	-0.01440 (19)	0.7318 (2)	0.44092 (18)	0.0557 (4)
H20A	-0.082 (4)	0.729 (3)	0.383 (3)	0.092 (11)*
H20B	-0.048 (3)	0.776 (3)	0.497 (3)	0.070 (9)*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Zn1	0.02461 (8)	0.02117 (8)	0.02345 (8)	0.00381 (6)	0.00452 (6)	0.00900 (6)
S1	0.02902 (18)	0.03198 (19)	0.02573 (17)	-0.00689 (14)	0.00212 (13)	0.01250 (15)
S2	0.02756 (17)	0.0354 (2)	0.02670 (18)	0.00130 (14)	0.00454 (13)	0.01668 (15)
S3	0.0560 (3)	0.02537 (18)	0.02544 (18)	-0.00262 (17)	0.01059 (17)	0.01015 (15)
S4	0.02671 (16)	0.02414 (17)	0.03090 (18)	0.00813 (13)	0.01197 (13)	0.01342 (14)
O1	0.0746 (10)	0.0502 (8)	0.0237 (6)	0.0060 (7)	0.0030 (6)	0.0132 (5)
O2	0.0744 (10)	0.0403 (7)	0.0630 (9)	0.0151 (7)	0.0259 (8)	0.0316 (7)
O3	0.0291 (6)	0.1148 (13)	0.0692 (10)	-0.0021 (7)	0.0074 (6)	0.0689 (10)
O4	0.0356 (7)	0.0524 (8)	0.0618 (9)	0.0251 (6)	0.0179 (6)	0.0229 (7)
O5	0.0985 (12)	0.0319 (6)	0.0513 (8)	0.0170 (7)	0.0449 (8)	0.0242 (6)
O6	0.0308 (6)	0.0364 (7)	0.0466 (7)	0.0042 (5)	0.0010 (5)	0.0021 (5)
N1	0.0255 (6)	0.0260 (6)	0.0290 (6)	0.0060 (5)	0.0052 (5)	0.0132 (5)
N2	0.0270 (7)	0.0479 (9)	0.0476 (9)	0.0152 (6)	0.0120 (6)	0.0253 (7)
N3	0.0239 (5)	0.0217 (5)	0.0234 (6)	0.0036 (4)	0.0068 (4)	0.0097 (5)
N4	0.0379 (7)	0.0219 (6)	0.0331 (7)	0.0078 (5)	0.0141 (6)	0.0119 (5)
C1	0.0325 (8)	0.0364 (9)	0.0334 (8)	0.0085 (7)	-0.0011 (6)	0.0040 (7)
C2	0.0257 (8)	0.0450 (10)	0.0570 (12)	0.0036 (7)	-0.0024 (8)	0.0156 (9)
C3	0.0425 (9)	0.0500 (11)	0.0373 (9)	0.0219 (8)	0.0164 (7)	0.0172 (8)
C4	0.0335 (8)	0.0311 (8)	0.0273 (7)	0.0101 (6)	0.0061 (6)	0.0087 (6)
C5	0.0377 (8)	0.0255 (7)	0.0294 (7)	0.0066 (6)	-0.0024 (6)	0.0085 (6)
C6	0.0351 (8)	0.0231 (7)	0.0342 (8)	0.0025 (6)	0.0018 (6)	0.0065 (6)
C7	0.0349 (8)	0.0307 (8)	0.0336 (8)	0.0105 (6)	0.0027 (6)	0.0133 (6)
C8	0.0248 (7)	0.0269 (7)	0.0361 (8)	0.0044 (5)	0.0028 (6)	0.0091 (6)
O10	0.0428 (8)	0.0457 (8)	0.0492 (8)	0.0068 (6)	0.0067 (6)	0.0197 (7)
O20	0.0445 (8)	0.0857 (12)	0.0441 (9)	0.0215 (8)	0.0168 (7)	0.0300 (9)

*Geometric parameters (Å, °)*

Zn1—N3	2.0727 (12)	N4—H4BN	0.93 (2)
Zn1—N1	2.0879 (13)	C1—C2	1.516 (2)
Zn1—S1	2.2927 (4)	C1—H1A	0.9700
Zn1—S3	2.3324 (4)	C1—H1B	0.9700
S1—S2	2.0511 (5)	C2—H2A	0.9700
S2—O2	1.4437 (14)	C2—H2B	0.9700
S2—O3	1.4539 (14)	C3—C4	1.510 (2)
S2—O1	1.4606 (13)	C3—H3A	0.9700
S3—S4	2.0332 (5)	C3—H3B	0.9700
S4—O4	1.4507 (12)	C4—H4A	0.9700
S4—O6	1.4546 (13)	C4—H4B	0.9700
S4—O5	1.4623 (13)	C5—C6	1.518 (2)
N1—C1	1.487 (2)	C5—H5A	0.9700
N1—C4	1.4876 (19)	C5—H5B	0.9700
N1—H1	0.83 (2)	C6—H6A	0.9700
N2—C2	1.485 (2)	C6—H6B	0.9700
N2—C3	1.489 (2)	C7—C8	1.511 (2)
N2—H2AN	0.95 (2)	C7—H7A	0.9700
N2—H2BN	0.93 (2)	C7—H7B	0.9700
N3—C5	1.4779 (19)	C8—H8A	0.9700
N3—C8	1.4820 (18)	C8—H8B	0.9700
N3—H3	0.837 (18)	O10—H10A	0.85 (3)
N4—C6	1.484 (2)	O10—H10B	0.76 (3)
N4—C7	1.491 (2)	O20—H20A	0.81 (3)
N4—H4AN	0.87 (2)	O20—H20B	0.74 (3)
N3—Zn1—N1	105.78 (5)	N1—C1—H1B	108.9
N3—Zn1—S1	110.79 (3)	C2—C1—H1B	108.9
N1—Zn1—S1	112.90 (4)	H1A—C1—H1B	107.7
N3—Zn1—S3	101.24 (4)	N2—C2—C1	109.22 (14)
N1—Zn1—S3	108.21 (4)	N2—C2—H2A	109.8
S1—Zn1—S3	116.788 (16)	C1—C2—H2A	109.8
S2—S1—Zn1	98.167 (18)	N2—C2—H2B	109.8
O2—S2—O3	112.85 (10)	C1—C2—H2B	109.8
O2—S2—O1	110.61 (9)	H2A—C2—H2B	108.3
O3—S2—O1	111.04 (10)	N2—C3—C4	109.77 (14)
O2—S2—S1	109.71 (6)	N2—C3—H3A	109.7
O3—S2—S1	107.00 (6)	C4—C3—H3A	109.7
O1—S2—S1	105.27 (6)	N2—C3—H3B	109.7
S4—S3—Zn1	101.05 (2)	C4—C3—H3B	109.7
O4—S4—O6	110.47 (8)	H3A—C3—H3B	108.2
O4—S4—O5	111.17 (9)	N1—C4—C3	113.09 (14)
O6—S4—O5	112.02 (9)	N1—C4—H4A	109.0
O4—S4—S3	110.45 (6)	C3—C4—H4A	109.0
O6—S4—S3	108.00 (6)	N1—C4—H4B	109.0
O5—S4—S3	104.53 (5)	C3—C4—H4B	109.0



C1—N1—C4	110.39 (12)	H4A—C4—H4B	107.8
C1—N1—Zn1	112.60 (10)	N3—C5—C6	113.06 (12)
C4—N1—Zn1	109.65 (9)	N3—C5—H5A	109.0
C1—N1—H1	105.4 (13)	C6—C5—H5A	109.0
C4—N1—H1	112.1 (13)	N3—C5—H5B	109.0
Zn1—N1—H1	106.6 (13)	C6—C5—H5B	109.0
C2—N2—C3	110.50 (14)	H5A—C5—H5B	107.8
C2—N2—H2AN	111.5 (13)	N4—C6—C5	110.10 (13)
C3—N2—H2AN	107.0 (14)	N4—C6—H6A	109.6
C2—N2—H2BN	107.5 (14)	C5—C6—H6A	109.6
C3—N2—H2BN	114.4 (14)	N4—C6—H6B	109.6
H2AN—N2—H2BN	106.1 (19)	C5—C6—H6B	109.6
C5—N3—C8	110.20 (12)	H6A—C6—H6B	108.2
C5—N3—Zn1	112.71 (9)	N4—C7—C8	110.19 (13)
C8—N3—Zn1	111.95 (9)	N4—C7—H7A	109.6
C5—N3—H3	109.2 (12)	C8—C7—H7A	109.6
C8—N3—H3	106.3 (12)	N4—C7—H7B	109.6
Zn1—N3—H3	106.2 (12)	C8—C7—H7B	109.6
C6—N4—C7	110.40 (12)	H7A—C7—H7B	108.1
C6—N4—H4AN	113.4 (13)	N3—C8—C7	112.29 (12)
C7—N4—H4AN	107.0 (13)	N3—C8—H8A	109.1
C6—N4—H4BN	114.3 (13)	C7—C8—H8A	109.1
C7—N4—H4BN	106.1 (13)	N3—C8—H8B	109.1
H4AN—N4—H4BN	105.1 (17)	C7—C8—H8B	109.1
N1—C1—C2	113.43 (15)	H8A—C8—H8B	107.9
N1—C1—H1A	108.9	H10A—O10—H10B	109 (3)
C2—C1—H1A	108.9	H20A—O20—H20B	100 (3)
C4—N1—C1—C2	52.0 (2)	C8—N3—C5—C6	-53.62 (19)
Zn1—N1—C1—C2	174.88 (12)	Zn1—N3—C5—C6	-179.47 (11)
C3—N2—C2—C1	59.1 (2)	C7—N4—C6—C5	-57.01 (18)
N1—C1—C2—N2	-56.1 (2)	N3—C5—C6—N4	55.66 (19)
C2—N2—C3—C4	-59.4 (2)	C6—N4—C7—C8	58.03 (18)
C1—N1—C4—C3	-51.76 (19)	C5—N3—C8—C7	54.16 (18)
Zn1—N1—C4—C3	-176.37 (11)	Zn1—N3—C8—C7	-179.56 (11)
N2—C3—C4—N1	56.0 (2)	N4—C7—C8—N3	-56.96 (19)

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

<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>
N1—H1 $\cdots$ O2 <sup>i</sup>	0.83 (2)	2.25 (2)	3.041 (2)	160 (2)
N2—H2AN $\cdots$ O6 <sup>ii</sup>	0.95 (3)	1.80 (3)	2.730 (2)	166 (2)
N2—H2BN $\cdots$ O10	0.93 (2)	1.89 (2)	2.811 (3)	170 (2)
N3—H3 $\cdots$ O3 <sup>i</sup>	0.84 (2)	2.03 (2)	2.853 (2)	166 (2)
N4—H4AN $\cdots$ O20	0.87 (2)	2.09 (2)	2.892 (2)	154 (2)
N4—H4BN $\cdots$ O5 <sup>iii</sup>	0.94 (2)	1.84 (2)	2.763 (2)	169 (2)
O10—H10A $\cdots$ O4	0.85 (3)	1.94 (4)	2.780 (2)	175 (3)
O10—H10B $\cdots$ O1 <sup>iv</sup>	0.76 (3)	2.02 (3)	2.777 (2)	176 (4)

---

O20—H20A···O1 <sup>v</sup>	0.82 (3)	2.02 (3)	2.804 (2)	163 (3)
O20—H20B···O5 <sup>vi</sup>	0.74 (3)	2.17 (3)	2.866 (2)	158 (3)
C3—H3A···O6 <sup>iv</sup>	0.97	2.45	3.221 (2)	136
C4—H4A···O3	0.97	2.49	3.175 (3)	128
C4—H4B···O4	0.97	2.54	3.463 (2)	159
C5—H5B···S3	0.97	2.86	3.453 (2)	120
C8—H8B···O2	0.97	2.50	3.318 (2)	142

---

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