

## Zinc(II) sulfate tetrahydrate

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## Key indicators

Single-crystal X-ray study  
 T = 150 K  
 Mean  $\sigma(\text{S}-\text{O}) = 0.008 \text{ \AA}$   
 R factor = 0.059  
 wR factor = 0.157  
 Data-to-parameter ratio = 9.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound crystallizes as centrosymmetric  $[\text{Zn}(\mu_2\text{-SO}_4)(\text{H}_2\text{O})_4]_2$  dimers. The six-coordinate geometry of the zinc(II) centre comprises four water molecules and two *cis*-located bridging sulfate anions in a distorted octahedral array within which the Zn—O interatomic distances and O—Zn—O interatomic angles fall into the narrow ranges 2.080 (8)–2.125 (7) Å and 83.7 (3)–96.7 (3)°, respectively. Strong O—H···O hydrogen bonds involving seven of the eight water-H atoms link the dimers to form a three-dimensional body-centred network.

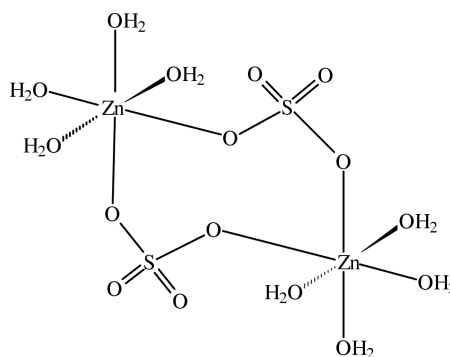
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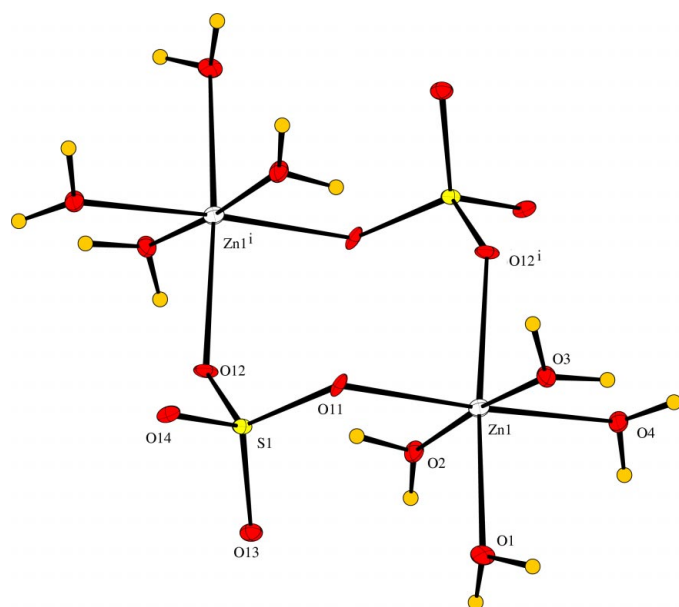
## Comment

Zinc sulfate tetrahydrate, (I), has long been considered to be an unstable material formed transiently during the thermal decomposition of zinc sulfate heptahydrate (Guenot *et al.*, 1969; Spiess & Gruehn, 1979), the stable hydrates being the heptahydrate (273–312 K), the hexahydrate (312–333 K) and the monohydrate (333–373 K) (Aylett, 1973). There is a dearth of information on its chemical and physical properties (Aylett, 1973). Its crystallization from an acetonitrile/diethyl ether mixture containing hydrated zinc tetrafluoroborate and 2,6-bis(2-mercapto-1-methylimidazole)pyridine was unexpected, and is assumed to result from decomposition/oxidation of the sulfur-bridged tridentate ligand.



(I)

The structure of zinc(II) sulfate tetrahydrate comprises centrosymmetric bis( $\mu$ -sulfato-*O:O'*)bis[tetraaquazinc(II)],  $[\text{Zn}(\mu_2\text{-SO}_4)(\text{H}_2\text{O})_4]_2$ , dimers with a Zn···Zn separation of 4.509 (2) Å (Fig. 1). Bis( $\mu$ -sulfato-*O:O'*)-bridged zinc(II) dimers are very rare, the motif having been reported for the first time in 2000 in bis( $\mu$ -sulfato-*O:O'*)bis[(2,9-dimethyl-1,10-phenanthroline)zinc(II)],  $[\text{Zn}(\text{dmp})(\mu_2\text{-SO}_4)]_2$  (Harvey *et al.*, 2000). The zinc(II) centres adopt distorted octahedral geometries with four water molecules [Zn—O 2.080 (8)–



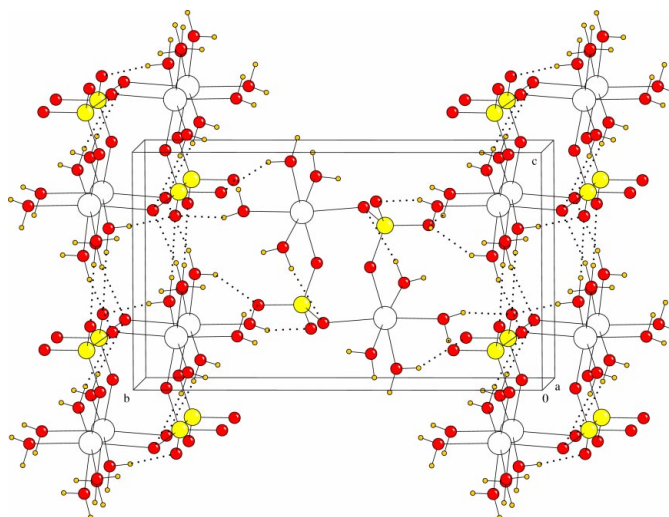
**Figure 1**

A view of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code:  $1-x, 1-y, 1-z$ .]

2.101 (7) Å] and two *cis*-located bridging sulfate anions [Zn—O 2.113 (7) and 2.125 (7) Å]. This arrangement is similar to that in the tetraqua(phenanthroline)zinc(II) cation,  $[\text{Zn}(\text{phen})(\text{H}_2\text{O})_4]^{2+}$  (Zn—O 2.083–2.130 Å; Zn—N 2.136 and 2.156 Å; Zhang *et al.*, 1999), the phenanthroline ligand replacing the two bridging sulfate anions.

The sulfate anions, despite the fact that two O atoms are coordinated to the metal centre and two are uncoordinated, adopt quite regular tetrahedral geometries within which the S—O interatomic distances and O—S—O interatomic angles fall into the narrow ranges 1.460 (7)–1.479 (7) Å and 108.2 (4)–111.3 (4)°, respectively. This behaviour differs from that in  $[\text{Zn}(\text{dmp})(\mu_2\text{-SO}_4)]_2$  (Harvey *et al.*, 2000) for which the coordinated O atoms form considerably longer S—O bonds [1.499 (2) and 1.513 (2) Å] than the non-coordinated ones [1.437 (2) and 1.439 (2) Å]. The difference may be attributed to the fact that the non-coordinated sulfate-O atoms in  $[\text{Zn}(\mu_2\text{-SO}_4)(\text{H}_2\text{O})_4]_2$ , but not those in  $[\text{Zn}(\text{dmp})(\mu_2\text{-SO}_4)]_2$ , act as hydrogen-bond acceptors.

The long-range structure of  $[\text{Zn}(\text{H}_2\text{O})_4(\mu_2\text{-SO}_4)]_2$  is dominated by O—H...O hydrogen-bonding contacts which link the dimers to form a three-dimensional body-centred network (Fig. 2). Six of the eight water-H atoms are involved in inter-dimer interactions, one is involved in an intradimer interaction and one is unused. Structural parameters for these contacts (Table 2), three of which have respective O...O and H...O distances shorter than 2.76 (1) and 1.95 Å (H—O = 0.82 Å) and O—H...O angles greater than 163°, are indicative of their significance.



**Figure 2**

A projection of the title phase on to (010), showing the O—H...O hydrogen-bonding contacts which link the dimers to form a three-dimensional body-centred network. Atoms are identified as follows: Zn, white circles; S, yellow circles; O, red circles; H, small orange circles.

## Experimental

Vapour phase diffusion of diethyl ether into the mixture formed by heating to reflux an acetonitrile solution of hydrated zinc tetrafluoroborate (0.106 g, 0.41 mmol) and 2,6-bis(2-mercapto-1-methylimidazole)pyridine (0.116 g, 0.38 mmol) gave, after a period of seven months, a small crop of tiny crystals of the title compound  $[\text{Zn}(\text{H}_2\text{O})_4(\mu_2\text{-SO}_4)]_2$ .

### Crystal data

$[\text{Zn}(\text{SO}_4)(\text{H}_2\text{O})_4]_2$   
 $M_r = 467.05$   
 Monoclinic,  $P2_1/n$   
 $a = 5.904$  (3) Å  
 $b = 13.519$  (6) Å  
 $c = 7.883$  (6) Å  
 $\beta = 90.26$  (6)°  
 $V = 629.2$  (6) Å<sup>3</sup>  
 $Z = 2$

$D_x = 2.465$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 48 reflections  
 $\theta = 10.5$ – $16.0$ °  
 $\mu = 4.23$  mm<sup>-1</sup>  
 $T = 150$  (2) K  
 Block, colourless  
 $0.09 \times 0.08 \times 0.03$  mm

### Data collection

Stoe Stadi-4 four-circle diffractometer  
 $\omega/\theta$  scans  
 Absorption correction: numerical (XRED; Stoe & Cie, 1997)  
 $T_{\text{min}} = 0.724$ ,  $T_{\text{max}} = 0.873$   
 1503 measured reflections  
 1101 independent reflections  
 775 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.085$   
 $\theta_{\text{max}} = 25.0$ °  
 $h = -6 \rightarrow 7$   
 $k = 0 \rightarrow 16$   
 $l = -8 \rightarrow 9$   
 3 standard reflections  
 frequency: 60 min  
 intensity decay: 7.1%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.059$   
 $wR(F^2) = 0.157$   
 $S = 1.08$   
 1101 reflections  
 115 parameters  
 H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.056P)^2 + 7.905P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.008$   
 $\Delta\rho_{\text{max}} = 0.85$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -1.18$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Zn1—O1	2.083 (8)	Zn1—O12 <sup>i</sup>	2.125 (7)
Zn1—O2	2.101 (7)	S1—O11	1.475 (7)
Zn1—O3	2.080 (8)	S1—O12	1.475 (7)
Zn1—O4	2.089 (7)	S1—O13	1.460 (7)
Zn1—O11	2.113 (7)	S1—O14	1.479 (7)
O1—Zn1—O2	91.9 (3)	O4—Zn1—O12 <sup>i</sup>	87.2 (3)
O1—Zn1—O3	83.7 (3)	O4—Zn1—O11	176.8 (3)
O1—Zn1—O4	92.4 (3)	O11—Zn1—O12 <sup>i</sup>	89.6 (3)
O1—Zn1—O11	90.6 (3)	O11—S1—O12	110.0 (4)
O1—Zn1—O12 <sup>i</sup>	171.3 (3)	O11—S1—O13	111.3 (4)
O2—Zn1—O3	175.5 (3)	O11—S1—O14	108.2 (4)
O2—Zn1—O4	87.2 (3)	O12—S1—O14	108.6 (4)
O2—Zn1—O11	93.7 (3)	O12—S1—O13	109.0 (4)
O2—Zn1—O12 <sup>i</sup>	96.7 (3)	O13—S1—O14	109.7 (4)
O3—Zn1—O4	91.8 (3)	Zn1—O11—S1	125.6 (4)
O3—Zn1—O11	87.6 (3)	Zn1 <sup>i</sup> —O12—S1	129.5 (4)
O3—Zn1—O12 <sup>i</sup>	87.7 (3)		

Symmetry code: (i)  $1 - x, 1 - y, 1 - z$ .**Table 2**

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H11 $\cdots$ O13 <sup>i</sup>	0.82 (2)	2.29 (10)	2.835 (10)	125 (10)
O1—H12 $\cdots$ O14 <sup>ii</sup>	0.82 (2)	1.95 (3)	2.746 (10)	163 (10)
O2—H22 $\cdots$ O12	0.83 (2)	2.358 (14)	3.185 (10)	172 (8)
O3—H31 $\cdots$ O14 <sup>iii</sup>	0.82 (2)	1.94 (2)	2.753 (10)	174 (10)
O3—H32 $\cdots$ O14 <sup>iv</sup>	0.82 (2)	2.05 (4)	2.838 (10)	160 (11)
O4—H41 $\cdots$ O13 <sup>ii</sup>	0.82 (2)	2.06 (4)	2.817 (10)	153 (9)
O4—H42 $\cdots$ O12 <sup>iv</sup>	0.82 (2)	1.95 (2)	2.758 (10)	170 (10)

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

A correction for linear isotropic crystal decay (7.1%) was applied during data processing. H atoms were located from  $\Delta F$  syntheses and refined with the O—H and H $\cdots$ H distances restrained to be 0.82 (1) and 1.33 (2) Å, respectively, and with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ .

Data collection: *STADIA* (Stoe & Cie, 1997); cell refinement: *STADIA*; data reduction: *XRED* (Stoe & Cie, 1997); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2001).

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