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The monodentate 4,4′-bipyridine complex tetraaquabis(4,4′-bipyridine)zinc(II) bis(4-carboxybenzenesulfonate)

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The molecule of the title salt, $[Zn(C_{10}H_8N_2)_2(H_2O)_4]$-$(C_7H_5O_5S)_2$, resides on a centre of symmetry and the coordination geometry of the Zn atom is octahedral. Each 4,4′-bipyridine ligand coordinates to the Zn atom in a monodentate fashion and the second N-atom donor of the 4,4′-bipyridine ligand forms a hydrogen bond with a sulfonate O atom. Hydrogen-bonding interactions between cations and anions generate a three-dimensional architecture and enhance the stability of the structure.

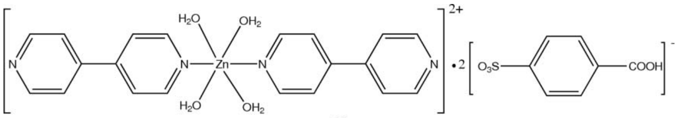
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.007 Å
R factor = 0.047
wR factor = 0.130
Data-to-parameter ratio = 12.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Numerous polymeric transition metal complexes with 4,4′-bipyridine (4,4′-bipy) have been synthesized and structurally characterized to date (Abu-Shandi *et al.*, 2001; Zhang *et al.*, 2004). In addition to the bridging mode in polymeric complexes, the 4,4′-bipy ligand also can exhibit dimeric linker (He *et al.*, 2005; Zhu & Kitagawa, 2003), protonated (Fan & Zhu, 2005; Fu *et al.*, 2005; Li *et al.*, 2004) or monodentate modes. The first monodentate 4,4′-bipy complex confirmed by single-crystal X-ray analysis was reported by Haim (Leopold & Haim, 1978). Although monodentate 4,4′-bipy complexes have been synthesized occasionally since 1978 (Abu-Shandi *et al.*, 2001; Attia & Pierpont, 1995; Julve *et al.*, 1987; Klevtsova *et al.*, 2001; Tong *et al.*, 1999), such investigations are still very limited. Recently, the combination of 4,4′-bipy and 4-sulfonatobenzoate with transition metals in our laboratory has produced several monodentate 4,4′-bipy complexes with variable structural topologies. Here, we present the synthesis and crystal structure of the title zinc complex, (I).



(I)

The title complex is a salt, as shown in Fig. 1. The cationic part is a monomeric species with two monodentate 4,4′-bipy ligands, in which the Zn atom, sitting on a special position of $\overline{1}$ site symmetry, adopts an octahedral geometry defined by four O atoms from four water molecules and two N donors from two 4,4′-bipy ligands. The 4-sulfonatobenzoic acid is an anion with one negative charge and retains the H atom of the carboxyl group. Each 4,4′-bipy ligand coordinates the Zn atom in a monodentate terminal fashion, which is a relatively rare phenomenon, as mentioned above. However, the other N-donor atom of each 4,4′-bipy ligand is engaged in intermolecular hydrogen bonding to a sulfonate, which completely blocks the bridging coordination mode of the 4,4′-bipy ligand.

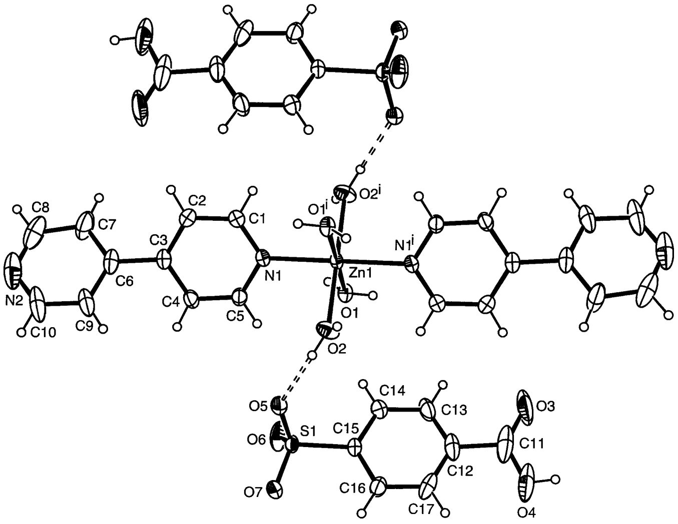


Figure 1

A view of the molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level. Hydrogen bonds are shown as dashed lines. [Symmetry code (i): $-x, 2-y, 1-z$.]

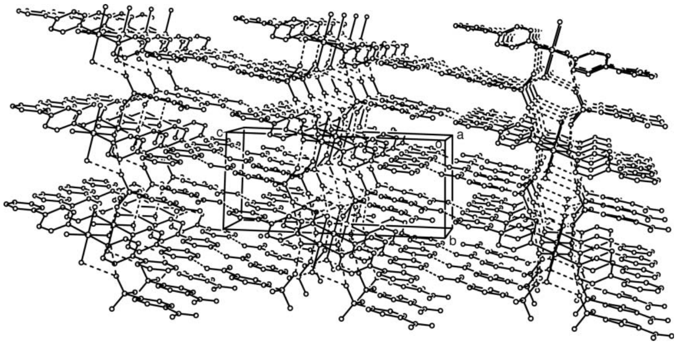


Figure 2

A view of the three-dimensional hydrogen-bonding network for (I). Hydrogen bonds are shown as dashed lines and H atoms have been omitted for clarity.

The two pyridyl rings of the 4,4′-bipy molecule in (I) are non-coplanar and are twisted, with a dihedral angle of 35.5 (2)°. The Zn—N distances in (I) are similar to those of polymeric or monodentate 4,4′-bipy–Zn complexes (Sen *et al.*, 1997; Liang *et al.*, 2001; Klevtsova *et al.*, 2001). The Zn—O*W* distances are also normal and similar to those of polymeric Zn complexes.

The crystal packing in (I) is controlled by hydrogen bonds between the 4-sulfonatobenzoic acid and 4,4′-bipyridine ligands, and between water molecules and sulfonates. The extended hydrogen-bonding network is a three-dimensional architecture, as shown in Fig. 2.

Experimental

A mixture of $ZnSO_4 \cdot 7H_2O$ (0.144 g, 0.5 mmol), potassium hydrogen 4-sulfonatobenzoate (0.120 g, 0.5 mmol), 4,4′-bipyridine (0.078 g, 0.5 mmol) and water (15 ml) was heated at 423 K for 24 h in a 30 ml Teflon-lined stainless steel autoclave. After cooling to room temperature, the mixture was filtered and the filtrate was set aside. After 1 d, pale-red block-shaped crystals of (I) were obtained.

Crystal data

$[Zn(C_{10}H_8N_2)_2(H_2O)_4](C_7H_5O_5S)_2$
$M_r = 852.14$
Triclinic, $P\overline{1}$
$a = 7.5086$ (4) Å
$b = 7.7202$ (4) Å
$c = 16.7277$ (9) Å
$\alpha = 92.256$ (1)°
$\beta = 93.660$ (1)°
$\gamma = 111.039$ (1)°
$V = 901.16$ (8) Å^3

$Z = 1$
$D_x = 1.570$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4470 reflections
$\theta = 2.8$–27.8°
$\mu = 0.87$ mm^{-1}
$T = 295$ (2) K
Block, pale red
0.37 × 0.29 × 0.23 mm

Data collection

Bruker APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{min} = 0.738$, $T_{max} = 0.824$
6510 measured reflections

3146 independent reflections
2947 reflections with $I > 2\sigma(I)$
$R_{int} = 0.014$
$\theta_{max} = 25.0°$
$h = -8 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.130$
$S = 1.10$
3146 reflections
262 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0639P)^2 + 1.2213P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.53$ e Å^{-3}
$\Delta\rho_{min} = -0.73$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Zn1—N1	2.114 (3)	S1—O5	1.446 (3)
Zn1—O1	2.116 (2)	S1—O7	1.446 (3)
Zn1—O2	2.161 (2)	S1—O6	1.449 (3)
N1—Zn1—O1	87.25 (10)	O5—S1—O7	111.52 (17)
N1—Zn1—O2	91.11 (11)	O5—S1—O6	114.6 (2)
O1—Zn1—O2	91.13 (10)	O7—S1—O6	111.21 (19)

Table 2

Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4*A*···N2^i	0.82	1.97	2.776 (6)	167
O1—H1*A*···O7^{ii}	0.85 (3)	1.89 (4)	2.730 (3)	174 (4)
O1—H1*B*···O6^{iii}	0.85 (3)	1.95 (2)	2.748 (4)	155 (5)
O2—H2*A*···O5	0.82 (3)	1.99 (3)	2.766 (4)	157 (3)
O2—H2*B*···O6^{iv}	0.86 (1)	2.25 (2)	3.059 (4)	157 (3)

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

All aromatic H atoms and the carboxyl H atom were positioned geometrically and refined as riding atoms, with C—H = 0.93 Å and O—H = 0.82 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$ and $U_{iso}(H) = 0.80$ Å^2, respectively. The water H atoms were located in difference Fourier maps and were refined with a distance restraint of O—H = 0.85 (1) Å and a fixed isotropic displacement parameter of $U_{iso}(H) = 0.08$ Å^2. The atoms of the terminal pyridyl ring and the carboxyl group have larger displacement parameters due to their freedom of libration.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

ORTEP3 for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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