# metal-organic compounds

# Aqua(thiosulfato-$\kappa^2 O,S$)-[2,4,6-tri-2-pyridyl-1,3,5-triazine-$\kappa^3 N^2,N^1,N^6$]zinc(II) hemihydrate

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The title compound, $[Zn(S_2O_3)(C_{18}H_{12}N_6)(H_2O)]\cdot 0.5H_2O$, contains two almost identical independent monomeric moieties composed of an octahedral Zn centre coordinated by a tridentate 2,4,6-tri-2-pyridyl-1,3,5-triazine (tpt) ligand, one aqua ligand and an $O,S$-chelating thiosulfate anion. The structure is stabilized by a solvent water molecule. Multiple strong hydrogen bonds with additional weaker $\pi$–$\pi$ interactions between tpt groups define a multiple column spatial organization.

## Comment

The coordination properties of thiosulfate have been extensively studied by our group with respect to $d\pi$–$p\pi$ bonding in sulfur oxoanions. The $(S_2O_3)^{2-}$ group has proved to be quite a versatile ligand, a behaviour related to its content of atoms classified as both soft and hard bases, according to Pearson (1973). This ligand is prone to producing a variety of coordination modes, especially when the metal ion is borderline



(I)
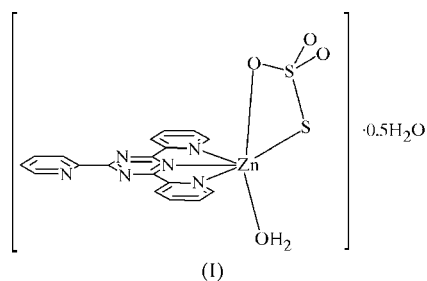
between Pearson classes '$a$' and '$b$'. In an earlier paper (Freire *et al.*, 2000), we presented a brief summary of the reported coordination modes of this anion to transition metals in coordination compounds. When the compound is monomeric,

the anion binds either through S (type 1 mode) or through S and O (type 3 mode), the former appearing more frequently than the latter [37 and 16 hits, respectively, in the Cambridge Structural Database (CSD, November 2005 Version; Allen, 2002)]. We present here the structure of the title compound, $[Zn(S_2O_3)(tpt)(H_2O)]\cdot 0.5H_2O$, (I) [tpt is 2,4,6-tri-2-pyridyl-1,3,5-triazine], (I), a monomeric structure where the coordination mode seems to lie somewhere in between these two cases.

The title compound crystallizes with two independent monomeric moieties, $A$ and $B$, in the asymmetric unit and one single water molecule of crystallization (Fig. 1). Both units are built up around six-coordinate $Zn^{II}$ cations (Zn1 and Zn2) bound to a tridentate tpt ligand, a water molecule and a thiosulfate anion. This last binds strongly *via* S, with Zn—S1 = 2.286 (3)/2.286 (4) Å (in the following discussion, values separated by a solidus, /, will indicate the corresponding values for moieties $A$ and $B$, respectively), and in a much weaker way through O, with Zn—O1 = 2.654 (4)/2.662 (4) Å. These latter distances are long enough to lie across the bonding/non-bonding borderline, and the 'bonding' assignment remained doubtful until some bond-valence calculations were carried out (Brown & Altermatt, 1985). These produced values of 0.076/0.075, compared with the lower limit of 0.06 proposed by Liebau (2000) for a cation–donor contact to be considered as a weak bonding interaction. This allows us to ascribe, with some confidence, a bidentate character to the anion, although the situation might be better described as a semi-coordination lying somewhere in between the definite $S,O$-bicoordinate character [with an $O_{coord}$ mean bond valence of 0.38 (13) for 16 cases in the CSD] and the $S$-monocoordinated situation, where the nearest-to-metal O atom presents bond valences of less than 0.01 (37 reported cases).

Having accepted the $S,O$-bicoordination of the thiosulfate group, both polyhedra around Zn can be described as two highly distorted octahedra, with atoms S1, N1, N2 and N3 defining the basal plane [maximum deviations from the mean plane are 0.20 (1)/0.22 (1) Å for atoms N2$A$ and N2$B$, respectively, and cation shifts of 0.34 (1)/0.40 (1) Å towards
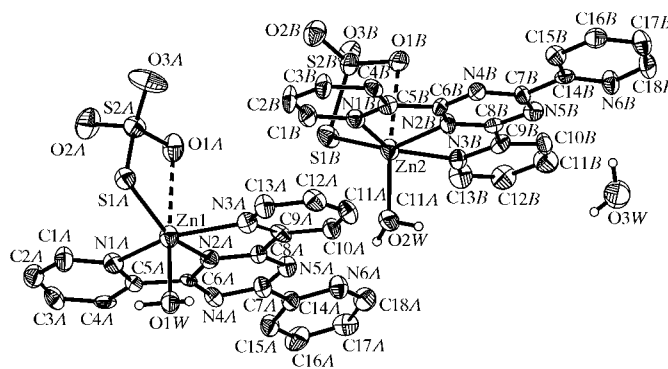


**Figure 1**
Views of the independent monomeric units of (I). Displacement ellipsoids are drawn at the 40% probability level and H atoms have been omitted for clarity.

the apical aqua molecule. The remaining apical site is occupied by the weakly bound atom O1. The apical axes thus defined are slightly 'offset', subtending angles at the corresponding metal sites of 172.9 (12)/170.3 (14)°; this deviation from linearity is due to the chelating character displayed by the thiosulfate group. Ascribable to the rigidity of the tpt skeleton, the basal angles around both Zn units show considerable variation around the expected value of 90° [in the ranges 73.42 (15)–104.13 (11)/73.94 (14)–104.64 (11)°]. The 'soft' Zn—O interactions, as expected, alter the thiosulfate characteristics, as S-coordinated anions typically do, with an enlargement of the S—S bond and a small contraction of the S—O bonds compared with ionic moieties (Baggio *et al.*, 1996).

The tpt ligand presents its most commonly found binding mode, *viz.* tridentate to one single cation. In 32 out of 44 entries in the CSD, the tpt group behaves in this fashion, coordinating through the central N2 atom from the triazine ring and through the lateral N1 and N3 atoms from two pyridine rings, leaving the third pyridyl group uncoordinated. In both moieties, the central Zn—N distances [Zn1—N2 = 2.067 (5)/2.069 (4) Å] are distinctly shorter than the lateral distances [range 2.215 (4)–2.287 (4) Å]. This behaviour has already been observed in all the above-mentioned group 12 tpt complexes and also in other [ZnN₃] cores, and it is due to the rather inflexible character of the tpt skeleton, which forces a closer approach of the central N atom [see Harvey *et al.* (2004) for a detailed discussion]. The tpt core deviates from planarity, mainly through the lateral pyridine rings, subtending angles of 7.7 (1) and 10.5 (1)/5.0 (1) and 4.1 (1)° at the central triazine. In addition, the uncoordinated pyridines are rotated with respect to the central ring (see below). As a result of all these factors, the ligand presents one of the most distorted geometries reported to date.
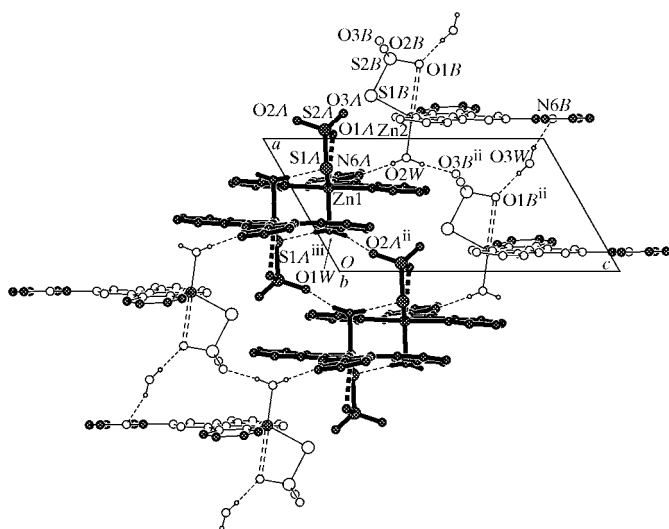


**Figure 2**
A packing view of (I) down the *b* axis, showing the different hydrogen-bonded columnar units propagating upwards along *a*. Heavy lines denote double columns of type *A*=*A* and thin lines denote columns of type *B*, laterally attached to the former to define a *B*=*A*=*A*=*B* structure (see *Comment*). Symmetry codes (ii) and (iii) are as in Table 2.

The two independent moieties are quite similar. In addition to geometric similarities (Table 1), both molecules have an approximate (non-crystallographic) pseudo-mirror plane defined by atoms S1*A*/O1*W*/Zn1/N2*A*/C7*A*/C17*A* (in molecule *A*). The differences between them can be linked to the deviations from a real *m* symmetry and to the relevant torsion angles. Note that the atomic coordinates reported for *A* and *B* reference molecules were chosen so as to facilitate the packing discussion and have opposite 'handedness', so that inversion-related torsion angles are quoted in Table 1.

Our analysis shows the main deviations to fall into three categories. Firstly, there is a slight rotation of the S₃ group around the Zn—S bond, constrained by the Zn—O1 interaction and leading to small and very similar Zn—S1—S2—O1 torsion angles [ΔΦ = 1.9 (2)°]. Secondly, there are different orientations of the terminal pyridyl groups with respect to the mean tpt plane. Their relative rotation around C4—C14 in opposite directions (ΔΦ ~10°; see the N5—C7—C14—N6 torsion angles in Table 1) can be related to π–π interaction with only one of them (*Cg*5; entry 2 in Table 3).

Finally, there is a different orientation of the aqua H atoms bound to atoms O1*W* and O2*W*, as the result of a rotation of the water molecule around the Zn—O$_{aqua}$ bond, shown by the N2—Zn—O$_{aqua}$—H$_{aqua}$ torsion angles in both moieties (Table 1 and Fig. 1). The two relative orientations of the aqua molecule are almost at right angles to one another. This major difference introduces a most significant effect in the molecular packing, namely completely diverse substructures involving the independent *A* and *B* moieties, which aggregate into dissimilar 'pure *A*' and 'pure *B*' columns, propagating along the very short *a* axis. Both array types are held together by hydrogen bonds involving the aqua H atoms. In the case of type *A* molecules, the bonds form double chains or strips (hereinafter symbolized as '*A*=*A*' and shown as heavy lines in Fig. 2) built up around symmetry centres (Table 2, entries 1 and 2). For type *B* molecules, they form a simple linear array ('*B*', thin lines in Fig. 2), with an additional bridging interaction provided by the solvent water molecule O3*W* (Table 2, entries 3–5).

These arrays interact with each other in turn through a strong hydrogen bond having O2*W* as donor and N6*A* as acceptor (entry 6 in Table 2), linking *A*=*A* and *B* columns into a strongly connected complex structure of the *B*=*A*=*A*=*B* type which behaves as the building block of the packing. These units interact with each other through much weaker C—H···O interactions (entries 7–9 in Table 2) and a few π–π contacts between interdigitated aromatic cycles belonging to different column types (Table 3).

## Experimental

2,4,6-Tri-2-pyridyl-1,3,5-triazine and zinc acetate were dissolved together in 96% ethanol and left to diffuse over an aqueous sodium thiosulfate solution, in a 1:1:1 molar ratio. After three months, colourless crystals of (I) suitable for X-ray analysis were obtained.

# metal-organic compounds

## Crystal data

[Zn(S$_2$O$_3$)(C$_{18}$H$_{12}$N$_6$)-
(H$_2$O)]·0.5H$_2$O
$M_r = 516.85$
Monoclinic, $P2_1/c$
$a = 7.550 (5)$ Å
$b = 44.57 (7)$ Å
$c = 13.791 (8)$ Å
$\beta = 119.88 (3)°$
$V = 4024 (7)$ Å$^3$
$Z = 8$

$D_x = 1.706$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25
    reflections
$\theta = 7.5–15°$
$\mu = 1.47$ mm$^{-1}$
$T = 295 (2)$ K
Block, colourless
$0.32 \times 0.16 \times 0.14$ mm

## Data collection

Rigaku AFC-6S diffractometer
$\omega/2\theta$ scans
Absorption correction: $\psi$ scan
    (North et al., 1968)
    $T_{min} = 0.650$, $T_{max} = 0.820$
15672 measured reflections
7771 independent reflections
4159 reflections with $I > 2\sigma(I)$

$R_{int} = 0.066$
$\theta_{max} = 26.0°$
$h = -9 \rightarrow 8$
$k = 0 \rightarrow 54$
$l = 0 \rightarrow 16$
3 standard reflections
    every 150 reflections
    intensity decay: none

## Refinement

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.083$
$S = 1.11$
7771 reflections
586 parameters
H atoms treated by a mixture of
    independent and constrained
    refinement

$w = 1/[\sigma^2(F_o^2) + (0.003P)^2 + 7.8876P]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.43$ e Å$^{-3}$
$\Delta\rho_{min} = -0.90$ e Å$^{-3}$

## Table 1
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Zn1—N2A | 2.067 (5) | Zn2—O2W | 2.005 (4) |
| Zn1—O1W | 2.083 (4) | Zn2—N2B | 2.069 (4) |
| Zn1—N3A | 2.215 (4) | Zn2—N3B | 2.251 (5) |
| Zn1—S1A | 2.286 (3) | Zn2—N1B | 2.254 (5) |
| Zn1—N1A | 2.287 (4) | Zn2—S1B | 2.286 (4) |
| Zn1—O1A | 2.654 (4) | Zn2—O1B | 2.662 (4) |
| S1A—S2A | 2.074 (2) | S1B—S2B | 2.055 (2) |
| S2A—O3A | 1.438 (4) | S2B—O2B | 1.449 (4) |
| S2A—O1A | 1.445 (4) | S2B—O3B | 1.455 (4) |
| S2A—O2A | 1.451 (4) | S2B—O1B | 1.461 (3) |
| | | | |
| Zn1—S1A—S2A—O1A | −14.37 (17) | N5B$^i$—C7B$^i$—C14B$^i$—N6B$^i$ | 5.3 (6) |
| Zn2$^i$—S1B$^i$—S2B$^i$—O1B$^i$ | −16.27 (19) | N2A—Zn1—O1W—H1WA | 107 (3) |
| N5A—C7A—C14A—N6A | −4.8 (7) | N2B$^i$—Zn2$^i$—O2W$^i$—H2WA$^i$ | 25 (3) |

Symmetry code: (i) $-x, -y, -z$.

## Table 2
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1W—H1WA···O2A$^{ii}$ | 0.85 (5) | 1.85 (5) | 2.694 (7) | 170 (4) |
| O1W—H1WB···S1A$^{iii}$ | 0.85 (3) | 2.32 (3) | 3.165 (6) | 172 (5) |
| O2W—H2WA···O3B$^{ii}$ | 0.86 (5) | 1.86 (5) | 2.710 (7) | 174 (5) |
| O2W—H2WB···N6A | 0.85 (3) | 1.92 (3) | 2.759 (7) | 168 (4) |
| O3W—H3WA···O1B$^{ii}$ | 0.85 (4) | 2.11 (4) | 2.951 (7) | 169 (4) |
| O3W—H3WB···N6B | 0.85 (4) | 2.47 (4) | 3.247 (8) | 152 (3) |
| C3A—H3A···O2B$^{iv}$ | 0.93 | 2.44 | 3.329 (8) | 160 |
| C17A—H17A···O3B$^v$ | 0.93 | 2.45 | 3.235 (8) | 143 |
| C16B—H16B···O1A$^{vi}$ | 0.93 | 2.40 | 3.228 (8) | 148 |

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

## Table 3
$\pi$–$\pi$ contacts in (I) (Å, °).

CCD is the centre-to-centre distance, SA is the (mean) slippage angle and IPD is the (mean) interplanar distance; $Cg1$ is the centroid of the ring N1A/C1A–C5A, $Cg2$ that of ring N2A/C6A/N4A/C7A/N5A/C8A, $Cg3$ that of ring N3A/C9A–C13A, $Cg4$ that of ring N1B/C2B–C5B and $Cg5$ that of ring N6B/C14B–C18B.

| $Cg$···$Cg$ | CCD | SA | IPD |
|---|---|---|---|
| $Cg1$···$Cg4^{iv}$ | 3.966 (7) | 27.1 (9) | 3.53 (3) |
| $Cg2$···$Cg5^{iv}$ | 3.560 (7) | 20.8 (15) | 3.33 (3) |
| $Cg3$···$Cg4$ | 3.663 (7) | 21.1 (7) | 3.42 (2) |

Note: symmetry code (iv) is as in Table 2.

H atoms attached to C atoms were included in their calculated positions, with C—H = 0.93 Å, and treated as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$. Water H atoms were found in a difference Fourier synthesis and refined with distance restraints of O—H = 0.82 (1) Å and H···H = 1.30 (2) Å, and with $U_{iso}(H) = 1.5U_{eq}(O)$. Two reflections partially eclipsed by the beam-stop were removed from the data set.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker, 2000); software used to prepare material for publication: *SHELXTL-NT* (Bruker, 2000) and *PLATON* (Spek, 2003).

## References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Baggio, R. F., Baggio, S., Pardo, M. I. & Garland, M. T. (1996). *Acta Cryst.* C**52**, 820–823.
Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.
Bruker (2000). *SHELXTL-NT*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Freire, E., Baggio, S., Suescun, L. & Baggio, R. (2000). *Aust. J. Chem.* **53**, 785–790.
Harvey, M. A., Baggio, S. & Baggio, R. (2004). *Acta Cryst.* C**60**, m498–m500.
Liebau, F. (2000). *Z. Kristallogr.* **215**, 381–383.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Pearson, G. R. (1973). *Hard and Soft Acids and Bases*. Stroudsburg, Pennsylvania: Dowden, Hutchinson & Ross.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.