

Tetraaquabis[5-(3-pyridyl- κ N)pyrimidine]zinc(II) bis(trifluoromethanesulfonate): a novel cationic complex and three-dimensional hydrogen-bonded network

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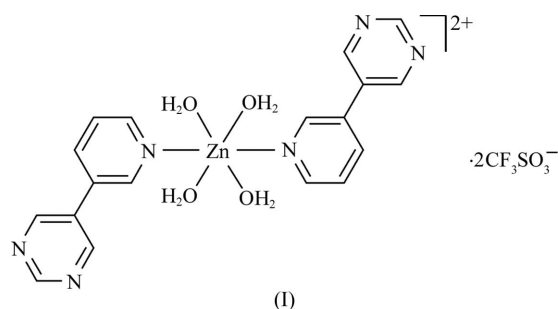
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The title compound, $[\text{Zn}(\text{C}_9\text{H}_7\text{N}_3)_2(\text{H}_2\text{O})_4](\text{CF}_3\text{O}_3\text{S})_2$, contains an octahedral $[\text{ZnL}_2(\text{H}_2\text{O})_4]^{2+}$ cationic complex with *trans* geometry (Zn site symmetry $\bar{1}$), and each 5-(3-pyridyl)pyrimidine (*L*) ligand is coordinated in a monodentate fashion through the pyridine N atom. In the extended structure, these complexes, with both hydrogen-bond acceptor (pyrimidine) and donor (H_2O) functions, are linked to each other by intermolecular water–pyrimidine $\text{O}\cdots\text{H}\cdots\text{N}$ hydrogen-bonding interactions, resulting in a double chain along the crystallographic *a* axis. The trifluoromethanesulfonate anions are integrated into the chains *via* $\text{O}\cdots\text{H}\cdots\text{O}$ hydrogen bonds between the coordinated water and sulfonate O atoms. These double chains are associated into a novel three-dimensional network through interchain water–pyrimidine $\text{O}\cdots\text{H}\cdots\text{N}$ hydrogen bonds. The asymmetric ligand plays an important role in constructing this unusual supramolecular structure.

Comment

Asymmetric organic ligands with various topologies and coordination natures are widely used by chemists in the construction of coordination polymers and supramolecular complexes. Some of the resulting materials exhibit encouraging potential for applications in magnetism (He *et al.*, 2006), luminescence (Allendorf *et al.*, 2009; Hou *et al.*, 2010) and nonlinear optics (Evans & Lin, 2002; Ye *et al.*, 2005). The geometry of the organic ligands is one of the most important factors in determining the structure of the framework. It is well known that the inclusion of different functional groups, such as pyrimidine and pyridine, can lead to different coordination modes and may play a crucial role in the construction of supramolecular complexes driven by coordinate interactions and hydrogen bonds. Previously, pyrimidine deriva-

tives have occasionally been used in supramolecular chemistry and coordination polymers with versatile structures, and potential properties have been reported. For example, Champness and co-workers have reported a highly unusual three-dimensional polymer, $[\text{Cu}_3\text{I}_3\{5-(4\text{-pyridyl})\text{pyrimidine}\}]_n$, in which the 5-(4-pyridyl)pyrimidine ligand bridges two-dimensional brick-wall $(\text{CuI})_n$ sheets (Thébaud *et al.*, 2006). Fujita *et al.* (2005) reported two M_8L_4 cages controlled by the guest molecules, based on the tridentate ligand 3,5-bis(3-pyridyl)-1-(pyrimidin-5-yl)benzene. In addition, some pyrimidine derivatives employed as nucleophilic linkers have received much attention in self-assembly with various hydrogen-bond donors (Georgiev *et al.* 2004). In this contribution, a new asymmetric organic ligand, 5-(3-pyridyl)pyrimidine (*L*), has been synthesized and used to create a novel Zn^{II} complex salt, $[\text{ZnL}_2(\text{H}_2\text{O})_4](\text{CF}_3\text{SO}_3)_2$, (I), the structure of which is reported.



Compound (I) crystallizes in the monoclinic space group $P2_1/n$ with one half of a $[\text{ZnL}_2(\text{H}_2\text{O})_4]^{2+}$ complex cation (Zn is on a centre of inversion) and one CF_3SO_3^- (trifluoromethanesulfonate) counter-anion in the asymmetric unit. The Zn^{II} centre lies in a highly regular octahedral $\{\text{ZnN}_2\text{O}_4\}$ coordination environment, which is composed of two pyridine N-atom donors from two *L* ligands in the axial positions and four O-atom donors from four coordinated water molecules in

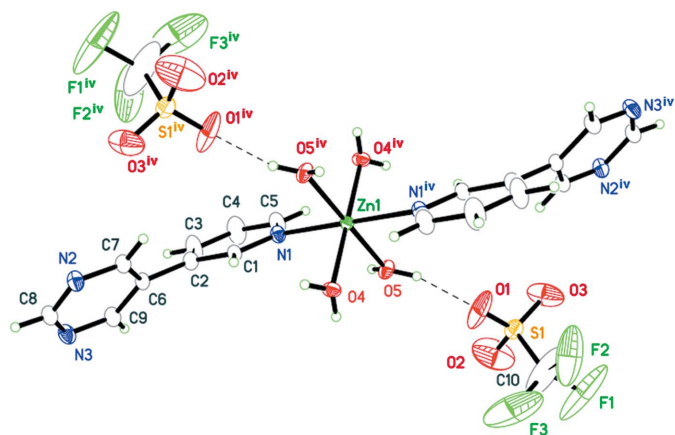
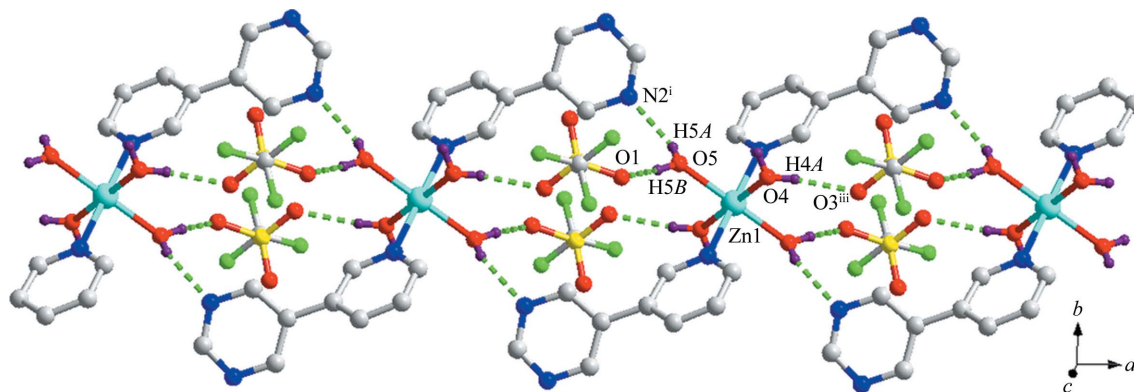


Figure 1
The Zn^{II} coordination environment of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level. Hydrogen bonds are shown as dashed lines. [Symmetry code: (iv) $-x + 1, -y + 1, -z + 1$.]


Figure 2

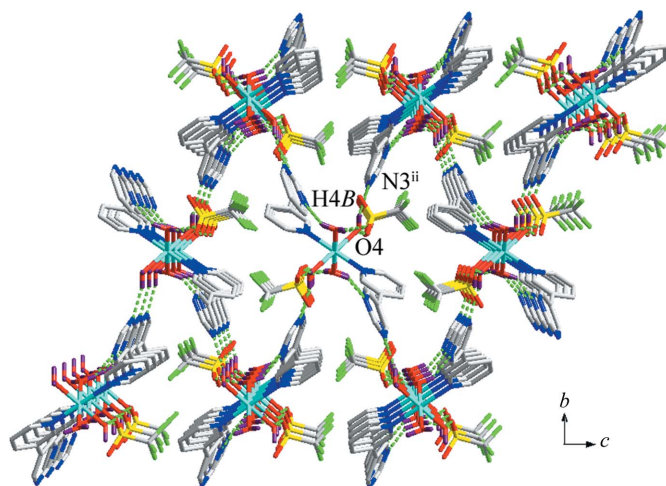
The hydrogen-bond-driven double chain formed along the crystallographic a direction of (I). Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $x - 1, y, z$; (iii) $x + 1, y, z$.]

the equatorial positions (Fig. 1). The fact that L acts as a monodentate ligand in this fashion proves that the pyridine group has a stronger coordination ability than the pyrimidine group in this case. The pyrimidine and pyridine rings in the ligand are significantly twisted. The dihedral angle between the two rings [$42.36(15)^\circ$] is distinctly larger than the value of $34.0(1)^\circ$ in $[\text{Cu}_3\text{I}_3\{5-(4\text{-pyridyl})\text{pyrimidine}\}]_n$ (Thébault *et al.*, 2006). For $[\text{ML}_2(\text{H}_2\text{O})_4]$ complexes with this type of asymmetric ligand, the two terminal groups of the ligand can be located on either the same or opposite sides of the central pyridine– M –pyridine unit, resulting in *cis* or *trans* conformations (Dong *et al.*, 2007; Zheng *et al.*, 2009), which is distinctly different from some $[\text{ML}_2(\text{H}_2\text{O})_4]$ complexes with non-symmetric ligands (Khanpour & Morsali, 2009; Peedikakkal & Vittal, 2008; Chen *et al.*, 2008). In (I), the two terminal pyrimidine groups of the $[\text{ZnL}_2(\text{H}_2\text{O})_4]^{2+}$ complex cation give rise to a *trans* conformation with respect to the central pyridine– Zn –pyridine unit, as required by the inversion symmetry. Though some similar *trans*-conformation complexes have been reported (Chen *et al.*, 2004; Cakir *et al.*, 2003; Zhu *et al.*, 2009), the specific combination of interacting groups in (I) leads to a novel three-dimensional network of interactions.

Given the strong hydrogen-bond capability of the uncoordinated pyrimidine groups (Horikoshi *et al.*, 2004; Georgiev *et al.*, 2004), it is not surprising that the $[\text{ZnL}_2(\text{H}_2\text{O})_4]^{2+}$ complex cation displays a robust hydrogen-bonding framework. The uncoordinated pyrimidine groups act as hydrogen-bond acceptors to link the complexes into double chains along the crystallographic a direction *via* $\text{O5}—\text{H5A} \cdots \text{N2}^i$ hydrogen bonds between coordinated water molecules and pyrimidine N atoms (Fig. 2) [symmetry code: (i) $x - 1, y, z$]. In the double chain, the $\text{Zn} \cdots \text{Zn}$ separation is $9.360(2)$ Å and this space is large enough to accommodate two uncoordinated CF_3SO_3^- anions, which are locked in the chain through $\text{O5}—\text{H5B} \cdots \text{O1}$ and $\text{O4}—\text{H4A} \cdots \text{O3}^{\text{iii}}$ hydrogen bonds between the coordinated water molecules and the CF_3SO_3^- anions [symmetry code: (iii) $x + 1, y, z$]. The CF_3SO_3^- anions thus play an important role in constructing the hydrogen-bonded supramolecular chain. Notably, the hydrogen-bond-driven chain here is distinctly different from that observed in the related compound $[\text{Zn}(\text{L1})_2(\text{CH}_3\text{CH}_2\text{OH})_2(\text{H}_2\text{O})_2](p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2)_n$,

(L1 is 1,2-bis[1-[1-(pyridin-3-ylmethyl)benzimidazol-2-yl]ethylidene]hydrazine; Zheng *et al.*, 2009) in which a (Zn complex) $\cdots p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^- \cdots (\text{Zn}$ complex) chain is constructed only by water–sulfonate $\text{O}—\text{H} \cdots \text{O}$ hydrogen bonds, without the participation of ligand L1 . In (I), the chain is generated from a combination of water–pyrimidine $\text{O}—\text{H} \cdots \text{N}$ and water–sulfonate $\text{O}—\text{H} \cdots \text{O}$ hydrogen bonds. Viewed along the crystallographic a direction, all the hydrogen-bond-driven chains are parallel and further extend into a three-dimensional framework *via* $\text{O5}—\text{H5B} \cdots \text{N3}^{\text{ii}}$ hydrogen bonds between double chains (Fig. 3) [symmetry code: (ii) $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$].

In summary, the introduction of both pyrimidinyl and pyridyl donor groups in the 5-(3-pyridyl)pyrimidine ligand leads to a $[\text{ZnL}_2(\text{H}_2\text{O})_4]^{2+}$ complex cation with multiple hydrogen-bonding capabilities which combines with the CF_3SO_3^- counter-anions to generate a novel three-dimensional network. This study demonstrates that such an asymmetric ligand plays an important role in constructing unusual supramolecular compounds, which may provide a new method for constructing novel functional materials in the future.


Figure 3

The three-dimensional framework of (I) formed *via* $\text{O4}—\text{H4B} \cdots \text{N3}^{\text{ii}}$ interactions (dashed lines) between double chains. [Symmetry code: (ii) $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$.]

Experimental

5-Bromopyrimidine (0.32 g, 2.0 mmol), 3-pyridylboronic acid (0.27 g, 2.2 mmol), [Pd(PPh₃)₄] (0.076 g, 0.066 mmol) and K₂CO₃ (0.83 g, 6.0 mmol) in EtOH–H₂O (3:1 v/v, 20 ml) were heated under reflux for 48 h. After removal of the solvents under vacuum, the residue was purified on silica gel using column chromatography with CH₂Cl₂–THF (10:1 v/v) as the eluent to give 5-(3-pyridyl)pyrimidine (*L*) as a colourless crystalline solid (yield 85%). IR (KBr pellet, ν, cm⁻¹): 3026 (*m*), 1638 (*m*), 1592 (*s*), 1574 (*s*), 1443 (*s*), 1418 (*s*), 1400 (*m*), 1354 (*m*), 1233 (*m*), 1026 (*m*), 994 (*m*), 805 (*m*), 729 (*s*), 708 (*s*), 634 (*s*); ¹H NMR (300 MHz, DMSO-*d*₆, TMS): δ 9.27 (*s*, 1H, C₄H₄N₂), 8.97 (*s*, 2H, C₄H₄N₂), 8.87 (*s*, 1H, C₅H₄N), 8.74–8.72 (*d*, 1H, C₅H₄N), 7.95–7.92 (*d*, 1H, C₅H₄N), 7.52–7.48 (*t*, 1H, C₅H₄N). Elemental analysis calculated for C₉H₇N₃: C 68.77, H 4.49, N 26.74%; found: C 68.54, H 4.57, N 26.83%.

A solution of Zn(CF₃SO₃)₂ (9.0 mg, 0.025 mmol) in CH₃CN (2 ml) was layered onto a solution of *L* (7.8 mg, 0.050 mmol) in CH₂Cl₂ (2 ml). The system was left for about three weeks at room temperature, after which time colourless crystals of (*I*) were obtained (yield 80%).

Crystal data

[Zn(C ₉ H ₇ N ₃) ₂ (H ₂ O) ₄](CF ₃ SO ₃) ₂	<i>V</i> = 1534.5 (4) Å ³
<i>M_r</i> = 749.93	<i>Z</i> = 2
Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Mo <i>K</i> α radiation
<i>a</i> = 9.3597 (15) Å	<i>μ</i> = 1.03 mm ⁻¹
<i>b</i> = 17.198 (3) Å	<i>T</i> = 298 K
<i>c</i> = 9.6857 (16) Å	0.30 × 0.25 × 0.22 mm
<i>β</i> = 100.187 (2)°	

Data collection

Bruker SMART APEX area-detector diffractometer	7904 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2003)	2854 independent reflections
<i>T</i> _{min} = 0.747, <i>T</i> _{max} = 0.805	2428 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.024

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.066	7 restraints
<i>wR</i> (<i>F</i> ²) = 0.199	H-atom parameters constrained
<i>S</i> = 1.04	Δ <i>ρ</i> _{max} = 1.24 e Å ⁻³
2854 reflections	Δ <i>ρ</i> _{min} = -0.93 e Å ⁻³
207 parameters	

Water H atoms were located in a difference Fourier map and included as riding atoms, with O–H = 0.82 Å and *U*_{iso}(H) = 1.5*U*_{eq}(O). Other H atoms were placed in idealized positions and treated as riding, with C–H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C).

The elongated displacement ellipsoids of the F atoms in the trifluoromethanesulfonate anion indicate possible disorder. However, attempts to refine the anion with split F-atom positions were unsuccessful, resulting in very poor geometry about the C atom. In order to keep the CF₃SO₃⁻ anion stable in the refinement, a series of C–F [1.40 (1) Å], C–S [1.65 (2) Å] and F⋯F [2.20 (2) Å] distance restraints were used.

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> –H⋯ <i>A</i>	<i>D</i> –H	H⋯ <i>A</i>	<i>D</i> ⋯ <i>A</i>	<i>D</i> –H⋯ <i>A</i>
O5–H5B⋯O1	0.81	1.89	2.677 (7)	162
O5–H5A⋯N2 ⁱ	0.82	2.07	2.762 (5)	142
O4–H4B⋯N3 ⁱⁱ	0.82	2.02	2.812 (5)	162
O4–H4A⋯O3 ⁱⁱⁱ	0.82	1.96	2.755 (7)	164

Symmetry codes: (i) *x* – 1, *y*, *z*; (ii) *x* – ½, –*y* + ½, *z* + ½; (iii) *x* + 1, *y*, *z*.

Data collection: SMART (Bruker, 2003); cell refinement: SMART; data reduction: SAINT (Bruker, 2003); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3296). Services for accessing these data are described at the back of the journal.

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