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Poly[[μ_2-4,4′-bipyridine-di-μ_3-sulfito-dizinc(II)] monohydrate]

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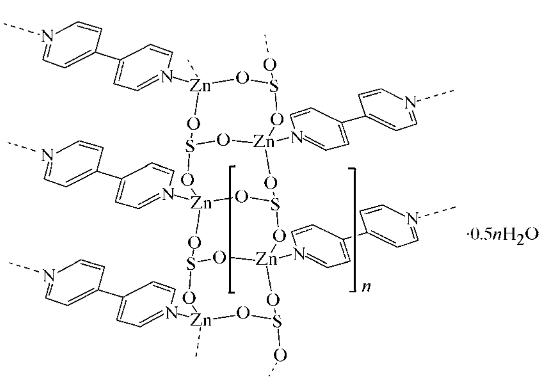
The title compound, $\{[Zn_2(SO_3)_2(C_{10}H_8N_2)]\cdot H_2O\}_n$, is a two-dimensional polymer built up of a $[ZnSO_3]_n$ chain evolving around a 2_1 axis and interconnected by a 4,4′-bipyridine spacer. The resulting two-dimensional structures are linked, in turn, by hydrogen bonding mediated by the solvent water molecule. The organic ligand lies on a centre of symmetry located on the mid-point of the bond between the rings, while the solvent water molecule is halved by a twofold axis passing through the O atom.

Comment

For some time now we have been interested in obtaining and characterizing novel thiosulfate and sulfite complexes of group XII metals. We have successfully explored the feasibility of producing these complexes through the decomposition of less common sulfur oxoanions, such as dithionite and pyrosulfite (Díaz de Vivar *et al.*, 2004, 2005). More recently, we have also attempted to build up supramolecular structures having the bidentate 4,4′-bipyridine (4,4′-bipy) ligand as a spacer (Díaz de Vivar *et al.*, 2007*a*,*b*). The present work represents a combination of both strands of our work: on the one hand, it is another application of the 'decomposition' method of synthesis as applied to sulfite, one of the anions present in the complex equilibrium of the dithionite–pyrosulfite system, while on the other, we intended to organize the resulting compound through the linkage of 4,4′-bipy ligands. The result is the title structure, (I), reported here. To the best of our knowledge, this is the first transition metal complex combining the sulfite anion and the 4,4′-bipyridine ligand. Fig. 1 shows a view of the structure of (I), while Table 1 displays relevant bonding parameters.

The Zn cation of (I) presents a slightly distorted tetrahedral environment, with three similar bonds to O atoms from three different sulfite groups [mean = 1.944 (12) Å and range = 1.935 (2)–1.956 (2) Å] and a slightly longer one to a terminal N atom of the 4,4′-bipy spacer [Zn—N = 2.030 (2) Å]. The sulfite anion, in turn, binds to three different Zn cations and its geometry is highly regular, with even S—O bond lengths [mean = 1.521 (4) Å and range = 1.517 (2)–1.523 (2) Å] and O—S—O angles [mean = 104.3 (18)° and range = 102.51 (12)–105.98 (13)°].



(I)

Perhaps the most interesting feature in the structure of (I) is the way in which the sulfite anion, acting in a μ_3,κ^3 mode, screws around a 2_1 axis and thus defines a neutral tubular chain (formulated as $[ZnSO_3]_n$) along the unique *b* axis. These chains are in turn interconnected *via* 4,4′-bipy spacers, which are almost perpendicular to the chain direction, resulting in a two-dimensional structure parallel to (101). Though unusual, this μ_3,κ^3 binding mode of the sulfite anion is not unique; we have observed it in a recent study of another polymeric zinc complex, poly[[aqua(1,10-phenanthroline)zinc(II)]-μ_3-sulfito-zinc(II)-μ_3-sulfito] (Díaz de Vivar *et al.*, 2005), the first zinc complex to exhibit this behaviour. A search of the Cambridge Structural Database (CSD, November 2006 release; Allen, 2002) showed at least nine more entries where this binding scheme of sulfite to different transition metals has been reported. Four of these are to Mo^{V} (CSD refcodes ALELUY, BEPJAI, BEPJEM and BEPJIG), three to V^{IV} (WUSXEN, JAPNUK and LAPCOV), one to Sn^{IV} (RUJGUY) and one to W^{VI} (SARTAH).

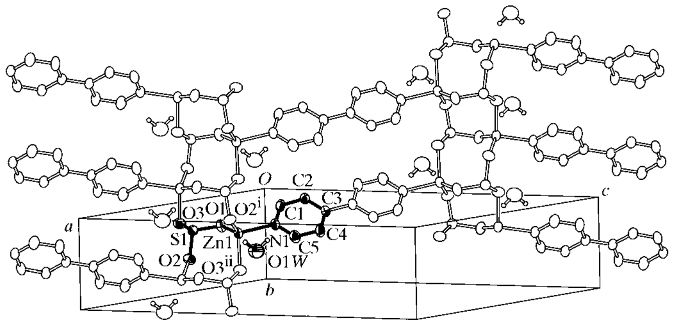


Figure 1
A packing diagram for (I), showing both the atom-numbering scheme and the way in which the two-dimensional structures parallel to (101) are formed. The independent part of the structure is drawn with full 50% probability displacement ellipsoids and black bonds, and the remainder of the structure is shown with open ellipsoids and hollow bonds. H atoms have been omitted, except for those pertaining to water. [Symmetry codes: (i) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.]

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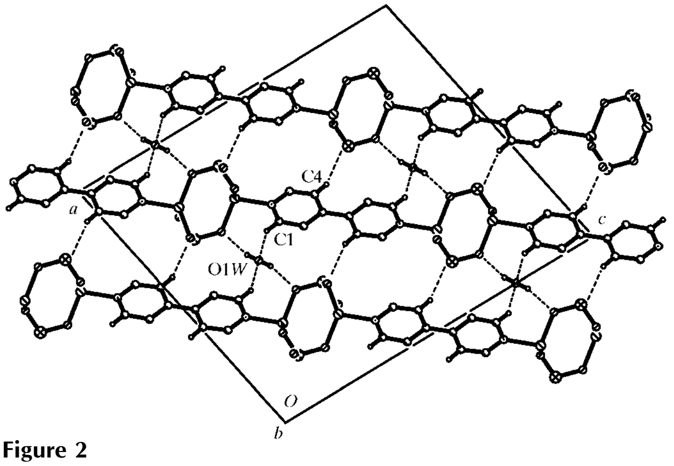

Figure 2
A projection of the structure of (I) along [010], showing the hydrogen-bonding interactions (dashed lines) linking the two-dimensional structures together.

For reasons of symmetry, the two pyridyl rings in the 4,4′-bipy spacer of (I) are coplanar, since the ligand lies on a centre of symmetry located on the mid-point of the bond between rings. Also, the solvent water molecule lies on a special position, being halved by a twofold axis.

The two-dimensional structures parallel to (101), displayed in Fig. 1, are interconnected by a medium strength O—H···O bond (that involving atom H1*W* in Table 2, and duplicated by symmetry into the second symmetry-related H atom on O1*W*), and two weaker C—H···O bonds, also presented in Table 2 and shown in Fig. 2.

No significant π–π contacts between adjacent pyridyl groups seem to be present, as the shortest centre-to-centre distance is 4.7819 (10) Å, *viz*. the *b* cell dimension.

Experimental

4,4′-Bipyridine (30 mg) and zinc acetate dihydrate (36.5 mg) were dissolved in methanol (4 ml) and left to diffuse slowly at room temperature over an aqueous solution (4 ml) of sodium dithionite dihydrate ($Na_2S_2O_4 \cdot 2H_2O$, 40.3 mg) plus potassium pyrosulfite ($K_2S_2O_5$, 85.2 mg) in a 1:1:1:2 molar ratio. The vessels were closed and left undisturbed. After four months diffusion at room temperature (estimated *T* range 291–295 K), small colourless prismatic crystals of (I) appeared, from which a sample suitable for X-ray analysis could be separated.

Crystal data

$[Zn_2(SO_3)_2(C_{10}H_8N_2)] \cdot H_2O$
$M_r = 465.06$
Monoclinic, $C2/c$
$a = 16.581$ (3) Å
$b = 4.7819$ (10) Å
$c = 19.230$ (4) Å
$\beta = 100.674$ (3)°

$V = 1498.3$ (5) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 3.52$ mm^{-1}
$T = 291$ (2) K
0.20 × 0.16 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min} = 0.51$, $T_{max} = 0.65$

5871 measured reflections
1668 independent reflections
1360 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.089$
$S = 1.02$
1668 reflections

105 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Zn1—O1	1.935 (2)	S1—O2	1.517 (2)
Zn1—O2^{i}	1.942 (2)	S1—O1	1.522 (2)
Zn1—O3^{ii}	1.956 (2)	S1—O3	1.523 (2)
Zn1—N1	2.030 (2)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*···O1	0.85	2.12	2.947 (3)	164
C1—H1···O1*W*^{iii}	0.93	2.43	3.237 (4)	145
C4—H4···O2^{iv}	0.93	2.43	3.296 (4)	154

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

H atoms attached to C atoms were placed in their calculated positions, with aromatic C—H = 0.93 Å, while the independent H atom pertaining to the solvent water molecule was located in a difference Fourier synthesis. All included H atoms were allowed to ride, with $U_{iso}(H) = xU_{eq}$(parent), where $x = 1.2$ for C and 1.5 for O atoms.

Data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINT-NT* (Bruker, 2001); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker, 2001); software used to prepare material for publication: *SHELXTL-NT* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3032). Services for accessing these data are described at the back of the journal.

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