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Journal of MOLECULAR STRUCTURE

Journal of Molecular Structure 829 (2007) 161-167

www.elsevier.com/locate/molstruc

Anion-tuned self-assembly of zinc(II)–fluconazole complexes: Crystal structures, luminescent and thermal properties

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> Received 12 April 2006; received in revised form 17 June 2006; accepted 17 June 2006 Available online 14 August 2006

Abstract

Four novel fluconazole-bridged Zn(II) complexes, $[Zn(HFlu)Cl_2(DMF)]_2$ (1), $\{[Zn(HFlu)_2(H_2O)_2](NO_3)_2 2DMF\}_n$ (2), $\{[Zn(HFlu)_2(H_2O)_2](NO_3)_2\}_n$ (3) and $\{[Zn(HFlu)(SCN)_2]H_2O\}_n$ (4) [HFlu = 2-(2,4-difluorophenyl)-1,3-bis(1,2,4-triazol-1-yl)-propan-2-ol], have been synthesized and structurally characterized by X-ray diffraction method. The structure of dimeric complex 1 consists of 20-membered macrometallacyclic ring-like structure, in which the Zn(II) ion is in a five-coordinated distorted trigonal bipyramidal geometry with the Zn···Zn distance of 10.265(3) Å across the*cis*HFlu ligand. Complex 2 shows infinite 1-D macrocyclic double chain structure with the central Zn(II) ions being six-coordinated by four HFlu ligands and two apical water molecules and with the intrachain Zn···Zn distance of 10.654(2) Å. The structure of complex 4 consists of infinite 1-D coordination polymeric chain with the tetrahedral coordination geometry of Zn(II) ion and with the intrachain Zn···Zn distance of 11.173(2) Å across the*cis*HFlu ligand. Complexes 1–4 show the similar fluorescence emission to the free HFlu ligand at ambient temperature and the thermal stabilities of the complexes have also been investigated.

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Keywords: Crystal structure; Fluconazole; Zn(II) complex; Self-assembly; Anion effect

1. Introduction

Crystal engineering has generated considerable interests due to the intriguingly aesthetic architectures, and/or the potential functional materials [1–11]. Self-assembly is one of the most successful approaches to construct the coordination supramolecules by the assembly of metal ions with the polyfunctional organic ligands (such as pyrazine, 4,4'byyridine, polycarboxylic acid and their analogues) as linkers [12–15]. The structure of the coordination polymer is significantly influenced by the coordination preference and geometry of the metal ions [16–19]. The anion can act not only as a charge-compensating component, but also

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as an auxiliary ligand to the metal sites to influence on the dimensionality of the coordination polymers [20–24]. Apart from these, the weak interactions (hydrogen bonding, π – π and hydrophobic interactions) are also significant to stabilize the structure and/or to form the high dimensional structures [12,25–29].

Poly(triazolyl)alkanes are attractive ligands for the design of the novel inorganic–organic hybrid frameworks and exhibit an extensive ability to bridge metal ions to afford polynuclear complexes [30–33]. We promote the poly(triazolyl)alkanes to the polyfunctional bis-triazole fluconazole. Fluconazole [2-(2,4-difluorophenyl)-1,3-bis(1,2,4-triazol-1-yl)-propan-2-ol, HFlu, Chart 1] is one of the first-line popular drugs used to treat invasive infections [34,35], and would be an interesting candidate to construct coordination polymers, since it combines the features required for coordination to metal ions through two

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Chart 1. The chemical structure of fluconazole (HFlu).

terminal triazoles and for extended intermolecular interactions (H-bonding functionality through alkoxyl group at the central carbon site and π - π interaction through the phenyl ring). Thus, the HFlu ligand is potential to construct a diversity of coordination architectures upon the metal complexation. In this work, we firstly describe the synthesis, crystal structures, fluorescent and thermal properties of four new Zn(II)-fluconazole complexes: [Zn(HFlu) Cl₂(DMF)]₂ (1), {[Zn(HFlu)₂(H₂O)₂](NO₃)₂·2DMF}_n (2), {[Zn(HFlu)₂(H₂O)₂](NO₃)₂}_n (3) and {[Zn(HFlu) (SCN)₂]-H₂O}_n (4), which are anion dependent.

2. Experimental

2.1. Materials and physical measurements

All chemicals were commercially available and used as received without further purification. Elemental analyses for C, H, N and S were carried out by using a *Vario* EL III Elemental Analyzer. Infrared spectra were recorded on a Bruker Equinox 55 FT-IR spectrophotometer as KBr pellets in the range of 4000–400 cm⁻¹. Electronic absorption spectra were recorded on a Hitachi U-3010 spectrophotometer in the range of 190–1100 nm. Luminescence spectra for solid samples and the solution were recorded with a Hitachi F-4500 fluorescence spectrophotometer. Differential scanning calorimeter–thermogravimetry analyses (DSC-TG) were performed on a simultaneous SDT thermal analyzer (STA449C, Netzsch) under a flow of N₂ at a heating rate of 10 °C/min between ambient temperature and 950 °C.

2.2. Preparations of complexes 1-4

2.2.1. $[Zn(HFlu)Cl_2(DMF)]_2(1)$

To a solution of $ZnCl_2$ (0.5 mmol, 0.0684 g) in H₂O (4 mL) was added a solution of HFlu (0.5 mmol, 0.1541 g) in DMF (5 mL). After refluxed for 60 min, the solution was filtered and kept at room temperature. Single crystals suitable for X-ray analysis were obtained by very slow evaporation of the solvent after 1 month. Yield:

48%. Anal. Calcd. for $C_{16}H_{19}Cl_2F_2N_7O_2Zn$: C, 37.27; H, 5.08; N, 19.01. Found: C, 37.51; H, 5.52; N, 19.05. IR (KBr pellet, cm⁻¹): 3277m, 3165w, 3126w, 1656s, 1619w, 1525m, 1420m, 1373m, 1278m, 1124s, 964m, 871m, 646m.

2.2.2. $\{[Zn(HFlu)_2(H_2O)_2](NO_3)_2 \cdot 2DMF\}_n$ (2)

The colorless block crystals of **2** suitable for X-ray analysis were obtained by a method similar to that of **1** except that ZnCl₂ was replaced by Zn(NO₃)₂·6H₂O. Yield 64%, Anal. Calcd. for $C_{32}H_{42}F_4N_{16}O_{12}Zn$: C, 39.05; H, 4.30; N, 22.77. Found: C, 39.21; H, 4.42; N, 22.97. IR (KBr pellet, cm⁻¹): 3126w, 1662s, 1618w, 1502m, 1382s, 1278m, 1136m, 966m, 858m, 669m.

2.2.3. $\{[Zn(HFlu)_2(H_2O)_2](NO_3)_2\}_n$ (3)

The colorless block crystals of **3** were obtained in the aqueous solution by a method similar to that of **2**. Yield 52%, Anal. Calcd. for $C_{26}H_{28}F_4N_{14}O_{10}Zn$: C, 37.26; H, 3.37; N, 23.40. Found: C, 37.01; H, 3.82; N, 23.22. IR (KBr pellet, cm⁻¹): 3283m, 1619m, 1505m, 1384s, 1277m, 1128s, 967m, 870m, 858m, 675m, 654m.

2.2.4. $\{[Zn(HFlu)(SCN)_2] \cdot H_2O\}_n$ (4)

The colorless rhombic crystals of **4** suitable for X-ray analysis were obtained in the aqueous solution by a method similar to that of **1** except that $ZnCl_2$ was replaced by $Zn(SCN)_2 \cdot 3H_2O$. Yield 37%. The crystal was not stable at room temperature and easily lost the lattice water to form powder after taken away from the mother liquid. Elemental analysis for the complex was performed after drying for 4 h at 120 °C. $C_{15}H_{12}F_2N_8OS_2Zn$: C, 36.93; H, 2.48; N, 22.97; S, 13.12. Found: C, 36.54; H, 2.94; N, 22.57, S, 12.98. IR (KBr pellet, cm⁻¹): 3657w, 3126m, 2090s, 1616m, 1533s, 1502m, 1421m, 1286s, 1132s, 993m, 966m, 864m, 671m, 655s.

2.3. X-ray structure studies

Intensities of complexes 1-4 were collected on a Bruker Apex II CCD diffractometer with graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å) at 293 K. Semi-empirical absorption corrections were applied by SADABS program [36], and the SAINT program was utilized for integration of the diffraction profiles [37]. The structures were solved by direct methods using SHELXS program of the SHEL-XL package and refined with SHELXL program [38,39]. The heavy atoms were located from the E-maps and other non-hydrogen atoms in successive difference Fourier syntheses. The final refinements were performed by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms on F^2 . The C-bound hydrogen atoms were generated with assigned isotropic thermal parameters, and those of water molecules were first located in the difference electron density map and then placed in their calculation positions with fixed thermal factors. Crystallographic data and structure refinement for 1-4 are summarized in Table 1.

Table 1 Crystal data and structure refinement information for 1-4

	1	2	3	4
Empirical formula	$C_{16}H_{19}Cl_2F_2N_7O_2Zn$	C32H42F4N16O12Zn	C ₂₆ H ₂₈ F ₄ N ₁₄ O ₁₀ Zn	$C_{15}H_{14}F_2N_8O_2S_2Zn$
Formula weight	515.65	984.19	838.00	505.83
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	P-1	C2/c	P-1	$P2_1/c$
a (Å)	8.8081(13)	9.514(5)	9.2306(16)	10.141(2)
b (Å)	10.7453(16)	19.218(9)	10.6540(18)	13.969(3)
<i>c</i> (Å)	11.7205(17)	23.633(11)	10.8611(18)	15.308(3)
α (°)	79.454(2)	90	61.450(2)	90
β (°)	77.595(2)	91.612(8)	73.159(2)	104.190(3)
γ (°)	87.350(2)	90	70.602(2)	90
$V(Å^3)$	1065.1(3)	4320(3)	873.8(3)	2102.3(7)
Z	2	4	1	4
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.608	1.513	1.592	1.598
μ (MoK α)(mm ⁻¹)	1.449	0.663	0.799	1.414
<i>F</i> (000)	524	2032	428	1024
θ range (°)	2.37-25.02	1.72-25.03	2.16-25.1	2.00-25.03
h	-9/10	-11/11	-10/10	-12/8
k	-12/12	-19/22	-12/9	-16/16
1	-13/12	-21/28	-12/11	-18/18
Reflections collected/unique $[R_{int}]$	$5822/3720 [R_{int} = 0.0114]$	$10,787/3809 [R_{int} = 0.0286]$	$4751/3032 [R_{int} = 0.0136]$	$11,244/3718 [R_{int} = 0.0278]$
Data/restraints/parameters	3720/0/274	3809/3/304	3032/0/251	3718/3/272
GOF	1.058	1.068	1.080	1.034
$R^{\rm a}/_{\rm w} R^{\rm b} [I \ge 2\sigma(I)]$	0.0265/0.0717	0.0420/0.1011	0.0287/0.0718	0.0350/0.0799
$R^{\rm a}/_{\rm w} R^{\rm b}$ (all data)	0.0314/0.0733	0.0547/0.1093	0.0358/0.0741	0.0523/0.0873
Residuals (e/Å)	0.389, -0.260	0.529, -0.317	0.198, -0.205	0.456, -0.329

$$^{a} R = \sum (||F_{o}| - |F_{c}||) / \sum |F_{o}|$$

^a $R = \sum (||F_{o}| - |F_{c}||) / \sum |F_{o}|.$ ^b $wR = [\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o})^{2}]^{1/2}.$

3. Results and discussion

3.1. Syntheses and general characterizations

Complexes 1-4 were prepared by reacting the corresponding zinc(II) salts with fluconazole ligand in the different solvent media under mild condition. Complexes 1 and 4 have 1:1 metal/ligand composition and 1:2 metal/ligand one was achieved for complexes 2 and 3, although the same metal/ligand molar ratio (1:1) was applied to the preparation process. For complexes 2 and 3, only the solvent is different in the preparation process. The IR spectra of complexes 1-4 matched well with the absorption bands of the characteristic skeletal vibrations of fluconazole at 3126, ~1618, 1278 (1286 for 4) and 966 cm^{-1} . On the other hand, several characteristic bands were observed at 1656 cm^{-1} attributed to the C=O stretching vibration of DMF molecules in 1, at 1662 and 1382 cm⁻¹ attributed to DMF molecules and nitrate anions in 2, and at 2090 cm^{-1} attributed to the SCN⁻ anions in 4, respectively. The C=O stretching vibration of lattice DMF molecule in 2 (1662 cm^{-1}) was observed to red shift to 1656 cm^{-1} due to its complexation to Zn(II) ion. The vibration of SCN⁻ at 2090 cm⁻¹ in **4**, lower than 2100 cm⁻¹, suggested a monodentate N-coordinated mode [40], which was conformed by X-ray structural analysis (vide infra). Electronic spectra of complexes 1–4 were measured in the solid state and aqueous solution. The UV/vis spectra show only intense bands in the UV region, at 266 nm ($\varepsilon = 707.6 \text{ dm}^3$ $mol^{-1} cm^{-1}$) and 261 ($\epsilon = 745.6 dm^3 mol^{-1} cm^{-1}$) in the DMF solution, which must be ligand-centered $\pi - \pi^*$ transitions.

3.2. Structural descriptions

 $[Zn(HFlu)Cl_2(DMF)]_2$ (1). The structure of 1 consists of M₂L₂ metallocyclic ring-like structure constructed by two ZnCl₂ units, two DMF molecules and two HFlu ligands as shown in Fig. 1a. Two HFlu ligands are both in *cis* coordination conformation to bridge two Zn(II) centers through triazolyl N atoms. Each Zn(II) center is pentacoordinated to one Cl- and two N atoms from two HFlu ligands in the equatorial plane, and one O atom of DMF molecule and one Cl⁻ at the axial positions to form a distorted trigonal bipyramid. The axial Zn(1)–Cl(2) bond length [2.4729(8) Å] is longer than the equatorial Zn(1)-Cl(1) one [2.2270(7) Å] (Table 2). The Zn(II) ion is displaced from the equatorial plane by 0.1965(6) Å towards the axial Cl⁻ ligand. The structural parameter τ is used to evaluate the coordination geometry of pentacoordinated metal center and is 0.83 for Zn(1), indicating a mediated distorted trigonal bipyramidal coordination environment [41]. The HFlu ligand adopts cis conformation to bridge two Zn(II) ions with intermetallic $Zn(1) \cdots Zn(1a)$ distance of 10.265(3) Å, and the two benzene ring planes are strictly parallel each other. The Cl(2)anion is hydrogen-bonded to the hydroxyl group of HFlu $(d_{O \dots Cl(2)} = 3.121 \text{ Å})$ to form 1-D chain structure along a axis (Table 3, Fig. 1b).



Fig. 1. (a) The asymmetric structure of dimeric complex 1 with the atom numbering scheme. (b) One-dimensional chain of complex 1 through $O-H\cdots Cl$ hydrogen-bonding interactions.

Table 2 Selected bond distances (Å) and angles (°) for 1–4 $\,$

Complex 1			
Zn(1)-N(1)	2.0423(19)	Zn(1)-N(6)#1	2.0501(18)
Zn(1)-Cl(1)	2.2270(7)	Zn(1)-O(2)	2.3235(17)
Zn(1)-Cl(2)	2.4728(8)		
N(1)-Zn(1)-N(6)#1	114.72(8)	N(1)-Zn(1)-Cl(1)	123.61(6)
N(6)#1-Zn(1)-Cl(1)	119.08(6)	N(1)-Zn(1)-O(2)	78.88(7)
N(6)#1-Zn(1)-O(2)	82.20(7)	Cl(1)-Zn(1)-O(2)	92.50(5)
N(1)-Zn(1)-Cl(2)	91.71(6)	N(6)#1-Zn(1)-Cl(2)	90.95(6)
Cl(1)-Zn(1)-Cl(2)	102.82(3)	O(2)-Zn(1)-Cl(2)	164.65(5)
Complex 2			
Zn(1) - O(2)	2.103(2)	Zn(1)-N(6)#2	2.154(2)
Zn(1) - N(1)	2.184(2)		
O(2)–Zn(1)–N(6)#2	89.44(9)	O(2) - Zn(1) - N(1)	90.65(9)
N(6)#2–Zn(1)–N(1)	89.69(9)		
Complex 3			
Zn(1)-O(2)	2.1691(14)	Zn(1)-N(6)#4	2.1352(15)
Zn(1) - N(1)	2.1422(15)		
N(6)#4– $Zn(1)$ – $O(2)$	89.19(6)	N(1)-Zn(1)-O(2)	92.47(5)
N(6)#4-Zn(1)-N(1)	90.04(6)		
Complex 4			
Zn(1)-N(7)	1.923(3)	Zn(1) - N(8)	1.945(3)
Zn(1)-N(6)#6	2.001(2)	Zn(1) - N(1)	2.016(2)
N(7) - Zn(1) - N(8)	116.49(12)	N(7)-Zn(1)-N(6)#6	117.30(11)
N(8)-Zn(1)-N(6)#6	103.71(11)	N(7)-Zn(1)-N(1)	109.28(11)
N(8) - Zn(1) - N(1)	103.16(11)	N(6)#6– $Zn(1)$ – $N(1)$	105.48(9)
N(7)-C(14)-S(2)	178.2(3)	N(8)–C(15)–S(1)	177.7(3)
#1: -v + 1 - v + 1	$-7 + 1 \cdot \# 2 \cdot \gamma$	r = 1/2 $v = 1/2$ $r = #3$	-r + 1 - r

#1: -x + 1, -y + 1, -z + 1; #2: x - 1/2, y - 1/2, z; #3 -x + 1, -y, -z + 1; #4: -x, -y + 1, -z; #5: -x, -y, -z; #6: x - 1, -y + 3/2, z - 1/2.

 $\{[Zn(HFlu)_2(H_2O)_2](NO_3)_2 \cdot 2DMF\}_n$ (2). The crystal structure of 2 consists of 1-D cationic macrocyclic double chain structure $[Zn(HFlu)_2(H_2O)_2]^{2+}$ (Fig. 2a), nitrate anions and lattice DMF molecules. Within the chain, the central Zn(II) ion is six-coordinated with a trans octahedral coordination environment, different from that in complex 1. The equatorial plane was defined by four N atoms from four HFlu ligands with the average Zn-N distance of 2.167(2) Å, longer than that found in 1 [2.046(2) Å]. The apical positions were occupied by two O atoms of two water molecules with the same bond length of 2.103(2) Å. The cis angles in the octahedron fall in the range of $89.35(9)-90.65(9)^\circ$, which deviate slightly from the ideal 90°. The structural parameter, defined as the sum of the deviations from 90° of the 12 *cis* angles [42], is 6.08 in this case, which suggests a weak octahedral distortion of Zn(II) coordination sphere. Although the HFlu ligand has the trans conformation in 2, different form the cis conformation in 1, the HFlu ligand coordinates to two Zn(II) ions as a bridging ligand and also form a 20-membered macrocyclic ring, which is further linked by Zn-N bonds to result in a 1-D structure as shown in Fig. 2. The shortest intrachain and interchain $Zn \cdot \cdot \cdot Zn$ distances are 10.722(3) and 9.514(3) Å, respectively. The uncoordinated nitrate is hydrogen-bonded to adjacent chains through one nitrato O atom with hydroxyl group and coordinated water molecule to extend the 1-D chains to a 2-D sheet structure (Table 3, Fig. 2b). The lattice DMF molecules cling to



Fig. 2. (a) One-dimensional double-bridged chain of complex **2** with the atom numbering scheme. Anions and lattice DMF molecules were omitted for clarity. (b) Supramolecular network in complex **2** through $O-H\cdots O$ hydrogen-bonding interactions.

Table 3 Selected intramolecular and intermolecular hydrogen-bonding interactions in complexes 1–4

Complex	D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	$\angle D - H \cdots A$ (°)
1	$O(1)-H(1)\cdots Cl(2)^{\#1}$	0.82	2.31	3.121	171
	$C(3)-H(3A)\cdots Cl(2)^{\#1}$	0.97	2.91	3.682	137
	$C(5)-H(5B)\cdots Cl(2)^{\#1}$	0.97	2.93	3.706	138
	$C(16)-H(16B)\cdots F(1)^{#2}$	0.96	2.53	3.428	157
2	$O(1)-H(1)\cdots O(3)^{\#3}$	0.82	1.93	2.745	173
	$O(2)-H(2B)\cdots O(3)^{#4}$	0.85	1.90	2.709	159
	$O(2)-H(2A)\cdots O(6)^{\#5}$	0.85	1.84	2.683	174
	$C(15)-H(15A)\cdots F(2)^{\#6}$	0.96	2.54	3.451	159
	$C(16)-H(16)\cdots O(4)^{\#6}$	0.93	2.37	3.248	157
3	$O(1)-H(1)\cdots O(5)^{\#7}$	0.82	2.00	2.813	175
	$O(2)-H(2A)\cdots O(5)^{\#8}$	0.85	1.98	2.811	166
	$O(2)-H(2B)\cdots O(3)^{\#7}$	0.85	2.23	2.973	146
	$C(1)-H(1A)\cdots O4^{\#8}$	0.93	2.28	3.028	137
	$C(10)-H(10)\cdots O4^{\#9}$	0.93	2.48	3.392	169
4	$O(2)-H(2B)\cdots O(1)^{#4}$	0.85	2.24	2.769	120
	$O(1)-H(1)\cdots O(2)^{#4}$	0.82	2.03	2.769	150
	$C(6)-H(6)\cdot\cdot\cdot S(2)^{\#10}$	0.93	2.91	3.78	157

Symmetry transformations used to generate equivalent toms: #1: -x, -y + 1, -z + 1; #2: -x + 2, -y + 1, -z; #3: -x + 1/2, -y + 1/2, -z + 1; #4: x, y, z; #5: x, y - 1, z; #6: -x, -y, -z + 1; #7: -x + 1, -y + 1, -z; #8: x, y - 1, z; #8: x, y - 1, z; #9: -x + 1, -y + 1, -z + 1; #10 -x + 2, -y + 1, -z + 1.

the 2-D structure through hydrogen bonding to the coordinated water molecules.

 ${[Zn(HFlu)_2(H_2O)_2] (NO_3)_2}_n$ (3). The crystal structure of 3 consists of 1-D cationic macrocyclic double chain structure $[Zn(HFlu)_2(H_2O)_2]^{2+}$ and nitrate anions, which is similar to complex 2. The average Zn–N distance in 3 is 2.1387(15) Å, slightly shorter than that in 2 (2.167(2) Å). The apical Zn–O distance is 2.1691 (14) Å, larger than that of 2.103(2) Å in 2. The structural parameter around the Zn ion [42] is 13.28, suggesting the stronger octahedral distortion than that observed in 2. The uncoordinated nitrate is hydrogen-bonded to the adjacent chains through two nitrato O atoms with hydroxyl group and coordinated water molecules to form a 2-D sheet structure (Table 3, Fig. 3).

 ${[Zn(HFlu)(SCN)_2] H_2O}_n$ (4). The structure of complex 4 consists of infinite 1-D zigzag polymeric $[Zn(HFlu)(SCN)_2]_n$ coordination chain and lattice water molecule (Fig. 4). Each Zn(II) ion is ligated by two triazole



Fig. 3. Supramolecular network in complex 3 through O–H \cdots O hydrogen-bonding interactions.



Fig. 4. The asymmetric unit of one-dimensional chain of complex 4 with the atom numbering scheme. The lattice water molecule was omitted for clarity.

nitrogen atoms from two HFlu ligands and two nitrogen atoms from SCN⁻ anions to form a distorted tetrahedral geometry. The average Zn–N_{triazole} distance [2.008 Å] is slightly longer than the average Zn–N_{SCN} distance [1.934 Å], and the N–Zn–N angles fall in the range of 103.71(11)–117.30(11) ° (Table 2). The HFlu ligand connects two Zn(II) ions in the *cis* conformation with the Zn···Zn distance of 11.173(2) Å and the Zn···Zn···Zn angle of 167.54 (11)°. The shortest Zn···Zn interchain distance in **4** is 7.182(2) Å, being shorter than the intrachain Zn···Zn distance. The lattice water molecules are hydrogen-bonded to the alkoxyl OH groups to accrete to the 1-D chain (Table 3).

The C–H $\cdot\cdot\cdot$ F(Cl) and F $\cdot\cdot\cdot$ F interactions play important roles in stabilizing the molecular packing in crystal engineering, which are reviewed by Hulliger et al. recently [43]. The C–H···F(Cl) interactions observed in complexes 1 and 2 are listed in Table 3, which are weaker than the classic hydrogen bonding interactions. It is very interesting to stress that the $F \cdots F$ interaction was only observed in 2 with the F \cdots F distance of 2.576(6) Å, and that no C–H \cdots F and $F \cdots F$ interactions were found in complexes 3 and 4. The dihedral angles between the best planes defined by the two triazoles and phenyl moieties of each HFlu ligand are listed in Table 4. Complexes 1-4 demonstrated that Zn(II) ions had the capacity to change the coordination geometries from tetrahedron to trigonal bipyramid to octahedron that are tuned by the anions, and the flexible HFlu ligand fulfills the requirement of the coordination geometry by the conformational change and the screw of the bis-triazole groups.

3.3. Thermal and luminescent properties

Thermogravimetric analysis (TGA) of complex 1 indicated that 1 lost 12.1% of the total molecular weight at 263 °C, corresponding to the loss of the coordinated DMF molecule (Calc. 14.2%) and gradually decomposed until 950 °C. However, complex 2 lost 18.9% of total molecular weight in the range of 69–211 °C, corresponding to the loss of two lattice DMF and two-coordinated water molecules (Calc. 18.5%). Then it decomposed to lose two HFLu ligands in the 220–675 °C with an experimental loss of weight of 61.4% (Calc. 62.2%), and above 675 °C, the resulting Zn(NO₃)₂ incompletely decomposed to form ZnO powder until 950 °C. The TGA curve of complex 3

Table 4					
Selected	dihedral	angles (°)	for	complexes	1–4

Complex	Plane 1–Plane 2	Plane 1–Plane 3	Plane 2–Plane 3
1	100.1	54.5	46.3
2	106.9	43.3	37.1
3	91.9	43.7	48.4
4	109.4	54.3	61.6

Plane 1 defined by triazole ring: N(1)-C(1)-N(2)-N(3)-C(3).

Plane 2 defined by triazole ring: N(4)–N(5)–C(6)–N(6)–C(7).

Plane 3 defined by phenyl ring: C(8)-C(9)-C(10)-C(11)-C(12)-C(13).

has three weight loss regions: the first observed weight loss in the range of 40–146 °C (5.0%) is in agreement with the calculated value of 4.3% for the loss of two-coordinated water molecules. The second weight loss in the range of 220–705 °C (71.0%) can be assigned to the removal of two HFlu ligands (73.0%). Above 705 °C, the resulting Zn(NO₃)₂ gradually also decomposed with the tendency to form ZnO powder. Complex **4** continuously lost the weight from the beginning with 1.8% of the total molecular weight (Calc. 3.6%) up to 125 °C, which confirmed the phenomenon during the preparation of the complex.

Metal–organic polymeric complexes with d^{10} configuration (Zn²⁺, Ag⁺, Cd²⁺ and so on) have been found to exhibit photoluminescence properties. Here, the photoluminescence of complexes 1–4 in the solid state and in the solution at room temperature was examined. The intense emission for 1–4 occurs at 284 nm upon excitation at 261 nm, but the intensity shows slightly alteration compared to that of free fluconazole ligand. The similar phenomenon was found in the ZnCl₂-HFlu system, which shows different crystal structure from polymer 1 [44,45]. Therefore, the emission was thought to be originated from a ligand-centered π – π * process of 2,4-difluorobenzyl group without significant influence by charge transfer character induced by the Zn(II) cation.

4. Conclusion

By self-assembly of fluconazole with different Zn(II) salts, three types of complexes with structural diversity varying from discrete dimer to one-dimension were firstly isolated. The fluconazole ligand shows good flexile nature to bridge two Zn(II) ions through two triazolyl nitrogen atoms with *trans-/cis*-conformations to fulfill the geometric requirement of Zn(II) ions. This study also shows that anions have great influence on the coordination geometries of Zn(II) ions through binding to Zn(II) or acting as counteranions, which offers a good opportunity in controlling the coordination networks. The fluorescence property of complexes 1–4 does not alter compared to that of the free fluconazole ligand because Zn(II) ions is far away from the fluorescence center without the electronic interactions with the luminescence center.

Acknowledgments

We are thankful for the financial support of the National Nature Science Foundation of China (No. 20501008) and Guangdong Provincial Laboratory for Green Chemical Technology. M.D. acknowledges the financial support from Tianjin Normal University.

Appendix A. Supplementary data

Crystallographic data for the structures described in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos 602704–602707. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (int.) +44 1223/336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc. 2006.06.028.

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