Poly[μ_2-trans-1,2-di-4-pyridylethylene-κ^2N:N'-μ_2-sulfato-κ^2O:O'-zinc(II)]

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The title compound, [Zn(SO$_4$)(C$_{12}$H$_{10}$N$_2$)]$_n$, features a layered structure based on [Zn(SO$_4$)]$_n$ spirals linked by 1,2-di-4-pyridylethylene (bpe) ligands, with the tetrahedral Zn and S atoms lying on twofold axes. The bpe ligands are centrosymmetric. The layers are linked by weak C—H···O interactions.

Comment

There has been considerable recent interest in the design and synthesis of supramolecular complexes due to their novel structural architectures and favourable properties in such fields as ion exchange, adsorption, non-linear optics and magnetism (Noro et al., 2000; Yaghi et al., 1998). Organic N-donors, such as bipyridine or related species, are often chosen to fabricate these complexes (Hagrman et al., 1999). The trans-1,2-di-4-pyridylethylene ligand (bpe) is also an attractive choice due to its multifunctional linking groups (Carlucci et al., 2003; Hagrman et al., 1998). Doubly charged anions such as sulfates are often known to enter the inner coordination sphere of metal complexes. Some examples of polymeric species containing both SO$_4^{2-}$ anions and bpe ligands have been reported in recent years, including one-dimensional (Li et al., 2005; Hu et al., 2005), two-dimensional (Hagrman et al., 1998)

(I)
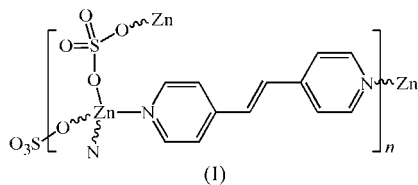
and three-dimensional structures (Carlucci et al., 2003; Lee et al., 2005; Sudik et al., 2006). All of them have water molecules and metal centres which often adopt octahedral geometry. Few examples report the combination of a tetrahedral metal centre and the tetrahedral SO$_4^{2-}$ anion, with the potential for four-connected structural topologies. In this paper, we report

such a novel two-dimensional coordination polymer, the title compound, [Zn(SO$_4$)(bpe)]$_n$, (I).

The structure of (I) features a layered structure based on [Zn(SO$_4$)]$_n$ spirals linked by bpe ligands. Both Zn and S atoms are on special positions with twofold symmetry, and the centre of inversion is located at the centre of the bpe ligand (Fig. 1). Thus, the Zn atom is coordinated by two O atoms from different SO$_4^{2-}$ anions and two N atoms from two symmetry-related bpe ligands. Each SO$_4^{2-}$ anion provides two O atoms to bridge two Zn atoms, with a Zn···Zn separation of 4.932 (2) Å. The tetrahedral [ZnO$_2$N$_2$] groups and tetrahedral SO$_4^{2-}$ anions are connected alternately, resulting in spirals along the b axis; the resulting spirals are further linked by the bpe ligands, forming a wave-like layer (Fig. 2). The Zn···Zn distance separated by the bpe ligand is 13.240 (2) Å. The two pyridine rings of the bpe ligand are parallel, as required by symmetry, with an interplanar distance of 0.546 (1) Å. As shown in Fig. 2, the sulfate–Zn spiral runs along the b axis, while the bpe ligands bridging the Zn atoms form a zigzag chain. The average best planes through the bpe ligands intersect the (004) plane through the sulfate–Zn spiral at 64.1°.

The layers are linked to complete the final three-dimensional structure by weak C—H···O interactions between two adjacent layers (Fig. 3 and Table 2), via the uncoordinated O1 atoms of the SO$_4^{2-}$ anions and two C atoms of two bpe ligands in an adjacent layer.
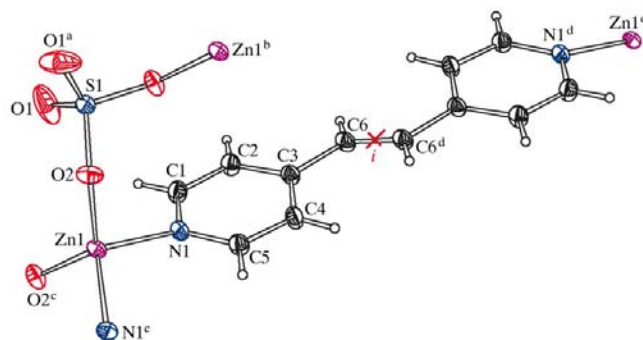

Figure 1
A view of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The centre of inversion is labelled with the letter i. [Symmetry codes: (a) $1 - x$, y, $\frac{1}{2} - z$; (b) $1 + x$, y, z; (c) $-x$, y, $\frac{1}{2} - z$; (d) $\frac{3}{2} - x$, $\frac{1}{2} - y$, $-z$.]
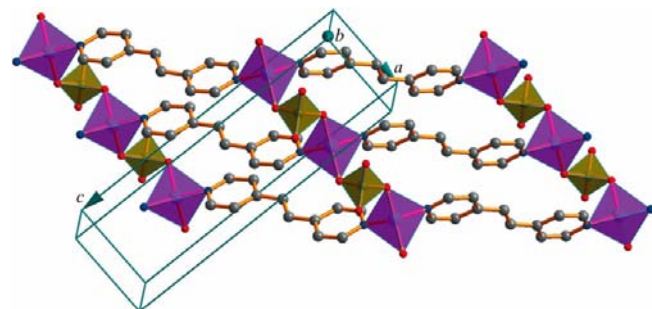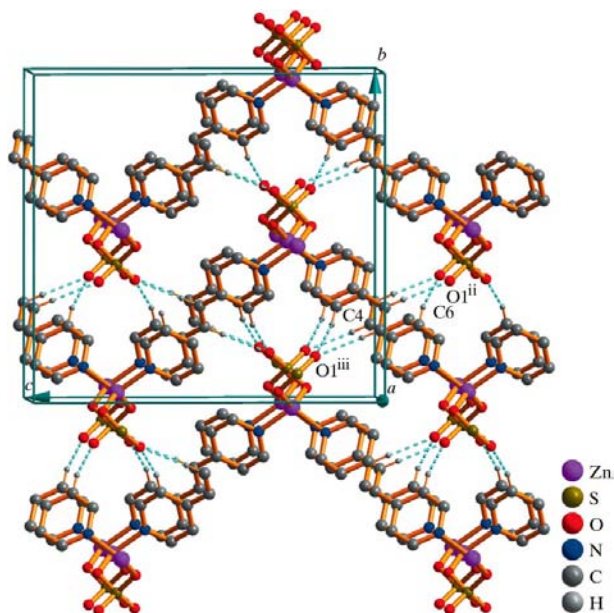

Figure 2
The layered structure of (I), showing the spirals bridged by bpe ligands. H atoms have been omitted for clarity.

metal-organic compounds

Some $[Zn(SO_4)]^{2-}$ structures containing the bpe ligand have been reported (Tong & Chen, 2000; Kondo *et al.*, 1999; Lee *et al.*, 2005). In these structures, the Zn atom adopts an octahedral geometry and the (bi)pyridine ligands link the $Zn–SO_4^{2-}$ chains to give three-dimensional structures. In the mixed bpe–SO_4^- system; the title compound appears to be the first layered structure containing spiral substructures and simple Zn^{II} tetrahedral units.

Figure 3
The packing structure of (I). Weak C—H···O interactions are shown as dashed lines (see Table 2).

Experimental

For the hydrothermal reaction, $ZnSO_4$ (1.0 mmol), *trans*-1,2-di-4-pyridylethylene (1.0 mmol) and H_2O (10 ml) were placed in a Parr Teflon-lined stainless steel vessel (20 ml), the vessel was sealed and heated to 433 K for 3 d, then cooled at a rate of 0.5 K min^{-1}, producing colourless crystals of (I) (yield 63%, based on Zn).

Crystal data

$[Zn(SO_4)(C_{12}H_{10}N_2)]$	$V = 1242.82$ (7) Å^3
$M_r = 343.68$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 4.9322$ (2) Å	$\mu = 2.16$ mm^{-1}
$b = 15.3739$ (5) Å	$T = 273$ (2) K
$c = 16.4044$ (5) Å	$0.24 \times 0.14 \times 0.10$ mm
$\beta = 92.388$ (2)°	

Data collection

Bruker SMART CCD area-detector diffractometer	5508 measured reflections
	1553 independent reflections
Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)	1106 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.058$
$T_{min} = 0.600$, $T_{max} = 0.800$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	92 parameters
$wR(F^2) = 0.077$	H-atom parameters constrained
$S = 0.91$	$\Delta\rho_{max} = 0.47$ e Å^{-3}
1553 reflections	$\Delta\rho_{min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—O2	1.9374 (18)	Zn1—N1	2.035 (2)
O2—Zn1—O2^i	129.04 (12)	O2—Zn1—N1^i	103.81 (8)
O2—Zn1—N1	104.32 (8)	O2^i—Zn1—N1^i	104.32 (8)
O2^i—Zn1—N1	103.81 (8)	N1—Zn1—N1^i	111.23 (12)

Symmetry code: (i) $-x, y, -z + \frac{1}{2}$.

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

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···O1^{ii}	0.93	2.35	3.276 (4)	178
C4—H4···O1^{iii}	0.93	2.34	3.206 (4)	154

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

H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART* and *SAINT* (Siemens, 1994); data reduction: *XPREP* in *SHELXTL* (Siemens, 1994); program(s) used to solve and refine structure, and prepare molecular graphics and publication material: *SHELXTL*.

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