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Three Zn(II)/Cd(II)/Mn(II) Coordination Polymers Based on a 2-Hydroxy-*N*-(1*H*-tetrazol-5-yl) Benzamide Ligand: Structures, Magnetic and Photoluminescence Properties

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Three coordination polymers, $\{[Zn(L)_2]\cdot H_2O\}_n$ **(1)**, $\{[Cd(L)_2]\cdot H_2O\}_n$ (**2**) and $\{[Mn(L)_2]\cdot H_2O\}_n$ (**3**) (HL = 2-Hydroxy-*N*-*1H*-tetrazol-5-ylbenzamide), have been prepared under hydrothermal conditions. The X-ray diffraction analysis reveals that compounds **1**- **3** are isomorphous, showing an interdigitated 3-D framework with 1-D channels. Fluorescence studies show that the emissions of complexes **1–2** are attributed to the ligand π–π* transition. Magnetic studies indicate that compound **3** exhibits antiferromagnetic properties.

Introduction

Coordination polymers,[1] a subset of coordination chemistry, comprise a wide range of materials. This kind of crystalline material has fascinating structures and potential versatile application in adsorption,[2] optics,[3] magnetism[4] and catalysis.[5] To obtain coordination materials with desired structures and properties, the design and synthesis of organic ligands are critical. Most of the ligands are carboxylate and aromatic N-heterocycles such as pyridine, imidazolate, triazolate, tetrazolate and their derivatives.[6] Among them, the 5-substituted tetrazolate is considered to be one of the most suitable candidates for the construction of coordination networks through versatile coordination modes because it can bridge metal ions using up to four electron-donating nitrogen atoms of tetrazole group, as well as the donor atoms of 5-substituent functional groups.[7] Meanwhile, amide functional ligands with the unique polar amide group (−CONH−) are now receiving increasing attention. Amide group has the potential to provide two types of hydrogen bonding sites. The –NH moiety acts as an electron acceptor and the –C=O group serves as an electron donor. Holdt's group has reported that amide functionalized imidazole ligands, which can construct robust supramolecular networks through amide−amide hydrogen bonds.[6a,b] In addition, a mass of coordination frameworks with the amide group are prepared.[8,9] However, the coordination product of the amide decorated tetrazole ligands has received little attention. Reports on the coordination polymers constructed by using amide decorated tetrazole ligands are currently quite limited.[10]

Taking inspiration from the above, and as a part of our enduring research on the construction of coordination materials with amide-modified ligands,[9,11] we report herein the synthesis, structure of three coordination frameworks $\{[Zn(L)_2]\cdot H_2O\}_n$ (**1**), $\{[Cd(L)_2]\cdot H_2O\}_n$ (**2**) and$\{[Mn(L)_2]\cdot H_2O\}_n$ (**3**) based on 2-Hydroxy-*N*-(1*H*-tetrazol-5-yl) benzamide (HL, a tetrazole ligand decorated with the amide group) under hydrothermal conditions. Complexes **1**-**3** are isostructures and each displays a 1D chain with tetrazole ring as a bridge. Hydrogen bonds between amide, phenol and tetrazole group play an important role in the formation of the final 3D architecture with 1D channel. The fluorescent properties of **1**, **2** and magnetic property of **3** were also investigated.

Experimental section

Materials and physical measurements

The ligand HL was prepared by using a modified version of a reported procedure.[12] All other reagents and solvents were commercially available and used without further purification. Elemental microanalyses (EA) were performed on a Perkin-Elmer CHN-2400 analyzer. Thermogravimetric analysis (TGA) was performed using a Pyris Diamond system with a heating rate of 10°C min^{-1} under an N_2 atmosphere. Powder X-ray diffraction measurements were recorded on a Bruker D8 ADVANCE using Cu-Kα radiation. Photoluminescence (PL) spectra were recorded using a Xe-lamp source and Edinburgh Instruments FLSP920 steady state spectrometer. Variable-temperature magnetic susceptibilities was measured on a Quantum Design MPMS XL-7 SQUID magnetometer in a magnetic field of 1000Oe under the temperature range 2–300K.

Preparation of complexes of 1, 2 and 3

Synthesis of 2-Hydroxy-*N*-1H-tetrazol-5-yl-benzamide (HL): 1.57g (10 mmol) sample of 2-hydroxybenzoyl chloride is added to a solution of 0.85g (10 mmol) of 5-aminotetrazole and 1mL of triethylamine in 80 mL of DMA. The mixture is stirred for 16 hrs, and then 400 mL water was added. White precipitate formed was filtered and the solid was washed with acetone, water, methanol and finally ether and further dried in vacuum. Yield = 1.18 g (57.5%). IR (KBr): ν/cm^{-1}): 3418(b), 3245(w), 3078(w), 1742(vs), 1688(vs), 1607(vs), 1548(s), 1487(s), 1455(s), 1385(s), 1300(s), 1255(m), 1196(vs), 1160(m), 1120(m), 1049(vs), 897(w), 754(vs), 692(m), 530(w).Elemental analysis: Calcd. for HL ($C_8H_7N_5O_2$, fw = 205.2): C, 46.83; H, 3.44; N, 34.13%. Found: C, 45.83; H, 3.61; N, 33.40%.

Synthesis of $\{[Zn(L)_2]\cdot1.5H_2O\}_n$ (1): A solvothermal reaction of $Zn(NO_3)_2\cdot6H_2O$ (320mg, 1.1 mmol) and HL (103 mg, 0.5 mmol) in 10 mL DMA-H_2O (3 : 2 volume ratio) was performed at 85°C for 5 days (Scheme 1). The colorless block crystals of **1** (35.3mg) were obtained in 28.7% yield (based on ligand). Elemental analysis: Calcd. for $C_{32}H_{29.6}N_{20}O_{10.8}Zn_2$: C, 38.51; H, 2.99; N, 28.07%. Found: C, 38.66; H, 2.94; N, 28.18%. IR (KBr, cm^{-1}): 3439(b), 3246(w), 3187(w), 3120(w), 1654(s), 1578(s), 1522(m), 1463(m), 1391(m), 1303(s), 1241(m), 1148(m), 1092(s), 1038(s), 908(m), 840(w), 796(w), 752(m), 725(m), 684(m), 647(m).

Synthesis of $\{[Cd(L)_2]\cdot3H_2O\}_n$ (2):2 was synthesized in a similar way as **1**, except that $Cd(NO_3)_2\cdot4H_2O$ was used instead of $Zn(NO_3)_2\cdot6H_2O$. Yield: 33.8% based on H_2L (48.6mg). Elemental analysis: Calcd. for $C_{32}H_{35.6}N_{20}O_{13.8}Cd_2$: C, 33.54; H, 3.13; N, 24.45%. Found: C, 33.70; H, 3.09; N, 24.56%. IR data (cm^{-1}): 3442(b), 3252(w), 3185(w), 3109(w), 1651(s), 1576(s), 1520(s), 1458(s), 1388(m), 1312(m), 1237(m), 1146(w), 1094(w), 1033(w), 909(w), 834(w), 793(w), 754(m), 688(m), 646(w).

Synthesis of $\{[Mn(L)_2]\cdot2H_2O\}_n$ (3): 3 was synthesized in a similar way as **1**, except that $MnCl_2\cdot4H_2O$ (0.031 g, 0.16 mmol) was used instead of $Zn(NO_3)_2\cdot6H_2O$. Yield: 63% based on H_2L (78.6mg). Anal. calc. $C_{32}H_{32.6}N_{20}O_{12.3}Mn_2$: C, 38.28; H, 3.27; N, 27.91%. Found: C, 38.14; H, 3.30; N, 27.80%. IR data (cm^{-1}): 3434(b), 3252(w), 3180(w), 3110(w), 1657(s), 1567(s), 1522(s), 1462(s), 1400(s), 1305(s), 1237(s), 1158(m), 1096(w), 1041(w), 911(m), 835(w), 789(m), 754(s), 734(m), 647(m).

X-Ray crystallography

All crystallographic data were carried out with a Bruker Smart APEX(II) area detector equipped with a graphite monochromatic Mo Ka (λ= 0.71073 Å). Lorentz polarization and absorption corrections were applied. The structures were solved by direct methods and refined by the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXS-97). Hydrogen atoms except for those of the uncoordinated water molecules were located geometrically and refined isotropically. Crystallographic data for the four compounds are listed in Table 1. Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC 1410608 (**1**), CCDC 1410609 (**2**) and CCDC 1410610 (**3**).

Results and discussion

Syntheses

Compounds **1–3** were synthesized under hydrothermal conditions. The synthetic conditions for **1–3** are the same, except for using different inorganic salts. The compounds **1–3** are isomorphous, in which the tetrazole ring links two metal ions *via* N2 and N5 atoms. All the two products are stable at ambient temperature and insoluble in common solvents such as methanol, ethanol, acetone, and acetonitrile. The same experiment was carried out on other transition metals such as Fe^{II}, Co^{II} , Ni^{II}, Cu^{II} but did not yield the desired results.

Description of structures

Crystal structure of $\{[Zn(L)]\cdot H_2O\}_n$ (1), $\{[Cd(L)]\cdot H_2O\}_n$ (2) and $\{[Mn(L)]\cdot H_2O\}_n$ (3).

Single crystal X-ray diffraction analysis reveals that **1** belongs to monoclinic system with space group *C*2/c, which is an interdigitated 3D network with 1D channel. Because the structures of **1–3** are isomorphous, compound **1** as a representation is described here in detail. The molecular structures and 3D network of complexes **1–3** are exhibited in the ESI† section (Fig. S1-3, Table S1, ESI†). The Zn(II) center lies in a distorted ZnN_4O_2 octahedral environment, which is provided by four nitrogen atoms and two oxygen atoms from four different L^- ligands. Among them, the equatorial nitrogen atoms and oxygen atoms (N2, $N2^i$, $N3^{ii}$ and O2) are coplanar with the center Zn^{II} ions, and the other nitrogen atom and oxygen atom ($N3^{iii}$ and $O2^i$) occupy the axial positions. The Zn1–N distances are ranging from 2.070(4) to 2.135(3) Å and Zn1–O distance is 2.135(3) Å. In contrast to **1**(Zn), the M-O bond lengths of compounds **2-3** are 2.306(3) Å for **2**(Cd), and 2.173(2) Å for **3**(Mn), the M-N bond lengths of compounds **2-3** are in the range of 2.254(3)- 2.321(3)Å for **2**, and 2.204(2)- 2.247(2)Å for **3**, which exhibit the phenomenon of bond distances shrinking for heavier metal ions in the same period and increasing down in the same group. Since the amide group can partially rotate, the flexibility can allow the sway of phenol and tetrazole group of the ligand to meet the coordination requirement of different metal ions and direct the final structures. The tetrazole and the phenyl rings are not coplanar, they show dihedral angles of 15.9° (between N2–N3–N4–N5-C8 and C1–C2–C3–C4–C5–C6 plane) for **1**, 18.6° for **2** and 20.2° for **3**. In **1**, each Zn^{II} ion is linked with two neighboring Zn^{II} ions by tetrazole group of four L^- ligands to form a 1D chain running along the *c*-axis. (Fig. 1(a)) The phenol group of the ligand acts as the bulge part of the 1-D chain motif. (Fig. 1(b) (c)) The bulges are interdigitated with those of the neighboring chains and have O–H···N and N–H···O hydrogen bonding (Fig S4 ESI†). Analysis of the crystal packing of **1** reveals the presence of π-π stacking interactions between the neighboring 1-D chains. The π-π stacking between phenyl rings of two adjacent ligands arranges in a parallel fashion and the centric distances of the phenyl rings are 4.243(2)Å (Fig S5 ESI†). Thus hydrogen bonds and π-π stacking interactions joined the 1-D chains together and further extended into a 3-D network with 1-D channels (Fig. 1(d), Fig S6, ESI†). The 1-D channels are along the *c*-axis with a cross section of 4.29×4.29 $Å^2$ (the channel size is measured after considering van der Waals radii for constituting atoms). The solvent water molecules cannot be accurately determined, because of the badly disordered structure of them that are further treated by the Platon Squeeze program.[13] The cavity volume is 364.6 $Å^3$ per unit cell, which is *ca.* 17.8% of the total crystal volume for **1** (455.0 $Å^3$, *ca.* 21.2% for **2** and 443.9 $Å^3$, *ca.* 20.7% for **3**) calculated by PLATON.[14]

Thermal stability analysis and powder X-ray diffraction (PXRD)analysis

To study the thermal stability of the complexes, thermogravimetric analyses (TGA) were performed under a nitrogen atmosphere from room temperature to 750 °C with a heating rate of 10 °C min^{-1}. The TGA curve of **1** reveals a weight loss of 5.2% in the region 40–370°C. This weight loss corresponds to six water molecules per formula unit (calcd. 5.4%) and is consistent with the elemental analysis. The residual framework decomposed beyond 390 °C in a series of complicated weight losses and was still continuing when heating ended at 800 °C. The thermal analysis of **2** shows one distinct weight loss of 9.5% in the region 40–320°C. This weight loss corresponds to twelve water molecules per formula unit (calcd. 9.4%). Upon further heating, a second weight loss of 67.03% was observed from 360 to 600 °C, which can be ascribed to the decomposition of organic ligand. The remaining residue corresponds to the formation of CdO (obsd 23.37%, calcd 21.74%). As for **3**, a weight loss of 7.3% is observed in the range of 50–350 °C, corresponding to the removal of eight water molecules per formula unit (calcd: 7.2%). The residual framework decomposed beyond 375 °C in a series of complicated weight losses and was still continuing when heating ended at 800 °C. (Fig. S7, ESI†). The powder X-ray diffraction (PXRD) patterns of the bulk amount of **1**- **3** are consistent with the simulated PXRD patterns, which confirmed the phase purity of the bulk sample (Fig. S8-S10, ESI†). A typical Type II isotherm of **1a**, **2a** and **3a** for N_2 sorption indicate that the desolvated frameworks are nonporous materials (Fig.S11, ESI†).

Fluorescent properties of 1 and 2

Owing to excellent luminescent properties of d^{10} complexes, the solid state luminescent spectra of the free ligand, **1** and **2** were investigated. As depicted in Fig. 2, the fluorescence spectrum of HL exhibits an emission maximum at 454 nm (λ_{ex} = 304 nm), complexes **1** and **2** exhibit one band with the maximum emission peaks a centered at *ca.* 392 (λ_{ex} = 243 nm) and 389 nm (λ_{ex} = 244 nm), respectively. However, no enhancement in the fluorescence intensity is realized, in fact the fluorescence intensity of **2** is virtually weakened. The emission color of free ligand was significantly affected by its incorporation into the Zn- and Cd-containing polymeric frameworks of **1** and **2**, as evidenced by the large shift in the emission. The emissions that occurred in compounds **1** and **2** can still be assigned to free ligand photoluminescence and the large blue-shift may be due to bad conjugation effects compared with those in the free ligand.[15]

Magnetic property of 3

The magnetic property of **3** has been studied over the temperature range of 2-300K. The temperature dependence of $\chi_M T$ is shown in Figure 3. The $\chi_M T$ value at room temperature is 3.87 $cm^3 K mol^{-1}$ lower than the spin-only value of 4.37 $cm^3 K mol^{-1}$ for one high-spin Mn^{II} ion (g = 2, S = 5/2). Within 25K to 300K, $\chi_M T$ did not obviously change, indicating paramagnetic behaviour. However, from 25 K to 2 K, $\chi_M T$ declines to 3.15 $cm^3\ mol^{-1} K$. These findings indicate an antiferromagnetic interaction between the adjacent Mn^{II} ions in **1**. The data can be well described by the Curie–Weiss law with $\theta = -3.91$ K throughout the entire temperature range (Fig. S13, ESI†). According to the structural data, the system can be treated as 1D uniform Mn^{II} chains. To determine the exchange parameters between Mn^{II} ions, χ_M was fitted using an infinite-chain model derived by Fisher, with $H = -2J\Sigma S_i \cdot S_{i+1}$.[16] The corresponding analytical expression for the χ_M product is as follows:

$$\chi_m = \frac{Ng^2\beta^2 S(S+1)}{3kT}\frac{1+u}{1-u} \qquad (1)$$

where,

$$u = \coth\left[\frac{JS(S+1)}{kT}\right] - \left[\frac{kT}{JS(S+1)}\right] \qquad S = 5/2$$

N, *g*, *β* and *k* are the Avogadro constant, Landé factor, Bohr magneton and Boltzmann constant, respectively, and *J* is the exchange coupling constant between adjacent Mn^{II} ions bridged by the tetrazolate-nitrogen atoms. The least-squares fitting of magnetic susceptibilities data led to $J = -0.11\ cm^{-1}$, $g = 1.91$ and $R = 3.6 \times 10^{-4}$ (the agreement factor defined as $R = \Sigma[(\chi_M)_{obsd} - (\chi_M)_{calcd}]^2/\Sigma[(\chi_M)_{obsd}]^2$). The exchange coupling constant indicates that the antiferromagnetic interactions between Mn^{II} centers are weak, and agrees with the long Mn···Mn distance (4.221Å), which induces very small coupling value because of the expanded metallic core and a mismatch in the orientation of magnetic orbitals. The same order (between −0.3 and −3K) has been previously reported.[17]

Conclusions

In summary, by the use of the amide-linked tetrazole ligand with different transition metal salts, three coordination polymers have been constructed under hydrothermal conditions. Complexes **1-3** are isostructures and each displays a 1-D chain with tetrazole ring as a bridge. Hydrogen bonds play an important role in the formation of the final interdigitated 3-D architecture with 1-D channels. Fluorescence studies show that the emissions of complexes **1-2** are attributed to the ligand π–π* transition. The variable-temperature magnetic susceptibility measurements indicate the existence of an anti-ferromagnetic interaction in **3**. More work in this direction is now under progress in our lab.

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Notes and references

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† Electronic Supplementary Information (ESI) available: tables of crystal **1-3** data and structure refinements, ball-and-stick and space-filling drawings of the crystal structures of **1-3**, PXRD data, TGA data, and crystallographic information files in CIF format. See DOI: 10.1039/b000000x/

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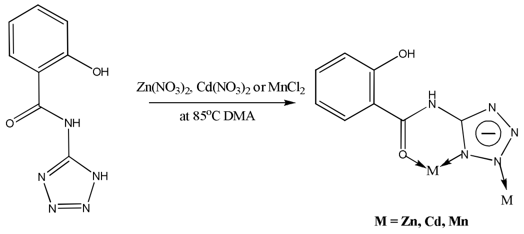

Scheme 1 Reaction and coordination mode of the ligand.

Table 1 Crystallographic data and structure refinement details for **1–3**

	1	**2**	**3**
Formula	$C_{32}H_{24}N_{20}O_{10}Zn_2$	$C_{32}H_{24}N_{20}O_{10}Cd_2$	$C_{32}H_{24}N_{20}O_{10}Mn_2$
M_r	979.45	1073.48	958.54
Crystal	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*
a (Å)	19.841(9)	21.091(9)	20.377(5)
b (Å)	14.971(7)	14.402(7)	14.889(4)
c (Å)	6.892(3)	7.062(3)	7.071(2)
β (°)	92.59(1)	93.23(1)	93.48(1)
V (Å^3)	2045.1(16)	2141.7(17)	2141.3(10)
Z	2	2	2
ρ calc (Mg	1.559	1.635	1.447
μ (mm^{-1})	1.250	1.067	0.662
F(000)	973	1045	946
θ range(°)	3.4–26.0	3.2–28.6	2.0-28.3
Limiting	$-24 \leq h \leq 19$	$-27 \leq h \leq 17$	$-26 \leq h \leq 24$

	1	2	3
indices	$-18 \le k \le 14$ $-7 \le l \le 8$	$-18 \le k \le 19$ $-9 \le l \le 9$	$-19 \le k \le 18$ $-9 \le l \le 8$
Reflns	5601	6834	6542
GOF on F^2	1.01	0.988	1.00
R_1/wR_2 [$I > 2\sigma(I)$]	$R_1 = 0.0558$ w$R_2 = 0.1270$	$R_1 = 0.0354$ w$R_2 = 0.1115$	$R_1 = 0.0492$ w$R_2 = 0.1500$
R_1/wR_2 (all data)	$R_1 = 0.0935$ w$R_2 = 0.1409$	$R_1 = 0.0406$ w$R_2 = 0.1150$	$R_1 = 0.0823$ w$R_2 = 0.1734$

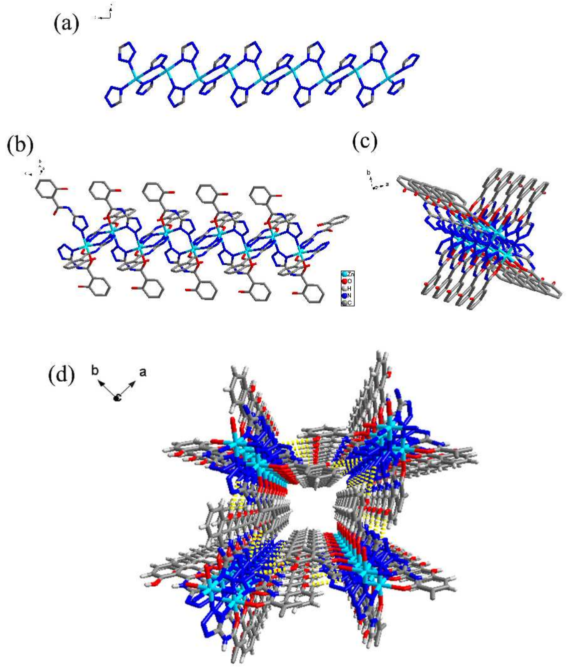

Fig. 1 The crystal structure of **1**. The solvent molecules in the 1-D channels and hydrogen atoms are omitted for clarity. (a)The tetrazole groups coordinate with the adjacent Zn^{II} to form 1 D chain along the *c*-axis. (b) The phenol group of the ligands act as the ridge part of the 1-D chain motif. (c) The 1D structure of **1** viewed from *c* direction. (d) The phenol group in a 1-D chain are interdigitated with those of neighboring 1-D chains using hydrogen bonds (yellow dotted line O1–H1···N5^i, N1–H1N···O1; Symmetry operator: i = -x+3/2, -y+3/2, -z+1) and π–π interactions to form a 3-D structure.

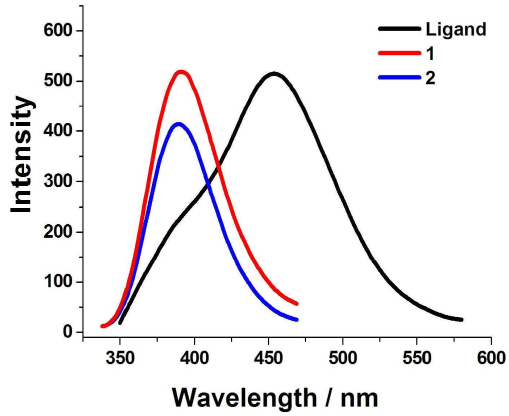

Fig. 2 Solid-state emission spectra of HL, **1** and **2** at room temperature.

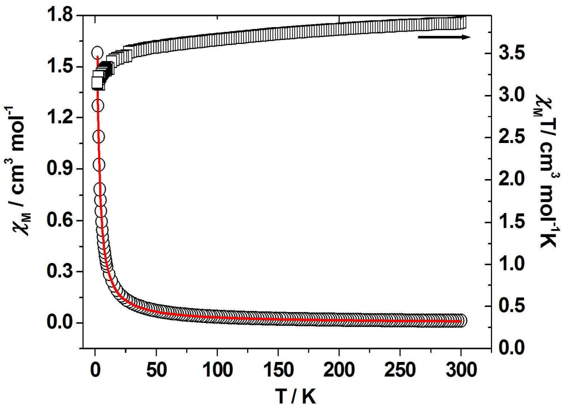

Fig. 3 Temperature dependence of χ_M (○) and $\chi_M T$ (□) for **3**. The solid line corresponds to the best fit according to the parameters in Eq (1) given in the text.