Acta Crystallographica Section C
Crystal Structure
Communications
ISSN 0108-2701

catena-Poly[[[tetraaquazinc(**II**)]-μ-4,4′-bipyridine] bis(4-hydroxybenzenesulfonate) trihydrate]

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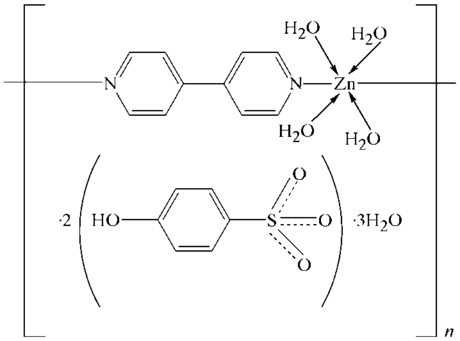
Received 22 August 2006
Accepted 22 September 2006
Online 14 October 2006

In the title compound, $\{[Zn(C_{10}H_8N_2)(H_2O)_4](C_6H_5O_4S)_2\cdot 3H_2O\}_n$, the Zn atom, the bipyridine ligand and one of water molecules are located on twofold rotation axes. The Zn atom is coordinated by four O atoms from four water molecules and two N atoms from two 4,4′-bipyridine molecules in a distorted octahedral geometry. The Zn^{2+} ions are linked by the 4,4′-bipyridine molecules to form a one-dimensional straight chain propagating along the *c* axis. The 4-hydroxybenzenesulfonate counter-ions are bridged by the solvent water molecules through hydrogen bonds to generate a two-dimensional layer featuring large pores. In the crystal packing, the intralayer pores form one-dimensional channels along the *c* axis, in which the one-dimensional $[Zn(C_{10}H_8N_2)(H_2O)_4]^{2+}$ chains are encapsulated. Electrostatic interactions between cations and anions and extensive hydrogen bonds result in a three-dimensional supramolecular structure.

Comment

Supramolecular chemistry and crystal engineering are active fields of chemistry owing to the intriguing structural topologies examined and potential applications in host–guest chemistry, catalysis and electrical conductivity (Biradha & Zaworotko, 1998; Yaghi *et al.*, 1995; Conn & Rebek, 1997). The key to successful construction of supramolecular architecture is the control and manipulation of coordination bonds and non-covalent interactions by careful selection of the coordination geometry of the metal centers and the organic ligands containing appropriate functional groups (such as carboxylic acid and pyridine; Tong *et al.*, 1999; Dong *et al.*, 2000). In the past few years, much effort has been devoted to the study of carboxylate-based supramolecular assemblies (Prior & Rosseinsky, 2001; Sun *et al.*, 2003). However, relatively little attention has been paid to sulfonate-based supramolecular assemblies, despite the fact that a sulfonate-containing ligand can provide three potential hydrogen-bond acceptors (Evans *et al.*, 1999). Recently, the combination of sulfonate-containing ligands with metal ions in our laboratory has produced several complexes with diverse structural topologies (Liu & Xu, 2005*a*,*b*). The hydrothermal reaction of $Zn(NO_3)_2$ with sodium 4-hydroxybenzenesulfonate (HBSNa) and 4,4′-bipyridine (bpy) yields the title complex, (I). We present its structure here.



(I)

The asymmetric unit of (I) consists of half of a $[Zn(bpy)(H_2O)_4]^{2+}$ cation, a HBS^- anion, and one and a half solvent water molecules. The cation is located on a twofold rotation axis that passes through atoms Zn1, N1, N2, C3 and C4. The Zn atom is six-coordinated by four O atoms from four water molecules in a distorted square-planar geometry, with two N atoms from two bpy molecules in apical positions (Fig. 1); the ZnO_4N_2 octahedron is slightly elongated (Table 1). The bond lengths involving the Zn atom are normal and are comparable to the values in related zinc(II) complexes (Zhang & Zhu, 2005; Huang *et al.*, 1998). As depicted in Fig. 2, the Zn ions are linked by the bpy molecules to produce a one-dimensional straight chain propagating along the *c* axis. The length of the repeat unit in the chain is equal to the length of the *c* axis. The two pyridine rings of the bpy system are not coplanar but make a dihedral angle of 5.1 (2)°, which is smaller than the corresponding angle of 39.2 (1)° in $[ZnCl_2(bpy)]_n$ (Hu & Englert, 2005).

The HBS^- anion is not involved in coordination but is hydrogen bonded to the $[Zn(bpy)(H_2O)_4]$ cation and solvent water molecules. As depicted in Fig. 3, the HBS^- anions are linked by the solvent water molecules (O2*W*) through hydrogen bonds between (*a*) water molecules and sulfonate O

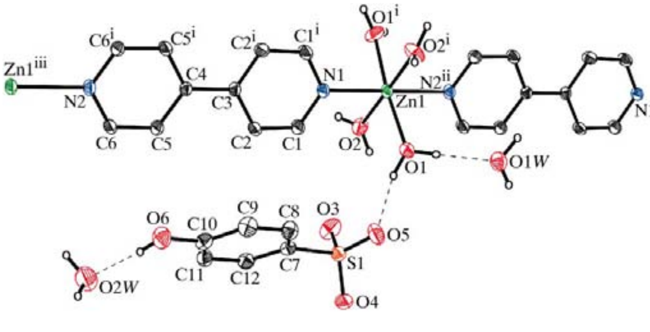


Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds. Aromatic H atoms have been omitted for clarity. [Symmetry codes: (i) $-x + 2, -y, z$; (ii) $x, y, z + 1$; (iii) $x, y, z - 1$.]

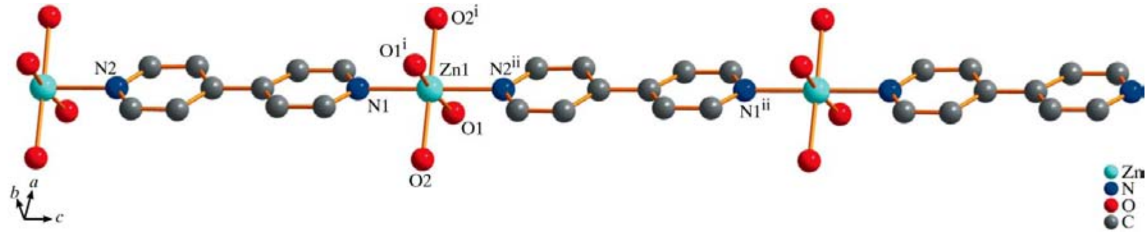


Figure 2
A view of the [Zn(bpy)(H_2O)$_4$] chain in (I). [Symmetry codes: (i) $-x + 2, -y, z$; (ii) $x, y, z + 1$.]

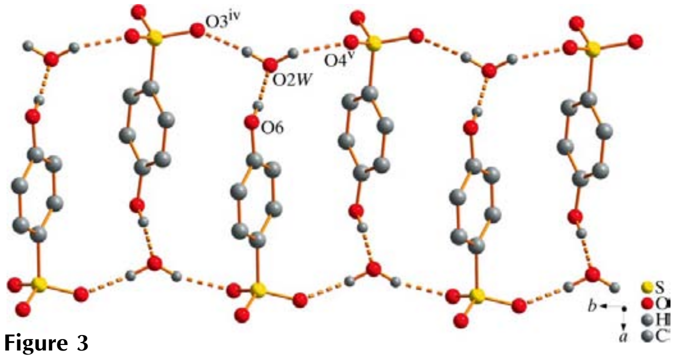


Figure 3
A perspective view of the one-dimensional ladder structure. Dashed lines indicate hydrogen bonds. [Symmetry codes: (iv) $-x + \frac{3}{2}, y + \frac{1}{2}, -z - 2$; (v) $-x + \frac{3}{2}, y - \frac{1}{2}, -z - 2$.]

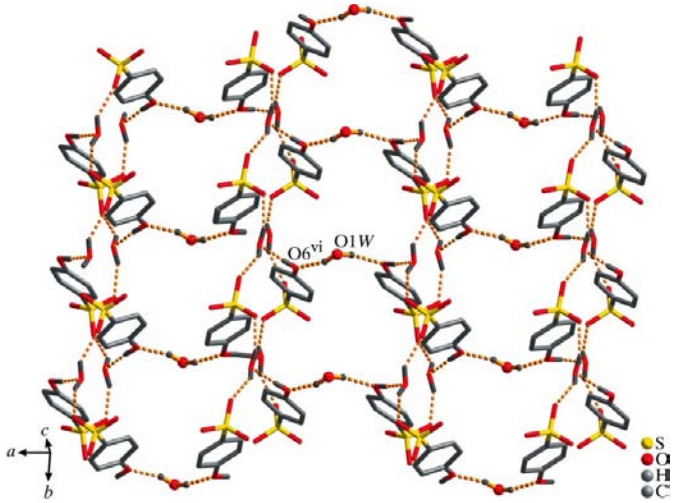


Figure 4
A perspective view of the two-dimensional layered structure. Dashed lines indicate hydrogen bonds. [Symmetry codes: (vi) $-x + 2, -y + 1, z + 1$.]

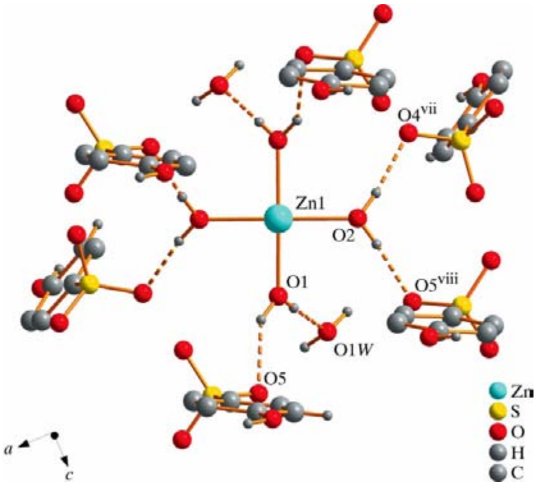


Figure 5
A perspective view of hydrogen bonds between the two-dimensional layer and the one-dimensional chain. Dashed lines indicate hydrogen bonds. [Symmetry codes: (vii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z - 1$; (viii) $x, y - 1, z$.]

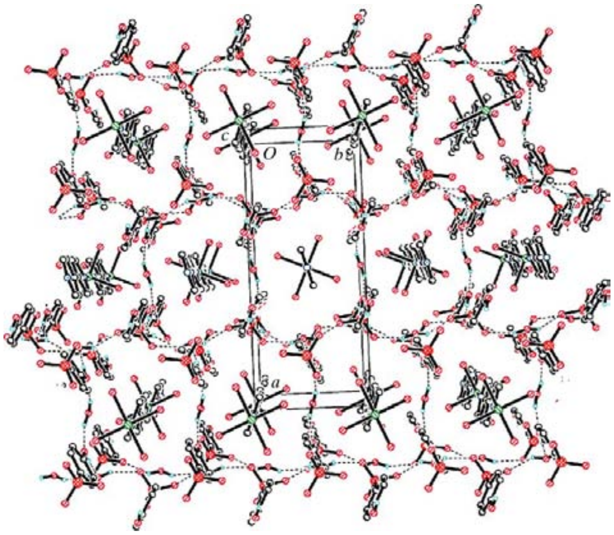


Figure 6
A view of the packing of (I) (viewed down the *c* axis), showing the cationic chains encapsulated in the one-dimensional channels. The hydrogen bonds between (*a*) cations and anions, and (*b*) cations and water molecules have been omitted for clarity.

atoms, and (*b*) hydroxy groups and water O atoms (Table 2), to form a one-dimensional ladder structure propagating along the *b* axis. In the one-dimensional ladder structure, the HBS$^-$ anion adopts alternating orientations as a result of the anions being stacked along a 2_1 screw axis (up and down sulfonate groups in Fig. 3) The planes of the benzene rings of adjacent HBS$^-$ anions in the stack intersect with a dihedral angle of 57.4 (1)°. The one-dimensional ladders are further linked by O1*W*—H1*W*$\cdots$O6^{vi} (see Table 2 for symmetry code) hydrogen bonds to produce a two-dimensional layered structure featuring large pores, as illustrated in Fig. 4. In the crystal packing, the intralayer pores form a one-dimensional channel along the *c* axis. A noteworthy feature of this compound is that the one-dimensional [Zn($C_{10}H_8N_2$)(H_2O)$_4$]$^{2+}$ chains are encapsulated in the host channels. The encapsulated cations interact with the negative layers *via* electrostatic interactions and hydrogen bonds between (*a*) coordinated water molecules and sulfonate O atoms, and (*b*) coordinated water molecules and solvent water molecules (Fig. 5 and Table 2). These interactions are responsible for the three-dimensional supramolecular framework structure (Fig. 6).

Experimental

The title compound was synthesized by a hydrothermal method under autogenous pressure. A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (148 mg, 0.5 mmol), sodium 4-hydroxybenzenesulfonate dihydrate (116 mg, 0.5 mmol), 4,4′-bipyridine (78 mg, 0.5 mmol) and distilled water (15 ml) was stirred under ambient conditions. The final mixture was sealed in a 25 ml Teflon-lined steel autoclave, heated at 438 K for 3 d and then cooled to room temperature. Colorless prism-shaped crystals of (I) were obtained, and these were recovered by filtration, washed with distilled water and dried in air (yield 33%). Analysis calculated for $C_{22}H_{32}N_2O_{15}S_2Zn$: C 38.15, H 4.66, N 4.05%; found: C 38.10, H 4.61, N 4.03%.

Crystal data

$[Zn(C_{10}H_8N_2)(H_2O)_4]$-$(C_6H_5O_4S)_2\cdot 3H_2O$
$M_r = 693.99$
Orthorhombic, $P2_12_12$
$a = 17.623$ (1) Å
$b = 7.2451$ (6) Å
$c = 11.3957$ (8) Å
$V = 1455.00$ (19) Å^3
$Z = 2$
$D_x = 1.584$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.06$ mm^{-1}
$T = 293$ (2) K
Prism, colorless
0.35 × 0.30 × 0.25 mm

Data collection

Rigaku Mercury7 diffractometer (2×2 bin mode)
ω scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku & Molecular Structure Corporation, 2000)
$T_{\min} = 0.698$, $T_{\max} = 0.768$
11370 measured reflections
3337 independent reflections
3066 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.074$
$S = 1.00$
3337 reflections
218 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 0.17P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.46$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0250 (16)
Absolute structure: Flack (1983), with 1401 Friedel pairs
Flack parameter: 0.030 (12)

Aromatic H atoms were placed in calculated positions and treated using a riding model [C—H = 0.93 Å and $U_{\rm iso}(H) = 1.2U_{\rm eq}(C)$]. H atoms bonded to O atoms were visible in a difference map and were refined with a DFIX (*SHELXL97*; Sheldrick, 1997*a*) restraint [O—H = 0.90 (1) Å and $U_{\rm iso}(H) = 1.5U_{\rm eq}(O)$].

Data collection: *CrystalClear* (Rigaku & Molecular Structure Corporation, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*) and *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXL97*.

Table 1
Selected geometric parameters (Å, °).

Zn1—O1	2.102 (2)	S1—O5	1.443 (2)
Zn1—O2	2.108 (2)	S1—O4	1.447 (2)
Zn1—N1	2.124 (2)	S1—O3	1.450 (2)
Zn1—N2^{ii}	2.164 (2)		
O1^{i}—Zn1—O1	173.51 (11)	O2—Zn1—N1	89.47 (6)
O1—Zn1—O2^{i}	89.77 (9)	O1—Zn1—N2^{ii}	86.76 (6)
O1—Zn1—O2	90.29 (9)	O2—Zn1—N2^{ii}	90.53 (6)
O2^{i}—Zn1—O2	178.94 (12)	N1—Zn1—N2^{ii}	180.0
O1—Zn1—N1	93.24 (6)		

Symmetry codes: (i) $-x+2, -y, z$; (ii) $x, y, z+1$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···O5	0.89 (3)	2.09 (2)	2.880 (3)	148 (3)
O1—H1B···O1W	0.89 (3)	1.89 (3)	2.777 (3)	178 (3)
O2—H2A···O4^{vii}	0.89 (3)	1.94 (3)	2.824 (3)	172 (3)
O2—H2B···O5^{viii}	0.90 (1)	1.92 (3)	2.810 (3)	174 (3)
O1W—H1W···O6^{vi}	0.89 (1)	1.93 (1)	2.801 (2)	163 (3)
O2W—H3W···O3^{iv}	0.90 (3)	1.94 (2)	2.750 (3)	149 (4)
O2W—H2W···O4^{v}	0.90 (3)	1.93 (2)	2.788 (3)	157 (4)
O6—H6A···O2W	0.88 (3)	1.76 (2)	2.568 (3)	152 (3)

Symmetry codes: (iv) $-x+\frac{3}{2}, y+\frac{1}{2}, -z-2$; (v) $-x+\frac{3}{2}, y-\frac{1}{2}, -z-2$; (vi) $-x+2, -y+1, z+1$; (vii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z-1$; (viii) $x, y-1, z$.

This work was supported by Jiangxi Normal University.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3042). Services for accessing these data are described at the back of the journal.

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