Synthesis, Structure and Properties of a 2D Cadmium(II) Coordination Polymer Based on Fluconazole and Isophthalate Ligands

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A Cd(II) complex based on fluconazole and isophthalate ligands, $\{[Cd(HFlu)(IPA)(H_2O)]\cdot H_2O\}_n$ (**1**), (HFlu = fluconazole; H_2IPA = isophthalic acid) has been synthesized. Single-crystal X-ray analysis reveals that complex **1** has a 2D network structure including unusual triple hydrogen bonds between hydroxyl and triazolyl groups. The complex has also been characterized by IR, UV/Vis and fluorescence spectroscopy, elemental analysis, and thermogravimetry.

Key words: Triple Hydrogen Bond, Coordination Polymer, Fluconazole, UV/Vis Spectra, Fluorescence, Thermogravimetry

Introduction

In recent years, much attention has been accorded to crystal engineering and the construction of coordination polymers with fascinating structural topologies due to their potential application in various fields such as optoelectronics, separation science, gas storage, catalysis, adsorption, host-guest chemistry, electrofunctional materials, luminescence, non-linear optics, and magnetism [1 – 5]. Because the Cd(II) ion with d^{10} configuration exhibits a wide variety of coordination geometries and modes, it is well suited for the construction of various coordination polymers [6].

Fluconazole is known as an antifungal drug first synthesized and reported in the literature by Richardson *et al.* as the outcome of their research initiated in 1970 [7, 8]. We have found that fluconazole as a ligand shows interesting coordinating characteristics to afford extended networks in a head-to-tail mode with good flexibility through rotating and twisting of the C–C and C–N bonds when coordinating to metal ions [9 – 12]. Besides, fluconazole can chelate metal ions with its endodentate nitrogen atoms (N^2) and alkoxo oxygen atom to form binuclear complexes [13]. Furthermore, the HFlu ligand has been proven to be a good candidate to construct polymeric networks because it has several available donors/acceptors [9 – 19].

Herein, we report the cadmium(II) coordination polymer $\{[Cd(HFlu)(IPA)(H_2O)]\cdot H_2O\}_n$ (**1**) (H_2IPA = isophthalic acid). Single-crystal X-ray analysis revealed that this complex is a 2D framework with π-π stacking interactions between adjacent two layers. Free water molecules as space fillers are accommodated in voids and further stabilize the structural framework through extensive hydrogen bonding. Complex **1** shows unusual triple hydrogen bonds between hydroxyl and triazolyl groups which are rarely reported. The thermal stability and fluorescence of this complex have also been studied.

Results and Discussion

Crystal structure description

Selected molecular geometry parameters of complex **1** are listed in Table 1 and the hydrogen bond data in Table 2. Single-crystal X-ray diffraction has revealed that complex **1** crystallizes in the triclinic system, space group $P\bar{1}$ with Z = 2. It forms a 2D framework containing uncoordinated water molecules as space fillers. As shown in Fig. 1, each Cd(II) center is in a distorted pentagonal bipyramidal geometry. Two chelating carboxylate groups from different IPA^{2-} ligands and one nitrogen atom from a fluconazole ligand comprise the equatorial basal plane. One water molecule and one nitrogen atom from another fluconazole ligand occupy the apical sites [O5–Cd1–N1A 158.13(11)°]. The Cd(II) center is displaced about

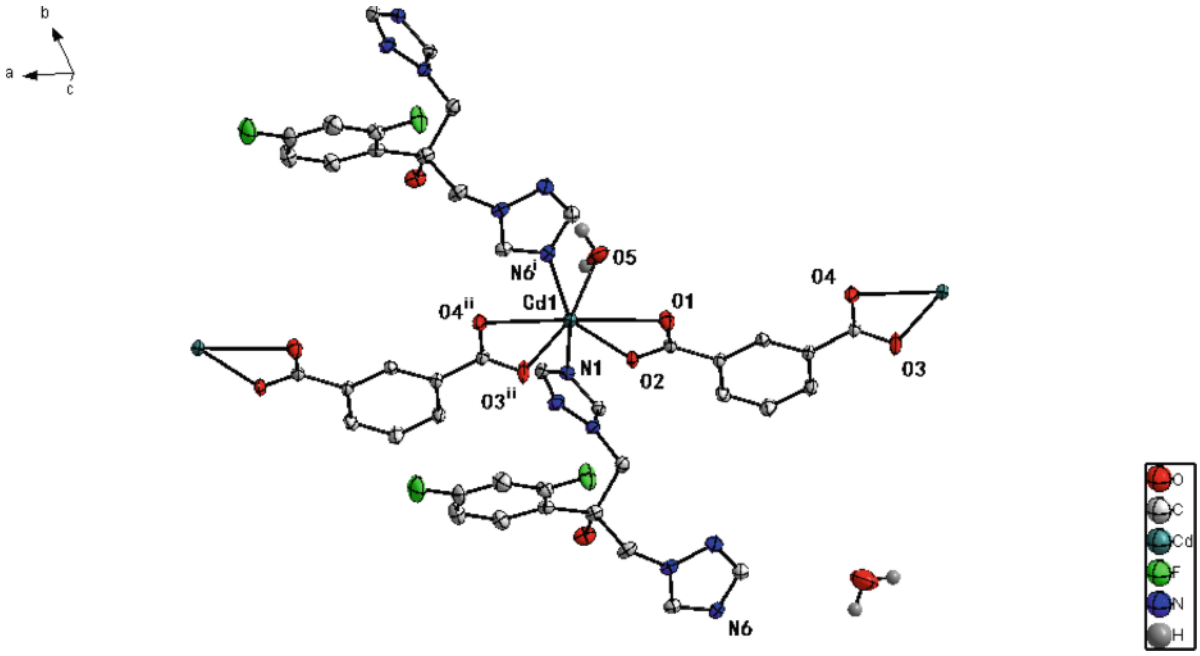

Fig. 1 (color online). Coordination environment of the Cd(II) ions in **1** with displacement ellipsoids at 30 % probability (hydrogen atoms except those of the water moleculs were omitted for clarity). Symmetry codes: (i) $x, y+1, z$; (ii) $x+1, y, z$.

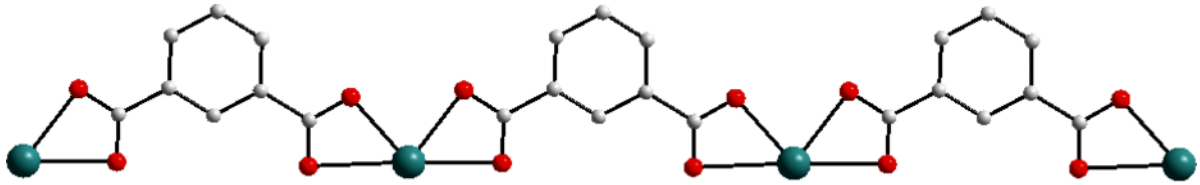

Fig. 2 (color online). View of a metal-carboxylate chain in **1**.

0.023 Å from the equatorial plane. The Cd–O and Cd–N bond lengths are in the ranges 2.306(2) – 2.672(3) Å and 2.307(3) – 2.375(3) Å, respectively, which are comparable to the reported values [20, 21]. However, these bond lengths are significantly different from those in the reported six-coordinated complex $\{[Cd(HFlu)_2(TPA)]\cdot(CH_3OH)_2\}_n$, where the Cd–O bond lengths are generally shorter than the Cd–N bond lengths [22]. The IPA^{2-} ligand acts as a chelating bis-bidentate ligand which bridges different Cd(II) centers giving rise to a metal-carboxylate chain (Fig. 2). The fluconazole ligand links adjacent chains into a (4,4) coordination 2D network with parallelogram grids (Fig. 3). However, unlike most of the known 2D (4,4) grid networks, it is not co-planar but undulated, due to the inherent bent conformations of the fluconazole molecules. The Cd···Cd distance for the atoms connected by IPA^{2-} ligands is 10.278(2) Å, and that between two adjacent cadmium atoms connected by fluconazole is 11.041(2) Å. The intersection angles for the parallelogram grid are 111.06(3)° and 68.94(3)°.

Another structural feature is that adjacent layers are in a face-to-face array (Fig. 4). Although the single-layered network contains a 10.278(2) × 111.041(2) $Å^2$ window (based on the Cd···Cd distances), the effective space of the channels are reduced due to a significant offset in the stacking of adjacent layers. There are π-π stacking interactions between the benzene rings of the IPA^{2-} ligands of adjacent layers with a centroid-to-centroid distance of 3.705(4) Å.

The hydroxyl group of the fluconazole unit forms a tricentered intramolecular hydrogen bond [23] [O(6)–H(6)···O(2)^{iv} 2.785(3) Å, O(6)–H(6)···N(3) 2.998(4) Å, (iv) $-x+2, -y+1, -z+2$] with a car-

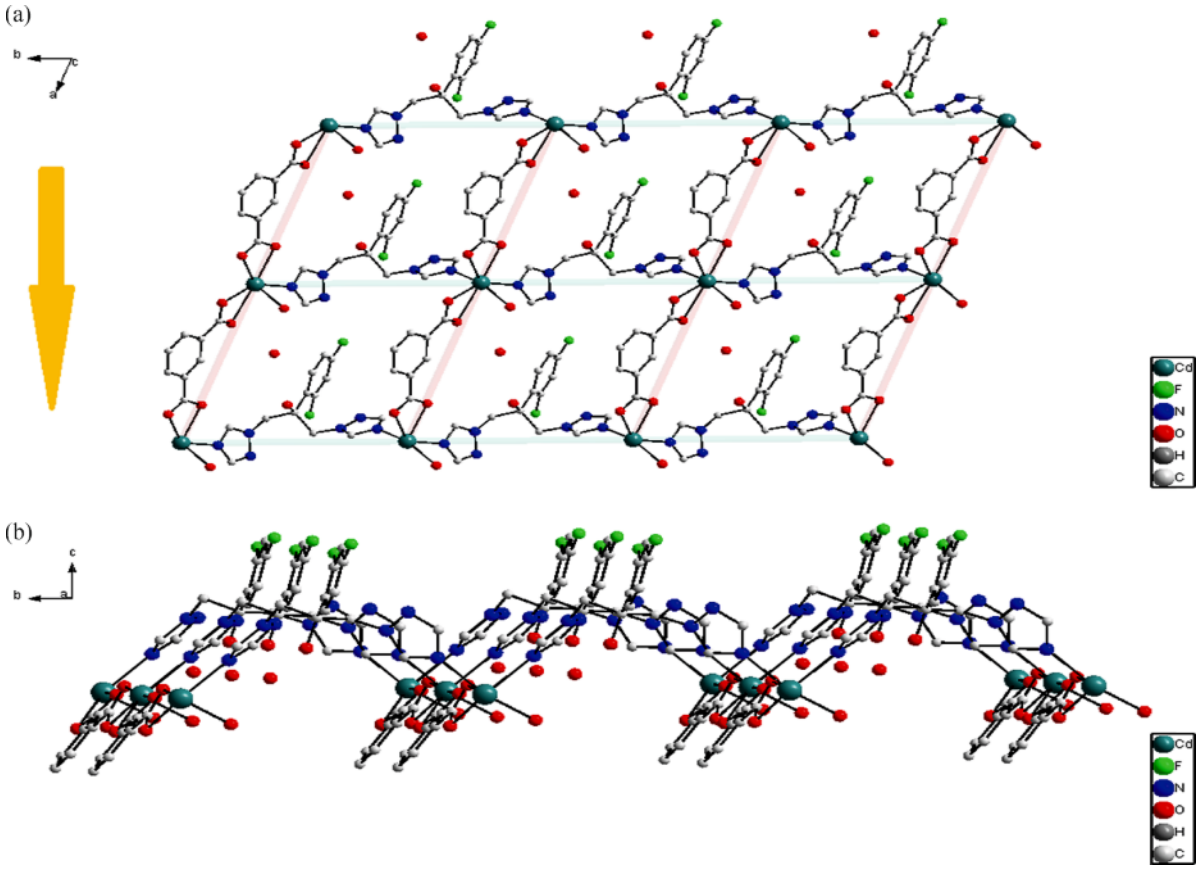

Fig. 3 (color online). (a) Top view and (b) side view of the 2-D network in **1** (hydrogen atoms are omitted for clarity).

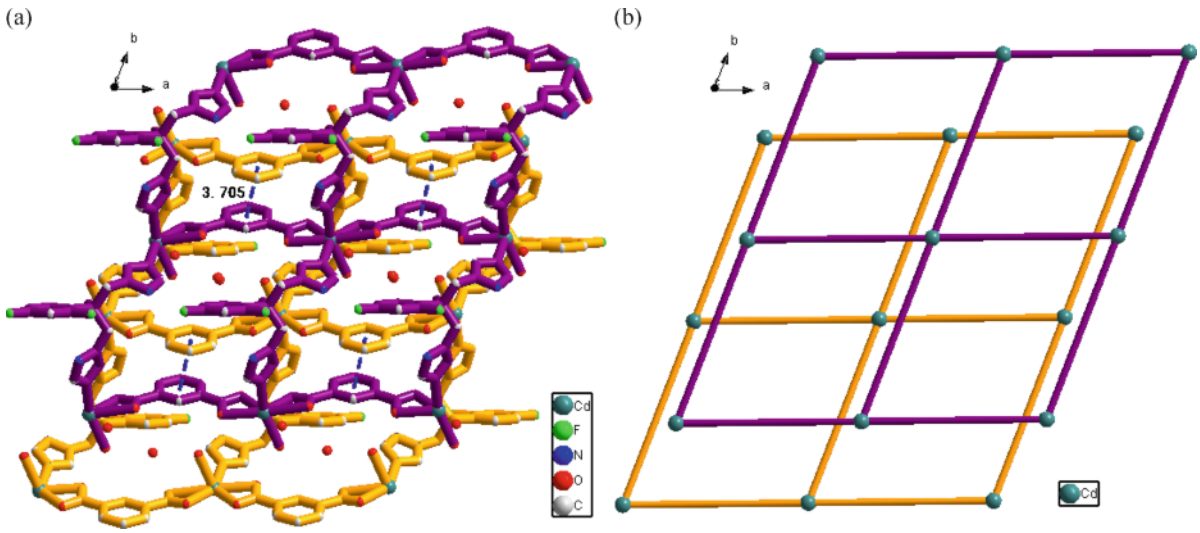

Fig. 4 (color online). (a) Two independent adjacent "wavy" face-to-face layers manner and the π-π stacking interactions in **1**. (b) Schematic illustration of offset stacking of adjacent layers in **1**.

Table 1. Selected bond lengths (Å) and angles (deg) for complex **1**[a].

Cd(1)–O(1)	2.672(3)	O1–Cd1–N1	82.62(10)
Cd(1)–O(2)	2.306(2)	O(2)–Cd(1)–O(5)	80.29(9)
Cd(1)–N(1)	2.307(3)	N(1)–Cd(1)–O(5)	158.13(11)
Cd(1)–O(5)	2.323(3)	O(2)–Cd(1)–N(6)^{i}	146.97(9)
Cd(1)–N(6)^{i}	2.375(3)	N(1)–Cd(1)–N(6)^{i}	90.70(10)
Cd(1)–O(3)^{ii}	2.395(3)	O(5)–Cd(1)–N(6)^{i}	80.84(10)
Cd(1)–O(4)^{ii}	2.461(2)	O(2)–Cd(1)–O(3)	78.89(8)
O(2)–Cd(1)–N(1)	96.93(9)	N(1)–Cd(1)–O(3)	94.79(10)
O(5)–Cd(1)–O(3)	105.81(11)	N(1)–Cd(1)–O(4)	90.86(9)
N(6)^{i}–Cd(1)–O(3)	132.59(9)	O(5)–Cd(1)–O(4)	107.21(10)
O(2)–Cd(1)–O(4)	132.02(8)	N(6)^{i}–Cd(1)–O(4)	79.65(9)
O(3)–Cd(1)–O(4)	53.26(9)	O1–Cd1–O5	78.67(10)
O1–Cd1–N6^{i}	97.97(10)	O1–Cd1–O3	129.45(9)
O1–Cd1–O4	173.05(8)	O1–Cd1–O2	51.73(8)

[a] Symmetry transformations used to generate equivalent atoms: (i) $x, y+1, z$; (ii) $x+1, y, z$.

Table 2. Hydrogen bond parameters for **1**[a].

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	<(D–H···A) (deg)
O(5)–H(5A)···O(4)^{iii}	0.850	2.017	2.712(4)	138.32
O(5)–H(5B)···O(6)^{iv}	0.850	2.245	2.929(4)	137.66
O(6)–H(6)···O(2)^{iv}	0.820	2.052	2.785(3)	148.47
O(6)–H(6)···N(3)	0.820	2.608	2.998(4)	110.74
O(7)–H(7A)···O(1)^{v}	0.850	1.947	2.797(5)	178.16
O(7)–H(7B)···O(5)^{vi}	0.850	2.120	2.969(5)	178.52

[a] Symmetry transformations used to generate equivalent atoms: (iii) $-x+1, -y+2, -z+2$; (iv) $-x+2, -y+1, -z+2$; (v) $x, y-1, z$; (vi) $-x+1, -y+1, -z+2$.

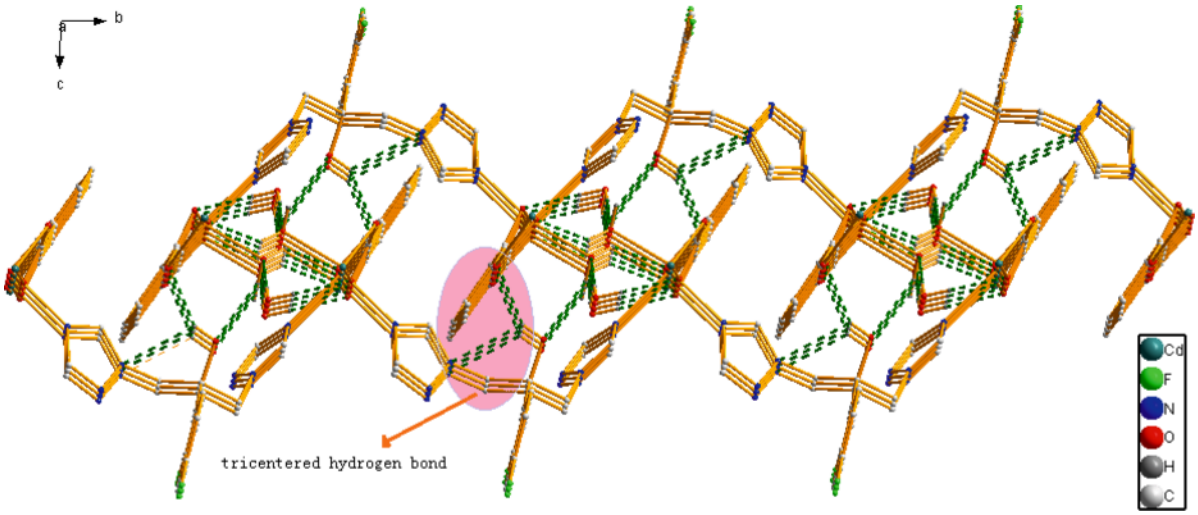

Fig. 5 (color online). A perspective view of hydrogen bonding interactions in **1**.

boxylate oxygen atom and a nitrogen atom of a triazolyl group of a fluconazole unit (Fig. 5). The angle O(6)–H(6)···O(2) is 148.71°, and the angle O(6)–H(6)···N(3) is 110.74°. Although some tricentered hydrogen bonds have been reported [24, 25], to our knowledge, tricentered hydrogen bonds between oxygen and nitrogen atoms are rare. Water molecules are accommodated in the residual voids and further stabilize the structural framework through hydrogen bonding interactions. The extensive hydrogen bond network comprises bonds between coordinated water molecules and carboxylate oxygen atoms of IPA^{2-} [O(5)–H(5A)···O(4)^{iii} 2.712(4) Å, (iii) $-x+1, -y+2, -z+2$], between coordinated water molecules and

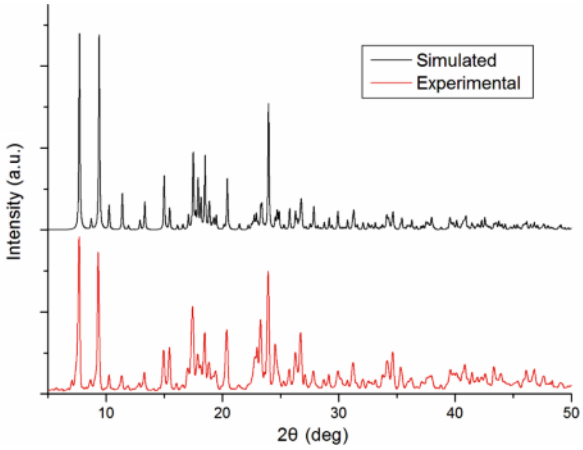

Fig. 6 (color online). Simulated (above) and experimental (below) PXRD patterns of **1**.

fluconazole hydroxyl groups [O(5)–H(5B)· · ·O(6)^{iv} 2.929(4) Å, (iv) $-x+2$, $-y+1$, $-z+2$], between free water molecules and carboxylate oxygen atoms of IPA^{2-} [O(7)–H(7A)· · ·O(1)^{v} 2.797(5) Å, (v) x, $y-1$, z], and between free water molecules and coordinated water molecules [O(7)–H(7B)· · ·O(5)^{vi} 2.969(5) Å, (vi) $-x+1$, $-y+1$, $-z+2$].

Powder diffraction

In order to confirm the phase purity of the polymer, the powder X-ray diffraction pattern was measured (Fig. 6). It is clearly seen that the peak positions in the experimental PXRD patterns are in good agreement with the corresponding simulated ones except for the differences in intensity, which indicate a pure phase of the bulk sample. The difference in reflection intensity between the simulated and experimental patterns may be due to preferred orientation of the crystallites.

Infrared spectroscopy

The IR spectrum of compound **1** exhibits characteristic bands of carboxylate groups at 1559 cm^{-1} for the antisymmetric stretching and at 1392 cm^{-1} for the symmetric stretching. The separation (Δ) between $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ shows that the carboxylate groups chelate to the metal atoms [26].

Electronic spectra

The UV/Vis spectrum of the $\{[Cd(HFlu)(IPA)(H_2O)]\cdot H_2O\}_n$ complex is shown in Fig. 7. It appears that intraligand bands are intense and mask any MLCT band at 254 nm.

Fluorescence properties

The fluorescence properties of the fluconazole ligand and of complex **1** have been studied in solid state at room temperature and the results are shown in Fig. 8. Under the 253 nm excitation, the fluconazole ligand emits strongly at 302 nm assigned to the $\pi^* \rightarrow \pi$ transition. Complex **1** gives a stronger fluorescence at 346 nm. The emission peak is red-shifted, which may be caused by the metal coordination as well as the introduction of the TPA ligand.

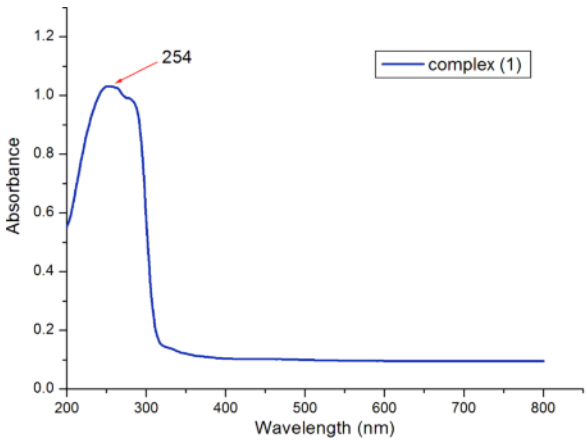

Fig. 7 (color online). UV/Vis spectra of **1** in the solid state at room temperature.

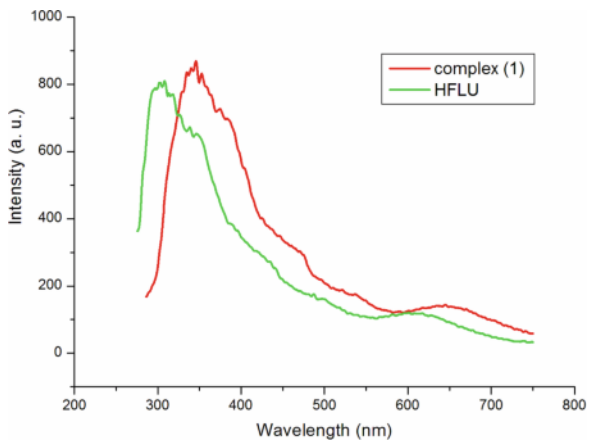

Fig. 8 (color online). Emission spectrum for HFlu and **1** in the solid state at room temperature.

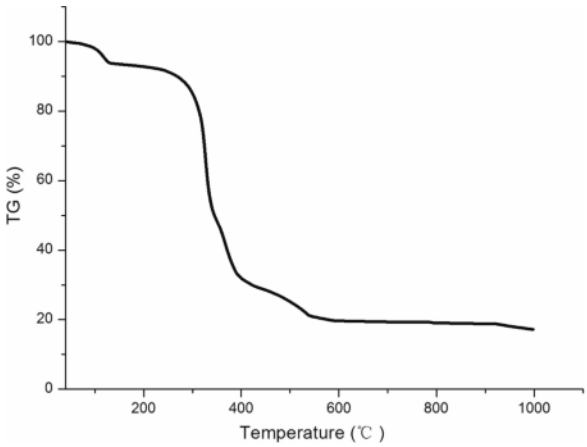

Fig. 9. The TG curve of **1**.

Thermal properties

Complex **1** was subjected to thermogravimetric analysis under nitrogen atmosphere at 10 °C min^{-1} in a temperature range of 40 – 1000 °C. As shown in Fig. 9, there are mainly two steps of weight loss. The first step with 6.6 % weight-loss from 74 to 150 °C corresponds to the release of lattice water and coordinated water molecules (calculated: 5.8 %). The second weight loss of 72.6 % between 222 and 580 °C corresponds to two consecutive pyrolysis processes for HFlu and TPA ligands (calculated: 73.4 %). The final residue of 19.8 % corresponds to CdO (calculated: 20.8 %).

Experimental Section

All chemicals were commercial materials of analytical grade and used as received. The FT-IR spectrum was obtained on a Nicolet 520 FT-IR spectrophotometer by Fourier transform methods in the 4000 – 400 cm^{-1} regions, using KBr pellets. Emission spectra were taken using a Perkin-Elmer LS55 fluorescence spectrometer. Elemental analysis for C, H, N was carried out on a Perkin-Elmer 2400 II elemental analyzer. The powder X-ray diffraction (XRD) pattern was obtained using a pinhole camera (Anton Paar) operating with a point-focused Ni-filtered CuK_α radiation in the 2θ range from 5° to 50° with a scan rate of 0.08° per second. The optical properties were analyzed by UV/Vis diffuse reflectance spectroscopy using a UV/Vis spectrophotometer Cary-500 (Varian Co.), in which $BaSO_4$ was used as the internal standard. Fluorescence spectra were recorded with a F-2500 FL spectrophotometer. Thermogravimetric analysis was performed on a Perkin-Elmer TG/DTA 6300 thermal analyzer under N_2 atmosphere at a heating rate of 10 °C min^{-1} in the temperature range 40 – 1000 °C.

*Preparation of {[Cd(HFlu)(IPA)(H_2O)]·H_2O}$_n$ (**1**)*

A mixture of fluconazole (153 mg, 0.5 mmol), isophthalic acid (83 mg, 0.5 mmol), $CdSO_4$ (208 mg, 1.0 mmol), 15 mL H_2O, and 4 mL ethanol was sealed in a 30 mL Teflon-lined stainless-steel container. An aqueous solution of sodium hydroxide was added dropwise with stirring to adjust the pH value of the solution to 6.0. The mixture was kept under autogenous pressure at 150 °C for 3 days before cooling to room temperature at a rate of 5 °C h^{-1}. Transparent crystals of **1** were obtained, washed with alcohol three times, and dried in a vacuum desiccator using silicagel (yield 71.8 %). Elemental analysis (%) for $C_{21}H_{20}F_2N_6O_7Cd$: calcd. C 40.76, H 3.26, N 13.58; found C 40.68, H 3.17, N 13.70. – IR (KBr, cm^{-1}): ν = 3165w, 3116m, 1606s, 1553s, 1504m, 1476w, 1435m, 1385s, 1282m, 1215w, 1134s, 1097w, 962w, 725m, 674m.

X-Ray data collection and structure refinement

X-Ray diffraction data for the complex were collected on on a Bruker SMART CCD diffractometer equipped with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) at 296(2) K. A suitable single crystal of

Table 3. Crystal structure data for **1**.

Empirical formula	$C_{21}H_{20}CdF_2N_6O_7$
Formula weight	618.83
Temperature, K	296(2)
Wavelength, Å	0.71073
Crystal size, mm^3	0.33 × 0.25 × 0.19
Crystal system	triclinic
Space group	$P\bar{1}$ (no. 2)
a, Å	10.133(2)
b, Å	10.855(2)
c, Å	11.53100(10)
α, deg	89.941(2)
β, deg	83.188(3)
γ, deg	68.940(2)
Volume, $Å^3$	1174.1(3)
Z	2
Calculated density, g cm^{-3}	1.75
Absorption coefficient, mm^{-1}	1.0
F(000), e	620
θ range for data collection, deg	2.01 – 25.00
Data / restraints / parameters	4063 / 0 / 335
Goodnessof-fit on F^2	1.075
$R1$ / $wR2$ [$I > 2\,\sigma(I)$]	0.0249 / 0.0812
$R1$ / $wR2$ (all data)	0.0284 / 0.0989
Largest difference peak / hole, e $Å^{-3}$	0.428 / −0.570

the complex was selected and mounted on a glass fiber to collect the data sets with the ω scan technique. Empirical absorption corrections were applied using the program SADABS [27]. The structure was solved by Direct Methods. All non-hydrogen atoms were refined with anisotropic displacement parameters by full-matrix least-squares based on F^2 using the SHELXTL package [28]. Further details of the structural analysis for the complex are given in Table 3. Selected bond lengths and angles of the complex are listed in Table 1, and hydrogen bond parameters are given in Table 2.

CCDC 943272 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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[1] Q. Liu, Y. Z. Li, Y. Song, H. Liu, Z. Xu, *J. Solid State Chem.* **2004**, *177*, 4701 – 4705, and refs. cited therein.
[2] J. Li, S. Meng, J. Zhang, Y. Song, Z. Huang, H. Zhao, H. Wei, W. Huang, M. P. Cifuentes, M. G. Humphrey, C. Zhang, *Cryst. Eng. Commun.* **2012**, *14*, 2787 – 2796.
[3] D. Niu, J. Yang, J. Guo, W. Kan, S. Song, P. Du, J. Ma, *Cryst. Growth Des.* **2012**, *12*, 2397 – 2410, and refs. cited therein.
[4] H. Wu, X. Dong, J. Ma, H. Liu, J. Yang, H. Bai, *Dalton Trans.* **2009**, 3162 – 3174.
[5] R. Li, Z. Wang, S. Gao, *Cryst. Eng. Commun.* **2009**, *11*, 2096 – 2101.
[6] E. V. Brusau, J. C. Pedregosa, G. E. Narda, G. Pozzi, G. Echeverria, G. Punte, *J. Coord. Chem.* **2001**, *54*, 469 – 480.
[7] K. Richardson, K. Cooper, M. S. Marriott, M. H. Tarbit, P. F. Troke, P. J. Whittle, *Rev. Infect. Dis.* **1990**, *12*, S267 – 271.
[8] K. Richardson, K. Cooper, M. S. Marriott, M. H. Tarbit, P. F. Troke, P. J. Whittle, N. Y. Ann, *Ann. N. Y. Acad. Sci.* **1988**, *544*, 4 – 11.
[9] L. Zhang, Y. Ling, F. Peng, M. Du, *J. Mol. Struct.* **2007**, *829*, 161 – 167.
[10] Y. Ling, L. Zhang, J. Li, A. X. Hu, *Cryst. Growth Des.* **2009**, *9*, 2043 – 2046.
[11] L. Zhang, Y. Ling, M. Du, *Inorg. Chim. Acta* **2007**, *360*, 3182 – 3188.
[12] Y. Ling, L. Zhang, *Acta Crystallogr.* **2007**, *E63*, m4 – m6.
[13] H. Y. Han, Y. L. Song, H. W. Hou, Y. T. Fan, Y. Zhu, *Dalton Trans.* **2006**, 1972 – 1980.
[14] Y. Gong, T. F. Liu, W. Tang, F. J. Wu, W. L. Gao, C. W. Hu, *J. Solid State Chem.* **2007**, *180*, 1476 – 1488.
[15] Y. Gong, W. Tang, W. B. Hou, Z. Y. Zha, C. W. Hu, *Acta Crystallogr.* **2006**, *E62*, m1827 – m1829.
[16] X. J. Zhao, Q. Wang, M. Du, *Inorg. Chim. Acta* **2007**, *360*, 1970 – 1976.
[17] Y. Q. Lan, S. L. Li, K. Z. Shao, X. L. Wang, Z. M. Su, *Dalton Trans.* **2008**, *29*, 3824 – 3835.
[18] Y. Gong, J. Z. Liu, C. W. Hu, W. L. Gao, *Inorg. Chem. Commun.* **2007**, *10*, 575 – 579.
[19] Y. Gong, C. W. Hu, Z. N. Xia, *J. Mol. Struct.* **2007**, *837*, 48 – 57.
[20] X. R. Meng, H. W. Hou, G. Li, B. X. Ye, T. Z. Ge, Y. T. Fan, Y. Zhu, H. Sakiyama, *J. Organomet. Chem.* **2004**, *689*, 1218 – 1229.
[21] C. P. Li, J. Chen, M. Du, *Cryst. Eng. Commun.* **2010**, *12*, 4392 – 4402.
[22] L. Zhang, Y. Ling, D. J. Li, J. Li, M. Du, *Inorg. Chim. Acta* **2010**, *363*, 1031 – 1038.
[23] G. R. Desiraju, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, Oxford, **1999**, p. 5.
[24] X. L. Zhang, X. M. Chen, *Cryst. Growth Des.* **2005**, *5*, 617 – 622.
[25] R. Murugavel, A. Choudhury, M. G. Walawalkar, R. Pothiraja, C. N. R. Rao, *Chem. Rev.* **2008**, *108*, 3549 – 3655.
[26] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, **1958**.
[27] G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen (Germany) **1996**.
[28] G. M. Sheldrick, SHELXTL (version 6.10), Software Reference Manual, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **2000**.