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Syntheses and Structures of Organic–Inorganic Hybrid Compounds Based on Metal–Fluconazole Coordination Polymers and the β-Mo_8O_{26} Anion

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Five organic–inorganic hybrid compounds, namely, $[Co_2(fcz)_4(H_2O)_4][\beta\text{-}Mo_8O_{26}]\cdot 5H_2O$ (**1**), $[Ni_2(fcz)_4(H_2O)_4][\beta\text{-}Mo_8O_{26}]\cdot 5H_2O$ (**2**), $[Zn_2(fcz)_4(\beta\text{-}Mo_8O_{26})]\cdot 4H_2O$ (**3**), $[Cu_2(fcz)_4(\beta\text{-}Mo_8O_{26})]\cdot 4H_2O$ (**4**), and $[Ag_4(fcz)_4(\beta\text{-}Mo_8O_{26})]$ (**5**), where fcz is fluconazole [2-(2,4-difluorophenyl)-1,3-di(1*H*-1,2,4-triazol-1-yl)propan-2-ol], were synthesized under hydrothermal conditions, and crystal structures of **1**–**5** have been determined by X-ray diffraction. In compounds **1** and **2**, metal cations are linked by fluconazole ligands to form hinged chain structures and $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions act as counterions. In compound **3**, Zn(II) cations are bridged by fluconazole ligands to form 2D (4,4) networks, and each pair of these networks is linked by $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions to form a sandwich double-layer structure. In compound **4**, Cu(II) cations are bridged by fluconazole ligands to form 2D (4,4) networks, and these networks are connected by $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions to form a 3D framework. In compound **5**, Ag^I cations and $[Ag_2]^{2+}$ units are bridged by fluconazole ligands to form 2D Ag–fcz layers, and these layers are further connected by $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions to form a complicated 3D structure with the topology of $(7^2\cdot 8^1)_2(7^3\cdot 8^3)(7^2\cdot 8^{11}\cdot 10^1\cdot 12^1)_2$. Thermogravimetric analyses for these compounds are also discussed in detail. The complexes exhibit antitumor activity in vitro, as shown by MTT experiments.

Introduction

Polyoxometalates (POMs), a unique class of metal−oxide clusters, have many properties that make them attractive for applications in catalysis, biology, magnetism, optics, medicine, etc.[1,2] Recently, an important advance in POMs chemistry is the coordination chemistry of polyoxoanions with classical transition metal coordination complexes or fragments. The transition metal complexes may adopt several roles: (1) as charge-compensating coordinated units, (2) as covalently bound subunits of the POM framework itself, and (3) as bridging "ligands" linking polyanion clusters into infinite extended networks. The introduction of metal complexes can not only enrich the frameworks of POMs but also ameliorate their electronic and magnetic properties.[3,4]

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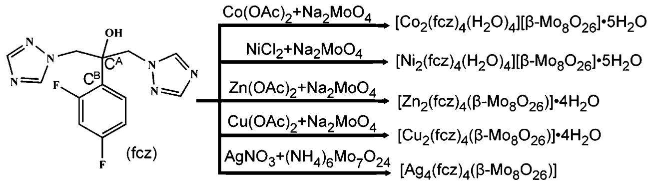
Hill has also pointed out that the versatility of the POMs and grafting organic and organometallic groups onto the POM surface can significantly increase their catalytic or medical applications,[5,2f] particularly the introduction of some medicine molecules into the POM surface.

Of the various POM structures, polyoxomolybdate is a remarkable family for their diverse structures including $\{Mo_4O_{13}\}$,[6a,b] $\{Mo_{36}\}$,[6c] $\{Mo_{154}\}$,[6d,e] $\{Mo_{176}\}$,[6f,g] $\{Mo_{368}\}$,[6h,i] et al., of which the octamolybdate is an interesting cluster with a variety of structural isomers.[7] As reported previously,[3] a lot of metal complexes with rigid ligands such as *o*-phenanthroline and 4,4′-bipyridine may act as 'bridging ligands' to link octamolybdate anion clusters into extended networks. However, the research on the introduction of metal complexes with flexible ligands into octamolybdate clusters is comparatively scarce. A 1,2,4-triazle derivative, fcz, is not only a widely used antifungal medicine but also a good flexible ligand to construct metal−organic polymers with optical properties and medical applications.[8] In this work, fcz was chosen as a flexible ligand, and five organic−inorganic hybrid compounds based on metal−fcz coordination polymers and the $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion were synthesized. $[Co_2(fcz)_4(H_2O)_4][\beta\text{-}Mo_8O_{26}]\cdot 5H_2O$ (**1**), $[Ni_2(fcz)_4(H_2O)_4][\beta\text{-}Mo_8O_{26}]\cdot 5H_2O$ (**2**), $[Zn_2(fcz)_4(\beta\text{-}Mo_8O_{26})]\cdot 4H_2O$ (**3**), $[Cu_2(fcz)_4(\beta\text{-}Mo_8O_{26})]\cdot 4H_2O$ (**4**), and $[Ag_4(fcz)_4(\beta\text{-}Mo_8O_{26})]$ (**5**) (Scheme 1). The systematic investigation of the modulated effect of different metal centers, coordination modes of $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions, and fcz ligands on the ultimate framework will be presented and discussed.

Scheme 1. Schematic View of the Syntheses of the Organic−Inorganic Hybrid Compounds in This Work



Experimental Section

Materials. All reagents and solvents for syntheses were purchased from commercial sources and used as received.

General Characterization and Physical Measurements. The C, H, and N elemental analyses were conducted on a Perkin−Elmer 240C elemental analyzer, and Mo, Co, Ni, Zn, Cu, and Ag were analyzed on a PLASMA-SPEC(I) ICP atomic emission spectrometer. The FT-IR spectra were recorded from KBr pellets in the range 4000−400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Thermogravimetric analyses (TGA) of the samples were performed on a Perkin−Elmer TG-7 analyzer heated from room temperature to 600 °C under nitrogen. Powder X-ray diffraction (XRD) patterns of the samples were collected on a Rigaku D_{max} 2000 X-ray diffractometer with graphite-monochromatized Cu Kα radiation (λ = 0.154 nm) and 2θ in the range 3−60°.

Synthesis of $[Co_2(fcz)_4(H_2O)_4][\beta\text{-}Mo_8O_{26}]\cdot 5H_2O$ (1). A mixture of $Co(OAc)_2\cdot 2H_2O$ (0.050 g, 0.2 mmol), $Na_2MoO_4\cdot 2H_2O$ (0.242 g, 1.0 mmol), and fcz (0.122 g, 0.4 mmol) in water (10 mL) was adjusted with HCl (6M) to pH 2. Then, the mixture was placed in a 23 mL Teflon-lined autoclave and kept under autogenous pressure at 150 °C for 3 days. After the mixture was cooled to room temperature at 10 $°C\cdot h^{-1}$, pink crystals of **1** were obtained. Yield: 54% based on $Co(OAc)_2\cdot 2H_2O$. Anal. Calcd for $C_{52}H_{66}Co_2F_8Mo_8N_{24}O_{39}$ (2688.67): C, 23.23; H, 2.47; N, 12.50; Mo, 28.55; Co, 4.38. Found: C, 23.21; H, 2.50; N, 12.53; Mo, 28.50; Co, 4.39. IR (cm^{-1}): 3846 (w), 3741 (m), 3676 (w), 3618 (w), 1622 (m), 1514 (s), 1463 (w), 1364 (w), 1280 (m), 1214 (w), 1132 (m), 932 (s), 887 (m), 848 (s), 716 (s), 667 (s), 517 (s).

Synthesis of $[Ni_2(fcz)_4(H_2O)_4][\beta\text{-}Mo_8O_{26}]\cdot 5H_2O$ (2). Compound **2** was prepared similarly to compound **1** by using $NiCl_2\cdot 6H_2O$ (0.048 g, 0.2 mmol) instead of $Co(OAc)_2\cdot 2H_2O$. Blue crystals of **2** were obtained in a 40% yield based on $NiCl_2\cdot 6H_2O$. Anal. Calcd for $C_{52}H_{66}F_8Mo_8N_{24}Ni_2O_{39}$ (2688.23): C, 23.23; H, 2.47; N, 12.51; Mo, 28.55; Ni, 4.37. Found: C, 23.20; H, 2.49; N, 12.50; Mo, 28.52; Ni, 4.40. IR (cm^{-1}): 3846 (w), 3741 (w), 3661 (w), 1621 (m), 1531 (s), 1421 (m), 1282 (m), 1215 (m), 1132 (s), 932 (s), 887 (s), 848 (s), 715 (s), 667 (s), 518 (s).

Synthesis of $[Zn_2(fcz)_4(\beta\text{-}Mo_8O_{26})]\cdot 4H_2O$ (3). A mixture of $Zn(OAc)_2\cdot 2H_2O$ (0.044 g, 0.2 mmol), $Na_2MoO_4\cdot 2H_2O$ (0.242 g, 1.0 mmol), and fcz (0.122 g, 0.4 mmol) in water (10 mL) was adjusted with HCl (6M) to pH 3.5. Then, the mixture was placed in a 23 mL Teflon-lined autoclave and kept under autogenous pressure at 150 °C for 3 days. After the mixture was cooled to room temperature at 10 $°C\cdot h^{-1}$, colorless crystals of **3** were obtained.

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Table 1. Crystal Data and Structure Refinements for Compounds **1**−**5**

	1	**2**	**3**	**4**	**5**
formula	$C_{52}H_{66}Co_2F_8Mo_8N_{24}O_{39}$	$C_{52}H_{66}F_8Mo_8N_{24}Ni_2O_{39}$	$C_{52}H_{56}F_8Mo_8N_{24}O_{34}Zn_2$	$C_{52}H_{56}Cu_2F_8Mo_8N_{24}O_{34}$	$C_{52}H_{48}Ag_4F_8Mo_8N_{24}O_{30}$
fw	2688.67	2688.23	2611.47	2607.81	2840.14
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	9.972(4)	9.950(4)	10.571(6)	12.042(9)	12.968(2)
b (Å)	13.484(5)	13.484(5)	11.737(6)	12.174(9)	23.220(2)
c (Å)	16.381(6)	16.367(7)	16.614(9)	15.041(1)	13.070(4)
α (deg)	90.054(6)	90.644(1)	78.773(2)	100.456(1)	90.000
β (deg)	98.811(6)	98.923(1)	86.208(3)	94.465(1)	92.188(5)
γ (deg)	90.094(6)	90.184(5)	82.351(2)	111.190(1)	90.000
V (Å^3)	2176.6(1)	2169.2(1)	2002.2(1)	1996.9(3)	3932.7(7)
Z	1	1	1	1	2
D_{calcd} [g cm^{-3}]	2.051	2.058	2.166	2.169	2.398
F(000)	1320	1322	1276	1274	2728
reflns collected/unique	13 473/9767	13 330/9690	12 148/8866	11 909/8789	23 913/9251
GOF on F^2	1.028	1.031	1.054	1.044	1.023
R1^a [$I > 2\sigma(I)$]	0.0268	0.0257	0.0259	0.0387	0.0268
wR2^b	0.0662	0.0647	0.0651	0.0995	0.0548

^{a} R1 $= \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} wR2 $= |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o{}^2)^2|^{1/2}$.

Yield: 54% based on $Zn(OAc)_2 \cdot 2H_2O$. Anal. Calcd for $C_{52}H_{56}F_8Mo_8N_{24}O_{34}Zn_2$ (2611.47): C, 23.95; H, 2.16; N, 12.89; Mo, 29.44; Zn, 4.86. Found: C, 23.96; H, 2.15; N, 12.91; Mo, 29.48; Zn, 4.82. IR (cm^{-1}): 3846 (w), 3741 (w), 3678 (w), 3617 (m), 1619 (m), 1532 (s), 1514 (s), 1425 (m), 1282 (m), 1129 (s), 951 (s), 889 (s), 840 (s), 668 (s), 516 (s).

Synthesis of [Cu_2(fcz)$_4$(β-Mo_8O_{26})]·$4H_2O$ (4). Compound **4** was prepared similarly to compound **1** by using $Cu(OAc)_2 \cdot H_2O$ (0.040 g, 0.2 mmol) instead of $Co(OAc)_2 \cdot 2H_2O$. Blue crystals of **4** were obtained in a 46% yield based on $Cu(OAc)_2 \cdot H_2O$. Anal. Calcd for $C_{52}H_{56}Cu_2F_8Mo_8N_{24}O_{34}$ (2607.81): C, 23.95; H, 2.16; N, 12.89; Mo, 29.43; Cu, 4.87. Found: C, 23.94; H, 2.18; N, 12.90; Mo, 29.41; Cu, 4.83. IR (cm^{-1}): 3845 (w), 3741 (w), 1612 (m), 1533 (s), 1425 (w), 1280 (m), 1126(s), 956 (s), 897 (s), 849 (s), 713 (s), 662 (s), 517 (s).

Synthesis of [Ag_4(fcz)$_4$(β-Mo_8O_{26})] (5). A mixture of $AgNO_3$ (0.068 g, 0.4 mmol), $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (0.124 g, 0.1 mmol), fcz (0.122 g, 0.4 mmol), and water (10 mL) was placed in a Teflon-lined autoclave (15 mL). After the mixture was heated at 150 °C for 3 days, it was gradually cooled to room temperature at a rate of 10 °C·h^{-1}. Colorless crystals of **5** were obtained. Yield: 48% based on $AgNO_3$. Anal. Calcd for $C_{52}H_{48}Ag_4F_8Mo_8N_{24}O_{30}$ (2840.14): C, 21.99; H, 1.70; N, 11.84; Mo, 27.02; Ag, 15.19. Found: C, 21.94; H, 1.71; N, 11.84; Mo, 27.02; Ag, 15.21. IR (cm^{-1}): 3845 (w), 3741 (m), 3679 (w), 3620 (w), 1620 (m), 1514 (s), 1275 (m), 1134 (s), 945 (s), 902 (s), 836 (s), 680 (s), 517 (s).

X-ray Crystallography. Single-crystal X-ray diffraction data for compounds **1**−**5** were recorded on a Bruker Apex CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Absorption corrections were applied using the multiscan technique. All of the structures were solved by direct methods with SHELXS-97[9] and refined by full-matrix least-squares techniques using the SHELXL-97 program[10] within WINGX.[11] Non-hydrogen atoms were refined with anisotropic temperature parameters. The hydrogen atoms of the organic ligands were refined as rigid groups. The hydrogen atoms of water molecules for the compounds were located from a difference Fourier map. The detailed crystallographic data and structure refinement parameters are summarized in Table 1.

Antitumor Activity Studies. The antitumor activity of compounds **1**−**5** on SMMC-7721 cells was tested by the MTT experiment.[12] The experimental details and results are provided in the Supporting Information.

Results and Discussion

Syntheses of the Compounds. Hydrothermal synthesis causes a reaction to shift from the kinetic to the thermodynamic domain, as compared with traditional aqueous reactions, and provides a powerful tool for the synthesis of hybrid materials.[7k] In addition, hydrothermal conditions can over-

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come the differential solubilities of the organic and inorganic components and are optimal for crystal growth.[13] Many organic−inorganic hybrid POMs with diverse structural architectures have been synthesized using this versatile method.[14] Compounds **1**−**4** were synthesized by conventional hydrothermal methods using HCl as a "mineralizer" or "solubilizer", while compound **5** was synthesized from $AgNO_3$ and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ under hydrothermal condition without using HCl.

Structure Description of 1 and 2. Selected bond distances and angles for compounds **1**−**5** are listed in Tables S1−S5 (see the Supporting Information). Compound **1** consists of $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions and Co−fcz polymeric chains. There are two kinds of crystallographically unique Co^{II} cations and two kinds of fcz ligands. As shown in Figure 1a, each Co^{II} cation is six-coordinated by four nitrogen atoms from four fcz ligands and two water molecules, showing a distorted octahedral geometry. The Co−N bond distances range from 2.126(2) to 2.204(2) Å, and the Co−O bond lengths are 2.101(2) Å for Co1 and 2.084(1) Å for Co2. Each fcz ligand coordinates to two Co^{II} cations in a 'C' shape. Co^{II} cations are bridged by fcz ligands to form 1D hinged chain structure containing $[Co_2(fcz)_2]^{4+}$ rings (Figure 1a).

The well-known $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion[15] consists of eight distorted corner- and/or edge-sharing $\{MoO_6\}$ octahedra. Therefore, the $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion contains four kinds of O atoms: μ_5-O, μ_3-O, μ_2-O, and terminal atoms (O_t). In compound **1**, the $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions do not coordinate to Co cations, only acting as counterions. The hydrogen-bonding mode of the $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion is shown in Figure 1b. Each $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion is hydrogen-bonded to four coordinated water molecules and four fcz hydroxyl groups from four Co−fcz polymeric chains. In the structure of compound **1**, Co−fcz polymeric chains are linked by $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions through hydrogen bonds to form a 3D supramolecular structure (Figure 1c).

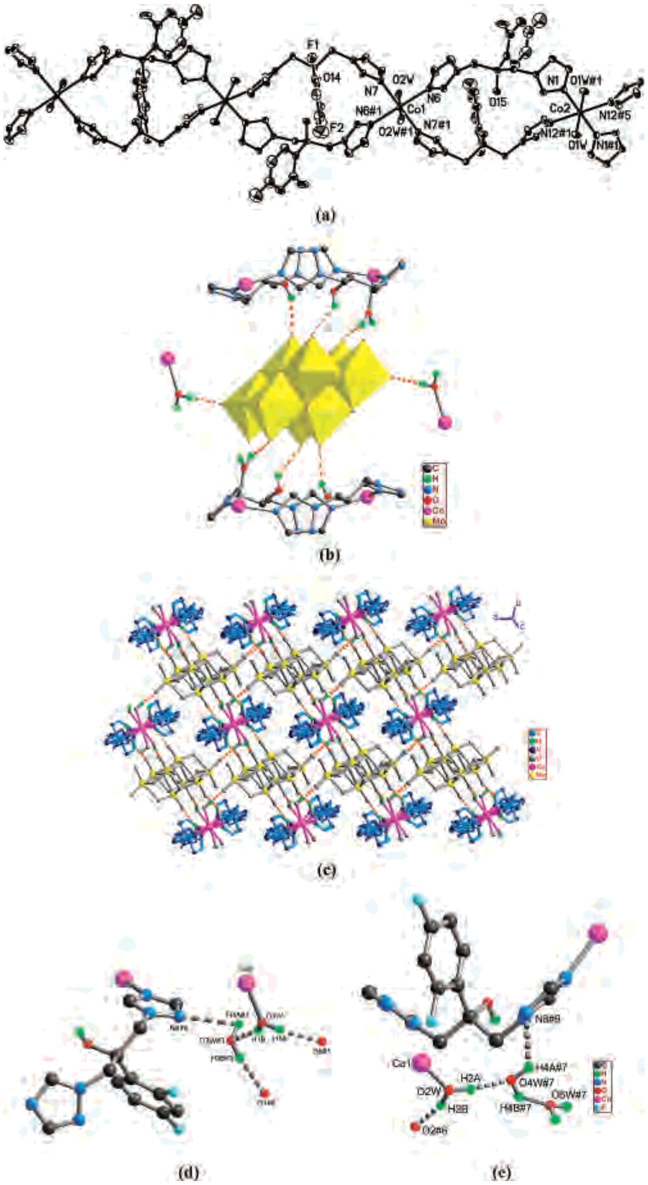

Figure 1. (a) Coordination environments for Co^{II} cations in **1**. (b) Hydrogen-bonding mode of the $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion. (c) View of the supramolecular network through hydrogen-bonding interactions of **1**. (d and e) Water clusters in the structure of **1**.

Water clusters have been widely studied both theoretically and experimentally.[16] A variety of water clusters, $[(H_2O)_n, n = 2-18]$ found in a number of crystal hosts have been characterized and display different configurations. Water molecules in **1** assemble themselves to form a hydrogen-bonded water dimer and trimer, and the geometrical parameters of the water clusters and their association with fcz ligands and $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions are provided in Table 2. As shown in Figure 1d, one coordinated water and one lattice water molecule in **1** assemble into a dimer with an OW⋯OW distance of 2.710(3) Å, while these distances in regular ice, liquid water, and water vapor are 2.74, 2.85, and 2.98

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Table 2. Hydrogen-Bonding Geometry for **1**−**5** (in Å and deg)[a]

	D−H···A	(D−H)	d(D···A)	(D−H···A)
1	O(1W)−H(1A)···O(5)#1	0.83(1)	2.702(3)	163(3)
	O(1W)−H(1B)···O(3W)#3	0.83(1)	2.710(3)	173(3)
	O(2W)−H(2B)···O(2)#6	0.84(3)	2.779(3)	172(3)
	O(2W)−H(2A)···O(4W)#7	0.79(3)	2.657(3)	163(3)
	O(4W)−H(4A)···O(5W)	0.82(4)	2.952(8)	142(5)
	O(14)−H(14)···O(7)#6	0.82	2.870(3)	140.2
	O(15)−H(15)···O(11)#8	0.82	2.860(2)	156.6
2	O(1W)−H(1B)···O(1)#6	0.85(1)	2.710(3)	167(3)
	O(1W)−H(1A)···O(5W)#3	0.85(1)	2.726(3)	174(3)
	O(2W)−H(2A)···O(13)#7	0.85(1)	2.781(2)	171(3)
	O(2W)−H(2B)···O(3W)#2	0.87(1)	2.672(3)	168(3)
	O(3W)−H(3B)···O(4W)	0.85(4)	2.979(7)	144(4)
	O(14)−H(14)···O(6)	0.82	2.871(3)	156.1
	O(15)−H(15)···O(11)#8	0.82	2.853(2)	140.6
3	O(1W)−H(1A)···O(13)	0.93(4)	2.948(6)	140(1)
	O(2W)−H(2A)···O(9)	0.86(4)	3.023(4)	130(1)
	O(14)−H(14A)···O(2W)#5	0.82	2.739(4)	150.9
	O(15)−H(13)···O(11)	0.82	2.828(3)	167.5
4	O(14)−H(13A)···O(2W)#7	0.82	2.68(1)	161.0
	O(15)−H(14)···O(1W)	0.82	2.934(7)	159.4
	O(2W)−H(2B)···O(6)	0.87(2)	2.84(1)	145(2)
5	O(14)−H(14)···O(5)#5	0.82	2.703(3)	168.6

[a] Symmetry codes: #1 −*x*, −*y*, −*z*; #2 −*x* − 1, −*y* − 1, −*z* − 1; #3 *x* − 1, *y* − 1, *z* − 1; #4 −*x*, −*y* + 2, −*z* + 1; #5 *x* + 1, *y* + 1, *z* + 1; #6 −*x*, −*y* + 1, −*z*; #7 *x*, *y*, *z* − 1; #8 −*x*, −*y* + 1, −*z* + 1 for **1**; #1 −*x*, −*y*, −*z*; #2 −*x* + 1, −*y* + 1, −*z* + 1; #3 −*x* + 1, −*y* + 1, −*z*; #4 *x* + 1, *y* + 1, *z* + 1; #5 *x* − 1, *y* − 1, *z* − 1; #6 *x* − 1, *y*, *z*; #7 *x*, *y*, *z* + 1; #8 *x* − 1, *y* − 1 , *z* for **2**; #1 *x*, *y* − 1, *z*; #2 −*x* + 2, −*y* + 1, −*z* + 2; #3 *x* − 1, *y*, *z*; #4 *x* + 1, *y*, *z*; #5 *x*, *y* + 1, *z* for **3**; #7 *x* + 1, *y* + 1, *z* for **4**; #1 −*x*, −*y* + 1, −*z* + 1; #2 −*x*−1, −*y* + 1, −*z* + 3; #3 *x* − 1/2, −*y* + 1/2, *z* + 3/2; #4 *x* + 1/2, −*y* + 1/2, *z* − 3/2; #5 *x* − 1/2, −*y* + 1/2, *z* − 1/2 for **5**.

Å, respectively. The coordinated water molecule O1W donates H-bonds to one terminal oxygen atom of $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion and O3W#3, which in turn donates to one terminal oxygen atom of $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion and one N atom from the fcz ligand. As shown in Figure 1e, the water trimer consists of one coordinated water molecule and two lattice water molecules with OW···OW distances of 2.657(3) and 2.952(8) Å. The coordinated water molecule O2W donates H-bonds to one terminal oxygen atom of the $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion and O4W#7, which in turn donates H-bonds to one N atom of the fcz ligand and O5W#7, which behaves completely as an acceptor.

Compound **2** is isomorphous with compound **1**. The M−O and M−N bond distances and related angles for compounds **1** and **2** are slightly different. Recently, Gong et al. reported the crystal structure of $[Ni_2(fcz)_4(H_2O)_4][\beta\text{-}Mo_8O_{26}]\cdot 6H_2O$ (**6**) from the reaction at 110 °C with $NiCl_2\cdot 6H_2O/Na_2MoO_4\cdot 2H_2O/fcz = 1{:}2{:}1$.[8c] Compounds **6** and **2** show the same structural motif, and the difference between **6** and **2** is a lattice water molecule.

Structure Description of 3. Compound **3** consists of one kind of crystallographically unique Zn^{II} cation and two kinds of unique fcz ligands. As shown in Figure 2a, Zn^{II} cation is coordinated by four nitrogen atoms (Zn−N = 1.978(2)−2.208(2) Å) from four fcz molecules and one terminal oxygen atom (Zn−O = 2.459(1) Å) from the $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion, showing a distorted square pyramidal coordination geometry. Two kinds of fcz molecules coordinate to two Zn^{II} cations in ‘C’ and ‘S’ shapes, respectively. Zn^{II} cations are bridged by fcz ligands to form a 2D (4,4) polymeric layer that contains 44-membered rings with a Zn^{II} cation at each corner and a molecule of fcz at each edge (Figure 2b). All 2,6-diflurophenyl (DFP) groups of the polymeric layer lie on the same side of polymeric layer.

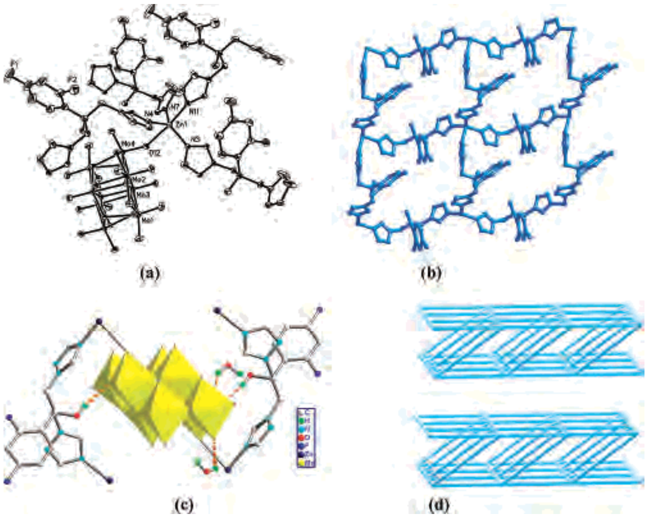

Figure 2. (a) ORTEP diagram showing the coordination environment for Zn cation in **3**. (b) View of the 2D Zn−fcz polymeric layer. (c) The coordination mode of $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion. (d) Schematic representation of the sandwich double-layer structure of **3**.

Each $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion coordinates to two Zn cations from adjacent Zn−fcz polymeric layers (Figure 2c). The cationic Zn−fcz polymeric layers are linked by $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions to form a sandwich double-layer structure with a thickness of 10.0 Å. DFP groups lie on both sides of the double layer (Figures 2d and S1).

Structure Description of 4. Compound **4** contains two kinds of crystallographically unique Cu^{II} cations. The coordination geometries of Cu^{II} cations are shown in Figure 3a. Each Cu^{II} cation lies on a center of symmetry and is coordinated by four nitrogen atoms from four fcz ligands (Cu1−N = 2.010(4)−2.035(4) Å and Cu2−N = 1.986(4)−2.021(3) Å) and two oxygen atoms from two $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions (Cu1−O = 2.433(3) Å and Cu2−O = 2.562(5) Å). Each fcz molecule coordinates to two Cu^{II} cations, and the Cu^{II} cations are bridged by fcz molecules to form a 2D (4,4) polymeric layer (Figure 3b). Unlike compound **3**, the DFP groups of the polymeric layer lie on both sides of the polymeric layer.

Each $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion coordinates to four Cu^{II} cations, and the Cu^{II} cations are bridged by $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions to form a 2D polymeric layer (Figure 3c). A 3D framework of **4** is formed by intersecting the Cu−fcz layers and Cu−$[\beta\text{-}Mo_8O_{26}]^{4-}$ layers (Figure 3d). If $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions are considered as four-connected nodes, the structure of **4** can be symbolized as a net with a $(3^2\cdot 6^2\cdot 7^2)(3^2\cdot 4^4\cdot 5^4\cdot 6^5)_2$ topology.

Structure Description of 5. Compound **5** contains two kinds of crystallographically unique Ag^{I} cations. As shown in Figure 4a, Ag1 is coordinated by two nitrogen atoms from two fcz ligands with Ag1−N distances of 2.181(3) and 2.174(3) Å and two oxygen atoms from the same $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion with Ag1−O distances of 2.589(2) and 2.814(3) Å. Ag2 is coordinated by two nitrogen atoms from two fcz

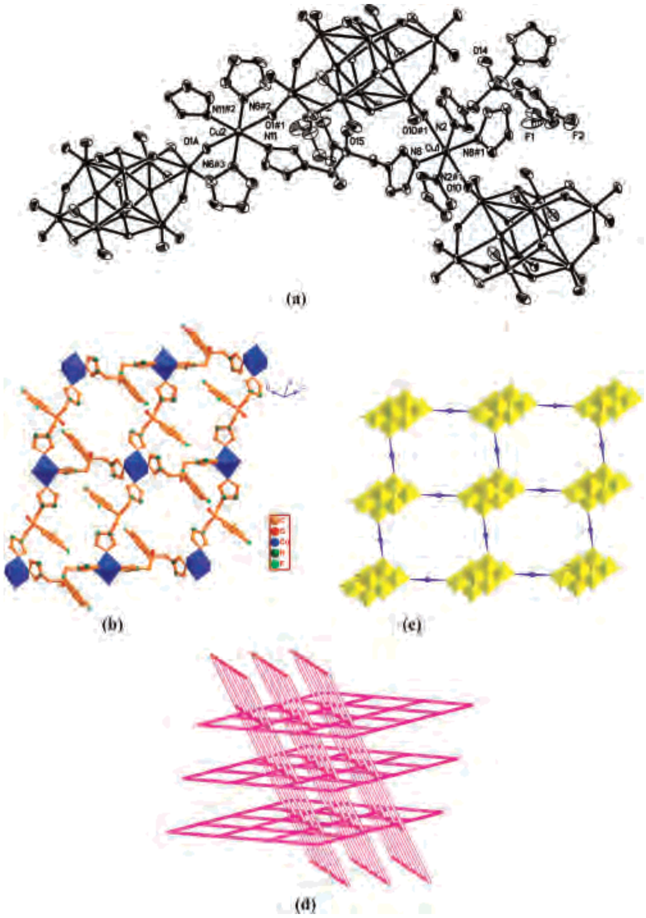

Figure 3. (a) Coordination environments for Cu^{II} cations in **4**. (b) View of the 2D Cu−fcz layer. (c) View of the 2D Cu−$[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ layer. (d) The schematic diagram of the 3D framework of **4**.

ligands and two oxygen atoms from two $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ anions with Ag2−O distances of 2.675 (2) and 2.754 (3) Å. In addition, two adjacent Ag2 cations are linked by Ag···Ag interaction to give a dinuclear $[\text{Ag2}-\text{Ag2}]^{2+}$ unit with a Ag···Ag distance of 2.820 (6) Å which is shorter than the van der Waals contact distance for Ag···Ag of 3.40 Å.[17] Each fcz molecule coordinates to one Ag1 cation and one Ag2 cation, acting as a bridging ligand. Ag1 cations and dinuclear $[\text{Ag2}-\text{Ag2}]^{2+}$ units are bridged by fcz ligands to form a 2D polymeric layer (Figure 4b). DFP groups of the same polymeric layer lie on both sides of the layer.

Each $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ anion coordinates to two Ag1 cations and four Ag2 cations, and these Ag^{I} cations are bridged by $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ anions to form an Ag−$[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ chain (Figure 4c). A 3D framework of **5** is formed by interconnecting the 2D Ag−fcz layers and the 1D Ag-$[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ chains (Figure 4d). If $[\text{Ag2}-\text{Ag2}]^{2+}$ units are considered as six-connected nodes (connecting to four fcz ligands and two $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ anions), $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ can be considered as four-connected nodes (connecting to two Ag1 cations and two $[\text{Ag2}-\text{Ag2}]^{2+}$ units), and Ag1 cations are considered as three-connected nodes. Then the structure of **5** can be symbolized as a net with a $(7^2\cdot8^1)_2(7^3\cdot8^3)(7^2\cdot8^{11}\cdot10^1\cdot12^1)_2$ topology. In addition, F atoms of one Ag−fcz layer are weakly coordinated to the Ag1 cations of another Ag−fcz layer with an Ag−F distance of 2.878 Å (Figure 5).[18]

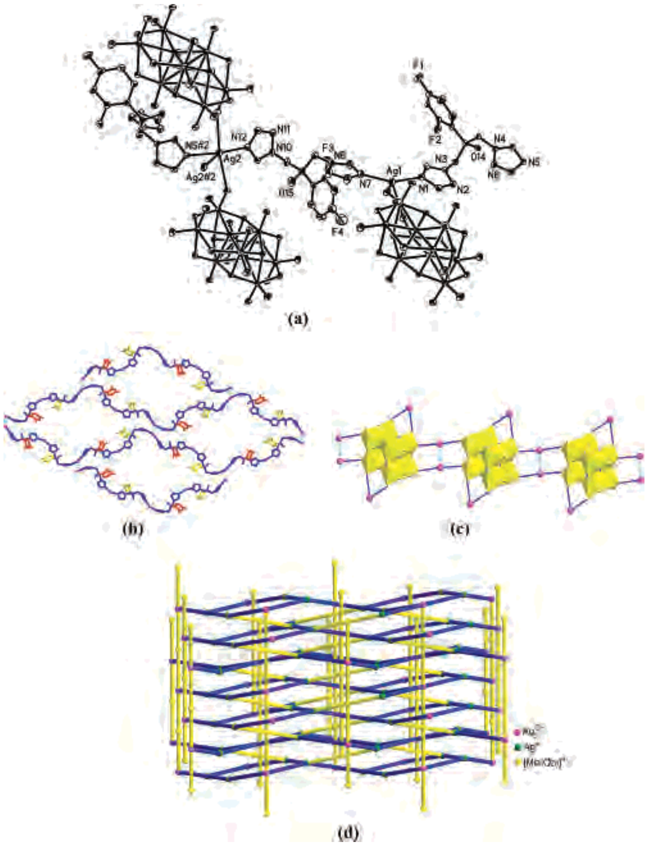

Figure 4. (a) Coordination environments for the Ag^{I} cations in **5**. (b) View of the 2D Ag−fcz layer. (c) View of a 1D Ag−$[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ chain. (d) The schematic diagram of the 3D framework of **5**.

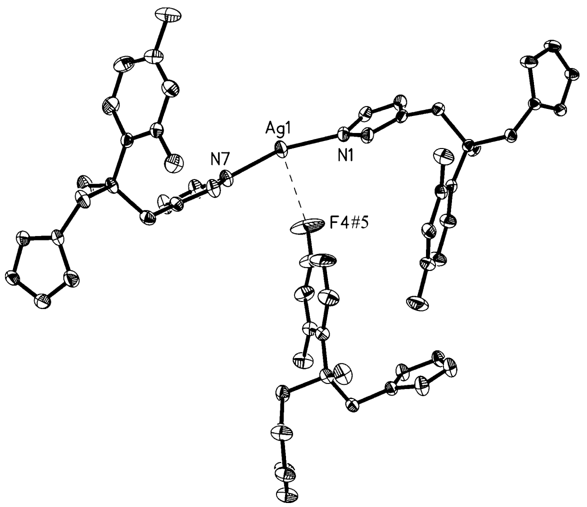

Figure 5. View of the Ag···F interaction in **5**.

Effect of Metal Cations on the Framework. Although 6 is the most common coordination number for the cations

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of Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}, these metal ions have different coordination behaviors. Due to its closed d^{10} electronic shell, Zn^{II} cation has no crystal field stabilization energy (CFSE) and the coordination numbers of Zn^{II} cations are more dependent on the steric effect of ligands than those of Co^{II}, Ni^{II}, and Cu^{II} cations. Moreover, due to the strong Jahn–Teller effect of its d^9 electronic configuration, Cu^{II} cation tends to form an elongated octahedral coordination geometry. For compounds **1**–**4**, since the coordination ability of the nitrogen atoms from fcz ligands is much stronger than water molecules and $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions, each metal cation is first coordinated by four nitrogen atoms. The coordination of the bulky $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion will produce a big steric hindrance which may force the metal cation to take a lower coordination number. For compounds **1** and **2**, although the coordination ability of the $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion is stronger than that of water, the coordination of $[MN_4]^{2+}$ is further completed by two water molecules because Co^{II} and Ni^{II} tend to be six-coordinate. For compound **3**, since the coordination number of Zn^{II} cation has a wider range than those of Co^{II} and Ni^{II} cations, the $[ZnN_4]^{2+}$ unit is further coordinated by one terminal oxygen atom of a $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion, showing a coordination number of 5 instead of 6. For compound **5**, due to the Jahn–Teller effect of the Cu^{II} cation, the $[CuN_4]^{2+}$ unit is further weakly coordinated by two terminal oxygen atoms from two $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions with long Cu–O distances of 2.429(3) and 2.563(5) Å to avoid the steric hindrance. Generally, the Ag^{I} cation shows a lower coordination number than Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} cations. The Ag/fcz molar ratio (1:1) of compound **5** is different from the M/fcz molar ratios (1:2) of compounds **1**–**4**. For compound **5**, each Ag^{I} cation is first coordinated by two fcz nitrogen atoms and the $[AgN_2]^{+}$ unit is further coordinated by two terminal oxygen atoms of $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions. In all, for compounds **1**–**5**, the coordination behaviors of metal ions strongly influence the coordination modes of $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions and finally result in different frameworks of these compounds.

Orientations of DFP Groups in Compounds 1–5. In compounds **1**–**5**, DFP groups of the fcz ligands display different orientations. It is believed that the orientations of DFP groups are influenced by two factors: (1) the steric repulsion between DFP groups and $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions and (2) the hydrogen-bonding interactions of the hydroxyl groups of fcz. In compounds **1** and **2**, the DFP groups direct to both sides of the $[MN_4]$ plane composed of metal cation and four coordinated N atoms. Because $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions do not coordinate to Co^{II} and Ni^{II} cations, the steric repulsion between $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions and DFP groups is very weak. The orientations of DFP groups are mainly determined by the hydrogen-bonding interaction of the hydroxyl group.

For compounds **3**–**5**, metal centers are bridged by fcz ligands to form 2D polymeric layers and the orientation of DFP group can be described by a parameter θ which is defined as the angle between the C^A–C^B bond of the DFP group (see Scheme 1) and the plane composed of metal centers of the polymeric layer. For compound **3**, all DFP groups of one Zn–fcz polymeric layer lie on the same side of the layer and $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions coordinate to the Zn^{II} cations from the other side of the polymeric layer. Therefore, the steric repulsion between $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions and DFP groups is very weak and the orientations of DFP groups with θ values of 34° and 76° are mainly determined by the hydrogen-bonding interaction of the hydroxyl group. For compound **4**, DFP groups of the Cu–fcz polymeric layer lie on both sides of the layer and $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions coordinate to Cu^{II} cations from both sides of the polymeric layer. The orientations of DFP groups with θ values of 17° and 29° are jointly determined the steric repulsion between $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions and DFP groups, as well as the hydrogen-bonding interactions of the hydroxyl groups of fcz. Like compound **4**, in compound **5**, DFP groups of the Ag–fcz polymeric layer lie on both sides of the layer and $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions coordinate to Ag^{I} cations from both sides of the polymeric layer. The orientations of DFP groups with θ values of 45° and 52° are jointly influenced by the steric repulsion between DFP groups and $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions, as well as the hydrogen-bonding interactions of the hydroxyl groups of fcz. The large θ values in **5** favor the formation of Ag···F weak interactions (Figure 5).

Coordination Modes of the $[\beta\text{-}Mo_8O_{26}]^{4-}$ Anion. According to previous studies, the $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions can coordinate to metal ions in a variety of coordination modes to form many attractive compounds with different dimensions.[19] Unambiguously, the coordination modes of $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions have a very significant effect on the final structures of compounds **1**–**5**. In compounds **1** and **2**, $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions act as the charge-compensating anions and space-filling structural subunits and do not coordinate to metal cations. In compound **3**, the $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion acts as a bidentate bridging ligand, coordinating to Zn^{II} centers through two terminal oxygen atoms. This coordination mode has been reported for the $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion.[20] In the structure of **4**, each $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion acts as a quadridentate ligand, coordinating to four copper cations through four terminal oxygen atoms. In compound **5**, the $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion acts as a special octadentate ligand, coordinating to six Ag^{I} cations. The coordination modes of $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions in compounds **4** and **5** have not been reported. These new coordination modes further enrich the coordination chemistry of the $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion.

FT-IR Spectroscopy. In the IR spectra of compounds **1**–**5**, bands in the range 1000–600 cm^{-1} are nearly identical to those of the reported $[\beta\text{-}Mo_8O_{26}]^{4-}$ except slight shifts of some peaks due to the effect of coordination.[21] This indicates

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that the polyanions in compounds **1**−**5** retain the basic [β-Mo_8O_{26}]$^{4-}$ structure. Furthermore, the bands at 3850−3600 and 1700−1000 cm^{-1} can be attributed to the fcz molecules.[8]

Thermal Analysis. In order to characterize the compounds more fully in terms of thermal stability, their thermal behaviors were studied by TGA (Figure S2). The experiments were performed on samples consisting of numerous single crystals of **1**−**5** under N_2 atmosphere with a heating rate of 10 °C min^{-1}.

For compounds **1** and **2**, the weight loss corresponding to the release of water molecules is observed from room temperature to 130 (**1**) and 132 °C (**2**), respectively. The anhydrous compounds begin to decompose at 305 (**1**) and 303 °C (**2**), respectively. Compound **3** lost its water molecules from room temperature to 240 °C. The anhydrous [$Zn_2(fcz)_4Mo_8O_{26}$] is stable up to 310 °C. For **4**, the weight loss of 2.9% (calcd 2.67%) in the range of 35−145 °C is attributed to the release of the crystal water molecules, and the departure of the fcz ligands occurs at 306 °C. Compound **5** is stable up to 308 °C where the framework structure begins to collapse.

Conclusion

In this paper, the hydrothermal reactions of the system of fcz ligand, MoO_4^{2-} anion and different metal ions have been studied. Five organic−inorganic hybrid compounds based on metal−fluconazole coordination polymers and the [β-Mo_8O_{26}]$^{4-}$ anion have been synthesized. It is found that metal ions with different coordination behaviors have significant effects on the formation and dimensionality of the resulting structures. In addition, this study also demonstrates that the flexible fcz molecule is a versatile ligand to construct organic−inorganic hybrid compounds.

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Supporting Information Available: X-ray crystallographic data (CIF); selected bond distances and angles; a diagram of the structure for compound **3**; TG curves for compounds **1**−**5**; simulated and experimental XRD patterns; and the antitumor activity studies of compounds **1**−**5** on SMMC-7721 cells. This material is available free of charge via the Internet at http://pubs.acs.org.

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