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catena-Poly[[[diaquazinc(II)]-bis[μ-2-(2,4-difluorophenyl)-1,3-bis(1,2,4-triazol-1-yl)-propan-2-ol-κ^2N^4:N^4]] bis(perchlorate)]

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.027
wR factor = 0.075
Data-to-parameter ratio = 11.4

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

The formula unit of the title one-dimensional coordination polymer, $\{[Zn(C_{13}H_{12}F_2N_6O)_2(H_2O)_2](ClO_4)_2\}_n$, which is twice the asymmetric unit, contains a Zn^{II} ion on an inversion centre, two fluconazole [or 2-(2,4-difluorophenyl)-1,3-bis(1,2,4-triazol-1-yl)propan-2-ol] ligands, two water molecules and two perchlorate anions. The fluconazole ligands connect the Zn^{II} atoms through their N^4 atoms in a head-to-tail fashion, resulting in the formation of a one-dimensional cationic macrocyclic chain structure. These one-dimensional cationic chains are connected by hydrogen bonds into a two-dimensional layer structure. There is also a π–π supramolecular interaction of the benzene rings of the flucanozole ligands between the chains.

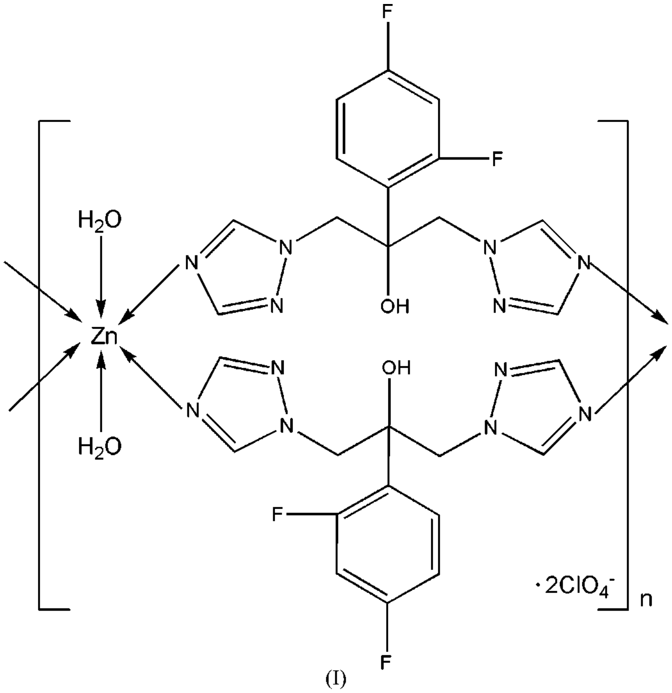
Comment

Organic ligands play an important role in the construction of coordination polymers with frameworks of different types and dimensionality. Flexible ligands, which have more than two σ bonds, are crucial ligands in building an intriguing variety of networks (Awaleh *et al.*, 2005; Chen *et al.*, 2005) which make the absorption, desorption and exchange of guest molecules possible (Hennigar *et al.*, 1997). Fluconazole [2-(2,4-difluorophenyl)-1,3-bis(1,2,4-triazol-1-yl)-propan-2-ol, HFlu] is one of the popular first-line drugs used to treat invasive infections (Ritter *et al.*, 1999; Caira *et al.*, 2004) and is also an interesting flexible ligand for the construction of coordination polymers. In previously reported structures, fluconazole acts not only acts as a chelating ligand with the endodentate N atom (N^2) and the O atom of the hydroxy group to form dinuclear metal complexes (Gong *et al.*, 2006), but also as a bridging ligand with the exodentate N atom (N^4) to construct chain or network structures (Han *et al.*, 2006; Zhang *et al.*, 2006).

In order to explore further the coordination chemistry of the Zn^{II}–HFlu system (Zhang *et al.* 2006), the title zinc(II) coordination polymer, (I), with HFlu was synthesized and the structure was characterized by single-crystal X-ray diffraction.

The title polymer consists of one-dimensional cationic macrocyclic chains, with a basic unit of $[Zn(HFlu)_2(H_2O)_2]^{2+}$, and perchlorate anions. The Zn^{II} ions are located on inversion centres and are thus have an all-*trans* octahedral coordination environment (Fig. 1, Table 1). The equatorial plane is defined by four N^4 atoms of four different HFlu ligands (N3, N3A, N6B and N6C in Fig. 1) with an average Zn—N distance of 2.1617 (15) Å. The axial positions are occupied by two O atoms of coordinated water molecules (O2 and O2A) with a Zn—O distance of 2.158 (13) Å.

The HFlu ligand has a *trans* conformation, as defined by Zhang *et al.* (2006), and coordinates to two Zn^{II} ions as a bridging ligand, forming a 20-membered macrocyclic ring, which is further linked by Zn—N bonds to generate a one-dimensional cationic chainlike structure running in the *b*-axis direction (Fig. 2). The Zn···Zn distance in the macrocyclic ring is 9.986 (2) Å, which is somewhat shorter than the value of 10.722 Å found in $\{[Zn(HFlu)_2(H_2O)_2](NO_3)_2{\cdot}2DMF\}_n$ (Zhang *et al.*, 2006). The two triazole rings in one HFlu ligand form a dihedral angle of 81.76 (8)°, larger than that of 73.13° in $\{[Zn(HFlu)_2(H_2O)_2](NO_3)_2{\cdot}2DMF\}_n$.



(I)

The uncoordinated perchlorate is hydrogen-bonded to adjacent chains through O—H···O and C—H···O interactions, extending the one-dimensional chain into a two-dimensional layer structure (Table 2, Fig. 2). There is also a supramolecular π–π interaction between the benzene rings of HFlu, with a centroid-to-centroid distance of 4.2745 (8) Å and a slip angle (defined as the angle between the centroid–centroid vector and the centroid–C10 vector) of 17.61 (5)°.

The photoluminescence of the title complex in a solution of ethanol (10 m*M* based on HFlu) at room temperature was examined. An intense emission (relative intensity 476) occurs at 288 nm, slightly stronger than that of the free ligand HFlu (relative intensity 378) upon excitation at 261 nm.

Experimental

The title complex was obtained by a diffusion reaction in an H-shaped tube, with an aqueous solution (14 ml) of zinc perchlorate hexahydrate (0.3729 g, 1 mmol) in one side and an ethanol solution (15 ml) of HFlu (0.3069 g, 1 mmol) in the other side. Colourless block-shaped crystals, suitable for X-ray diffraction, were obtained after several days; these were filtered off and washed with diethyl ether (yield 48%). CHN analysis, found: C 34.20, H 3.15, N 18.51%; calculated for $C_{26}H_{28}Cl_2F_4N_{12}O_{12}Zn$: C 34.18, H 3.07, N 18.40%.

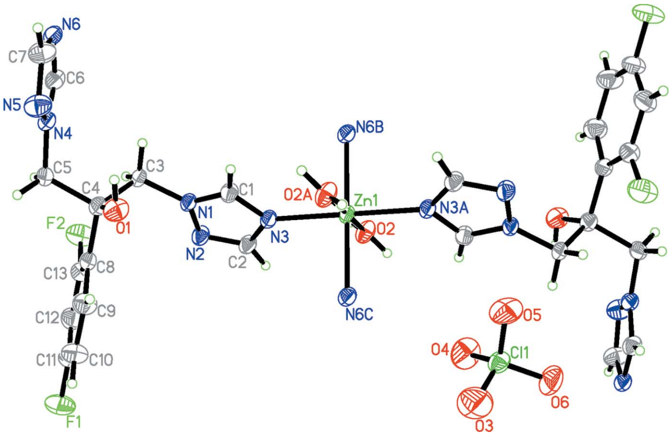


Figure 1
Part of the polymeric structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes (A): $-x + 1, -y + 1, -z$; (B): $-x + 1, -y, -z$; (C): $x, y + 1, z$.]

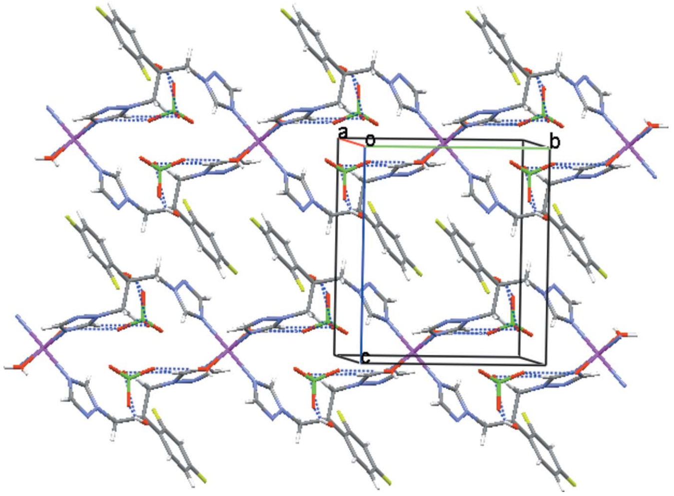


Figure 2
The cationic macrocyclic chain structure of the title polymer, showing π–π stacking between the benzene rings of two chains. Dashed lines indicate hydrogen bonds.

Crystal data

$[Zn(C_{13}H_{12}F_2N_6O)_2(H_2O)_2](ClO_4)_2$
$M_r = 912.87$
Triclinic, $P\overline{1}$
$a = 7.9134$ (17) Å
$b = 9.986$ (2) Å
$c = 11.494$ (3) Å
$\alpha = 90.194$ (3)°
$\beta = 94.070$ (3)°
$\gamma = 111.031$ (3)°
$V = 845.2$ (3) Å^3
$Z = 1$
$D_x = 1.793$ Mg m^{-3}
Mo *Kα* radiation
$\mu = 0.99$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.28 × 0.22 × 0.20 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.873$, $T_{max} = 1.000$ (expected range = 0.716–0.820)
4602 measured reflections
2952 independent reflections
2658 reflections with $I > 2\sigma(I)$
$R_{int} = 0.013$
$\theta_{max} = 25.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.075$
$S = 1.09$
2952 reflections
260 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0422P)^2 + 0.2716P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—N3	2.1438 (15)	Zn1—N6^{i}	2.1797 (16)
Zn1—O2	2.1580 (13)		
N3—Zn1—O2^{ii}	91.14 (6)	O2—Zn1—N6^{iii}	89.86 (6)
N3^{ii}—Zn1—O2^{ii}	88.86 (6)	N3—Zn1—N6^{i}	90.13 (6)
N3—Zn1—N6^{iii}	89.87 (6)	O2—Zn1—N6^{i}	90.14 (6)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$O3^{iv}	0.82	2.50	3.169 (3)	139
O1—H1$\cdots$O4^{iv}	0.82	2.64	3.272 (3)	135
O2—H2$B\cdots$O6^{v}	0.85	1.99	2.833 (2)	173
O2—H2$A\cdots$N2^{vi}	0.85	2.14	2.983 (2)	173
C1—H1$A\cdots$O4^{iv}	0.93	2.64	3.368 (3)	136
C1—H1$A\cdots$O6^{iv}	0.93	2.47	3.392 (3)	171
C2—H2$\cdots$O5^{vii}	0.93	2.29	3.227 (3)	176
C3—H3$B\cdots$O4^{iv}	0.97	2.42	3.243 (3)	143
C5—H5$A\cdots$O3^{viii}	0.97	2.56	3.501 (4)	164
C6—H6$\cdots$O5^{viii}	0.93	2.39	3.280 (3)	159

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

The water H atoms were located in a Fourier difference map and refined subject to an O—H restraint of 0.85 (2) Å and an H$\cdots$H restraint of 1.39 (4) Å. Other H atoms were introduced in calculated positions, with C—H = 0.93–0.97 Å and O—H = 0.82 Å, and refined using a riding model. The hydroxyl group was allowed to rotate around the C—O bond. For all H atoms, $U_{iso}(H) = 1.2U_{eq}$(parent atom).

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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