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Tetraaqua(3,4,7,8-tetramethyl-1,10-phenanthroline-κ^2N,N')zinc(II) thiosulfate

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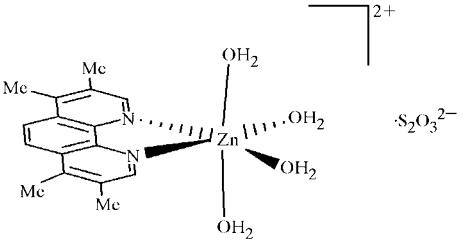
In the title complex of zinc(II) with 3,4,7,8-tetramethyl-1,10-phenanthroline (tmph), *viz*. $[Zn(C_{16}H_{16}N_2)(H_2O)_4](S_2O_3)$, the metal atom has a monomeric octahedral ZnN_2O_4 complex environment comprising two N-atom donors from the tmph group and four aqua O-atom donors. The complex cation is connected to four thiosulfate anions through a compact hydrogen-bonding network involving all coordinated aqua H-atom donors and all the outer acceptors (O and S) of the anion.

Comment

The thiosulfate anion, $S_2O_3^{2-}$, is a highly versatile ligand, and metal complexes in which it does not bind to the cation are not common. A search of the April 2004 version of the Cambridge Structural Database (CSD; Allen, 2002) shows that the group acts as a counter-ion in fewer than 20% of the reported structures containing thiosulfate; in the remaining cases, it coordinates in a variety of different binding modes [for a brief review on the subject, see Freire, Baggio, Suescun & Baggio (2000), and references therein]. This behavior contrasts with those of some closely related oxyanions, *e.g.* sulfate, where the ratio rises to *ca* 50%.

When the anion does not coordinate, it tends to be involved in non-bonding interactions that are unusual either by virtue of their nature, as in $[Ni(bpy)_3](S_2O_3)\cdot7H_2O$ (bpy is 2,2′-bipyridine; Freire, Baggio, Mombrú & Baggio, 2000), where two neighboring thiosulfates approach linearly head-to-head *via* a strikingly short S$\cdots$S contact of 3.25 Å, or because of their quantity, as in the organic clathrate $C_{36}H_{60}N_8^{6+}\cdot S_2O_3^{2-}\cdot 4ClO_4^{-}\cdot 11H_2O$ (Maubert *et al.*, 2001), in which the anion in involved in 12 strong hydrogen-bonding interactions.

We present here the structure of the monomeric zinc(II) complex with thiosulfate and 3,4,7,8-tetramethyl-1,10-phenanthroline (tmph), *viz*. $[Zn(tmph)(H_2O)_4](S_2O_3)$, (I), one of the infrequent cases in which the anion does not bind to the cationic unit directly but is multiply connected through a dense network of hydrogen bonds.



(I)

The structure is shown in Fig. 1. The N_2O_4 environment about the Zn atom is achieved through two N-atom donors of the tmph ligand [which imposes the only distortion to the coordination polyhedron through its small bite angle, 77.6 (2)°] and four water donor molecules. The result is a slightly distorted octahedral coordination with a narrow range of metal–N,O bond lengths [2.084 (5)–2.138 (6) Å; Table 1].

Analogous monomeric complexes with unsubstituted 1,10-phenanthroline instead of tmph molecules have been reported previously in the form of $[Zn(phen)(H_2O)_4]^{2-}$, the counter-ion(s) being either SO_4^{2-} (Zhang *et al.*, 1999) or $2NO_3^-$ (Zhang & Janiak, 2001). No major differences are observed between these complexes and the present structure; a least-squares fit yielded mean deviations of 0.15 (1) and 0.12 (1) Å, respectively, for the 19 atoms that they have in common.

The tmph group is essentially planar [the mean deviation from the plane is 0.02 (1) Å] and binds to the cation with a small, though detectable, tilt [the angle between the N1/Zn/N2 and tmph planes is 6.4 (1)°].

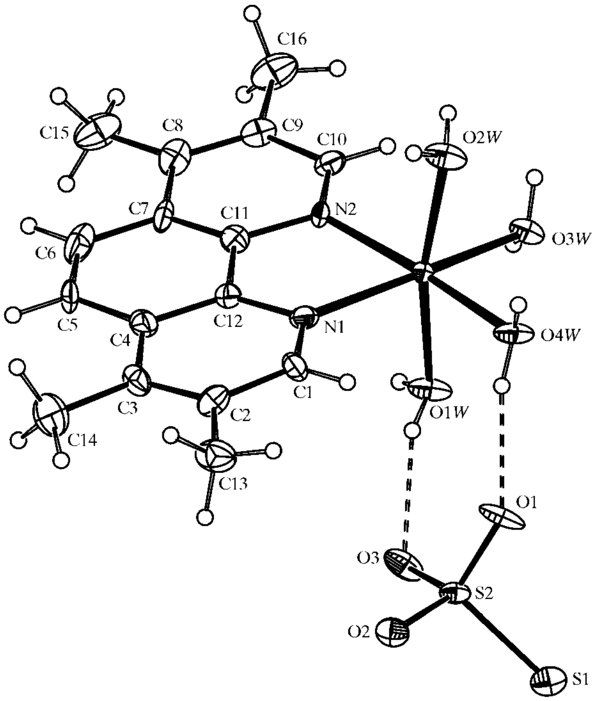


Figure 1
A molecular diagram and the atom-numbering scheme for (I). Displacement ellipsoids are drawn at the 50% probability level.

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As expected, the thiosulfate anion has an undistorted structure, with three S—O bond lengths that are indistinguishable within experimental error. A slight departure from the ideal arrangement is observed for the S—S—O angles, presumably arising from asymmetries in non-bonding contacts.

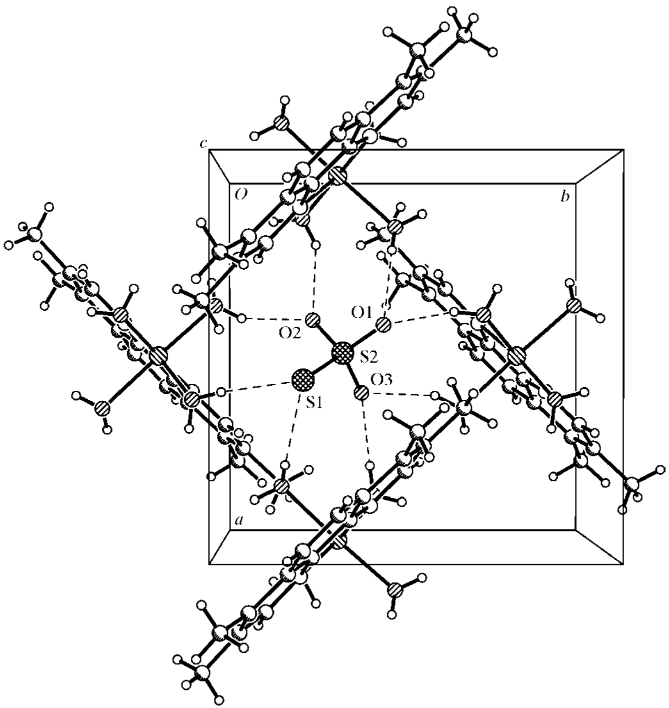

Figure 2
A packing diagram showing the hydrogen-bonding interactions leading to the formation of extended two-dimensional structures. H atoms attached to C atoms have been omitted for clarity.

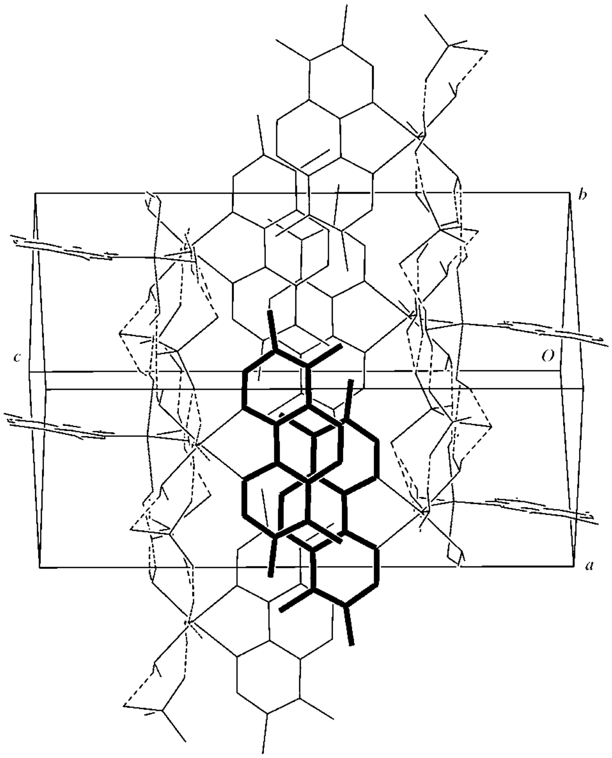

Figure 3
A schematic view of the two-dimensional structures interacting with one another through the overlap of interleaved dmph groups (in order to clarify the figure, two of these groups have been highlighted).

The packing of the structure is governed by the hydrogen-bonding interactions involving, as donors, all eight water H atoms and, as acceptors, the outer atoms of the thiosulfate anion (one S and three O), all of them fulfilling the role of double acceptors. This 'one-to-one' correspondence results in an approximately square geometry (in projection) of the hydrogen-bonding network around the thiosulfate anion (Fig. 2), and leads in turn to a two-dimensional structure perpendicular to the c axis in which each complex interacts with four counter-ions and *vice versa* (Table 2). The two-dimensional frameworks thus defined are concentrated in narrow regions at $z \simeq 0.25$ and $z \simeq 0.75$, with the bulky dmph groups protruding outwards from opposite 'faces' of the two-dimensional arrays, those on one side being at 90° to those on the other (Fig. 3). Neighboring planes are related by inversion centers promoting the interleaving of parallel aromatic groups at graphitic distances from each other. These π–π interacting groups are separated by 3.48 (1) Å, with overlapping rings slipped by 18.3 (1)° [where the slippage angle is that subtended by the ring normal and the center-to-center line (Janiak, 2000)].

Experimental

The title compound was obtained by allowing a 96% ethanol solution of 3,4,7,8-tetramethyl-1,10-phenanthroline to diffuse into an equimolar aqueous solution containing zinc acetate and sodium thiosulfate (5 ml of each solution, all concentrations being 0.025 *M*). After *ca* six weeks of slow evaporation, a few (colorless) prismatic crystals suitable for X-ray analysis were obtained.

Crystal data

$[Zn(C_{16}H_{16}N_2)(H_2O)_4](S_2O_3)$
$M_r = 485.86$
Monoclinic, $P2_1/n$
$a = 9.894$ (2) Å
$b = 9.887$ (2) Å
$c = 20.016$ (4) Å
$\beta = 90.909$ (4)°
$V = 1957.9$ (7) Å^3
$Z = 4$
$D_x = 1.648$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 112 reflections
$\theta = 2.3$–21.1°
$\mu = 1.51$ mm^{-1}
$T = 299$ (2) K
Prism, colorless
0.28 × 0.16 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan [*SADABS* (Sheldrick, 1996) in *SAINT-NT* (Bruker, 2000)]
$T_{min} = 0.75$, $T_{max} = 0.83$
15 814 measured reflections
4386 independent reflections
1863 reflections with $I > 2\sigma(I)$
$R_{int} = 0.072$
$\theta_{max} = 28.1°$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.141$
$S = 0.81$
4386 reflections
277 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0446P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.012$
$\Delta\rho_{max} = 0.89$ e Å^{-3}
$\Delta\rho_{min} = -0.52$ e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

Zn—O2*W*	2.084 (5)	Zn—N1	2.138 (6)
Zn—O4*W*	2.097 (5)	S1—S2	1.989 (3)
Zn—O3*W*	2.097 (5)	S2—O1	1.475 (5)
Zn—O1*W*	2.108 (5)	S2—O3	1.482 (5)
Zn—N2	2.124 (6)	S2—O2	1.482 (5)
O1—S2—O3	111.2 (3)	O1—S2—S1	106.2 (3)
O1—S2—O2	109.4 (3)	O3—S2—S1	110.8 (2)
O3—S2—O2	108.7 (3)	O2—S2—S1	110.4 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···O3	0.82 (2)	2.048 (17)	2.785 (7)	150 (3)
O1*W*—H1*WB*···S1^{i}	0.82 (4)	2.439 (19)	3.219 (6)	160 (5)
O2*W*—H2*WA*···O1^{ii}	0.81 (4)	2.07 (4)	2.716 (8)	136 (6)
O2*W*—H2*WB*···O2^{iii}	0.813 (16)	1.969 (14)	2.714 (7)	153 (3)
O3*W*—H3*WA*···O3^{i}	0.820 (16)	2.036 (16)	2.818 (7)	159 (4)
O3*W*—H3*WB*···S1^{iii}	0.82 (2)	2.499 (12)	3.275 (5)	158 (3)
O4*W*—H4*WA*···O1	0.813 (13)	1.964 (16)	2.760 (6)	166 (6)
O4*W*—H4*WB*···O2^{ii}	0.82 (3)	2.05 (3)	2.811 (7)	156 (5)

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

H atoms on C atoms which were unambiguously defined by the stereochemistry were placed at calculated positions (C—H = 0.93 Å) and allowed to ride. In addition, terminal dmph methyl groups (C—H = 0.96 Å) were allowed to rotate, although their low rotational energy barrier may make the positions less well defined. Water H atoms were located from difference Fourier syntheses and refined with restrained O—H and H···H distances of 0.82 (1) and 1.36 (2) Å, respectively. All $U_{\rm iso}$(H) values were fixed at $1.2U_{\rm eq}$ of the parent atoms.

Data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINT-NT* (Bruker, 2000); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL*/*PC* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1648). Services for accessing these data are described at the back of the journal.

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