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Synthesis and Structures of Copper(II) and Cadmium(II) Compounds Based on Pyridazine Derivative Ligands[1]

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Abstract—The two new compounds $[Cu(HODA)_2(H_2O)_2] \cdot 3H_2O$ (**I**) and $[Cd(HODA)_2(H_2O)_3]$ (**II**) (HODA = 6-oxo-1,6-dihydropyridazine-4-carboxylic acid) based on pyridazine derivation ligands have been synthesized and characterized by elemental analysis, infrared spectrum and X-ray single crystal diffraction. X-ray analysis shows that in compound **I**, Cu^{2+} ion is four-coordinated with a plane square geometry while Cu^{2+} ion in compound **II** is seven-coordinated with a distorted pentagonal bipyramid geometry. Both of the two units are all connected as 3D supramolecular structures by the intermolecular hydrogen bonds. Moreover, thermal gravimetric analysis of two compounds has been also investigated.

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INTRODUCTION

Nowadays, the design and construction of metal-organic materials have drawn enormous interests in modern inorganic chemistry, which not only due to their promising applications asfunctional materials in fields, including catalysis, gas adsorption, nonlinear optics, magnetism and luminescence but also their fascinating structural topologies [1–5]. It is well known that the resulting structures are mainly dependent upon several factors, such as the chemical nature of organic ligands and the coordination preference of metal ions and so on, while the match of mental centers with suitable ligands which is one of the most important factors [6]. Ligands containing nitrogen and carboxyl, which have been employed to construct many metal-organic frameworks (MOFs) with novel structures and properties, may play different roles [7–9]. Usually the further connection of the frameworks by nitrogen-containing ligands will devote to tuning the structures and properties of the final products, bringing about high dimensional coordination polymers, carboxyl ligands link metal ions into neutral 1D chains or 2D networks, as well as their versatile coordination conformations and strong coordination ability.

In the construction of MOFs, flexile pyrazine derivative ligands were well used for the construction of complexes due to their ready availability and strong coordination ability to transition metal ions. Meanwhile, the combination of N-donors and carboxyl-coordination groups in a promising metal organic ligand may raise a higher interest for structural evolution [10–12]. Inspired by the former considerations, we pushed our attention on exploring various MOFs which can be formed via a mixed ligand system containing N-donors and carboxyl-co-ligand. In the present work, the rigid 6-oxo-1,6-dihydropyridazine-4-carboxylic acid (HODA) ligand has been employed as a building block, which based on the following considerations: (1) The nitrogen-donor ligands have been widely used as an auxiliary recent years, thus the introduction of them is an effective method on the structure of metal compounds owing to the fact that they can satisfy and even mediate the coordination needs of the metal centers and consequently generate more meaningful architectures [13, 14]. (2) The carboxyl-ligands have been intensely investigated, which can donate to the building of the structures with high dimensions. (3) Coordination polymers constructed from the combination of N-donor and carboxyl-ligands remain largely unexplored, therefore, the research of much work is still on the way, and is truely a good originality for the construction of novel topology and networks.

Considering the above-mentioned aspects, the two new compounds, $[Cu(HODA)_2(H_2O)_2] \cdot 3H_2O$ (**I**) and $[Cd(HODA)_2(H_2O)_3]$ (**II**), have been prepaered hydrothermal synthesis. They were well characterized by elemental analysis, infrared spectroscopy (IR) and X-ray single crystal diffraction. Thermo gravimetric analysis (TGA) of two compounds was also used to investigate.

EXPERIMENTAL

Materials and methods. HODA was purchased and used without further purification. All the other starting

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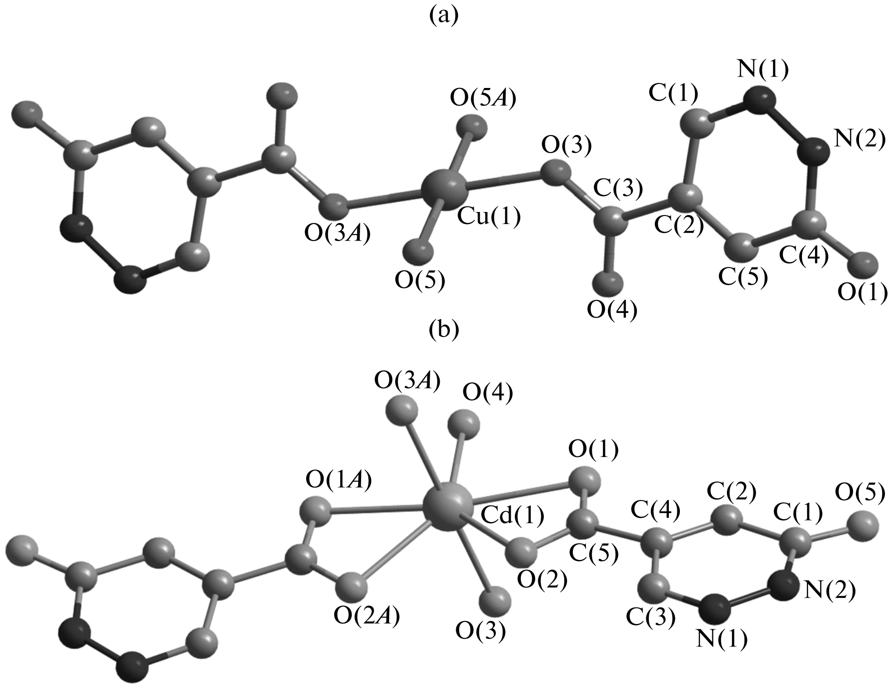

Fig. 1. Molecular structures of **I** (a) and **II** (b).

chemicals and solvents were of reagent grade and were used as received. The FT-IR spectra were obtained from KBr pellets on a Bruker Vectorm 22 spectrometer in the 400–4000 cm^{-1} region. TGA was carried out on a Sta449c thermal analyzer from room temperature to 1000°C with a heating rate of 10°C min^{-1}.

Synthesis of I and II. Compound **I** was synthesized by adding $Cu(NO_3)_2 \cdot 3H_2O$ (0.06024 g, 0.25 mmol) to an ethanol solution in which contains HODA (0.07042 g, 0.5 mmol) and distilled water. Then it was put into a stainless-steel reactor with Teflon liner, heated to 150°C and kept at constant temperature for 72 h. After cooling to room temperature, green crystals of compound **I** were obtained. The yield was 55%.

For $C_{10}H_{18}N_4O_{12}Cu$ (**I**)			
anal. calcd., %:	C, 26.78;	H, 4.020;	N, 12.50.
Found, %:	C, 26.67;	H, 4.000;	N, 12.44.

IR (KBr; ν, cm^{-1}): 3025, 1760, 1600, 1320, 950, 725, 710.

Compound **II** was prepared following the same synthetic procedure as that for compound **I**, except that $Cd(NO_3)_2 \cdot 4H_2O$ was used instead of $Cu(NO_3)_2 \cdot 3H_2O$. Light yellow crystals of compound **II** were obtained. The yield was 63%.

For $C_{10}H_{12}N_4O_9Cd$ (**II**)			
anal. calcd., %:	C, 27.13;	H, 2.713;	N, 12.67.
Found, %:	C, 27.02;	H, 2.702;	N, 12.61.

IR (KBr; ν, cm^{-1}): 3160, 1754, 1610, 1335, 955, 725, 715.

X-ray crystallography. Single-crystal X-ray diffraction measurements were performed on Brucker Smart Apexccd diffractometer with a graphite-monochromated MoK_α radiation at 296(2) K. Absorption corrections were applied to the date using SADABS program. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restrains, while the non-hydrogen atoms were treated with common anisotropic displacement factors and included in the final refinement with geometrical restrains. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using the SHELXL program. The details of the crystal parameters, data collections and refinements for compounds **I** and **II** are summarized in Table 1, selected bond distances and angles are listed in Table 2.

RESULTS AND DISCUSSION

The single-crystal X-ray diffraction analysis reveals that compound **I** is a 3D supramolecular polymer. It contains one Cu^{2+} ion, two HODA ligands, two coordinated water molecules and three lattice water molecules, in which the Cu^{2+} ion is four-coordination. The molecular structure of the compound **I** is shown in Fig. 1a. The plane is occupied by two carboxylic oxygen atoms (O(3), O(3*A*)) from two different HODA ligands and two other oxygen atoms (O(5), O(5*A*))

Table 1. Crystallographic data and structural refinement details of complexes **I** and **II**

Parameter	Value	
	I	**II**
Color/shape	Green/block	Light yellow/block
Formula weight	449.82	444.64
Wavelength, Å	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$Fdd2$
Unit cell dimensions:		
a, Å	6.2777(8)	12.8227(13)
b, Å	6.9141(9)	36.088(4)
c, Å	10.7504(14)	6.1875(6)
α, deg	72.986(2)	
β, deg	77.784(2)	
γ, deg	73.604(2)	
Z; V, Å^3	1; 423.80(9)	8; 2863.3(5)
ρ_{calcd}, mg/m^3	1.763	2.063
Absorption coefficient, mm^{-1}	1.363	1.585
F(000)	231	1760
θ Range for data collection, deg	2.00–26.05	3.37–26.77
Reflections collected	2296	3903
Independent reflection (R_{int})	1627 (0.0142)	1456 (0.0239)
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	1627/6/133	1456/1/127
Goodness-of-fit on F^2	1.122	1.079
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0348$, $wR_2 = 0.1126$	$R_1 = 0.0239$, $wR_2 = 0.0635$
R indices (all data)	$R_1 = 0.0391$, $wR_2 = 0.1398$	$R_1 = 0.0253$, $wR_2 = 0.0644$
Largest diff. peak and hole, e/Å^3	0.316 and –0.593	0.290 and –0.272

from coordinated water molecules. The length of the Cu(1)–O(3) bond is 1.933(2) Å and that of Cu(1)–O(5) is 1.984(2) Å, which form a plane square structure. As the Table 2 shows, the bond angle of O(3)Cu(1)O(5) do not significantly deviate from orthogonal, ranging from 87.6(10)° to 92.4(10)°.

In compound I, there are three kinds of the intermolecular H-bonds interactions. As shown in Fig. 2a, one kind of hydrogen bonds of N–H···O type has been observed between the hydrogen atoms from the lattice water molecules and the nitrogen atoms from the HODA ligands (2.823 Å for N(2)···O(2)). The second kind of hydrogen bonds existing between the lattice water molecules and the coordinated water molecules has been found (2.727 Å for O(5)···O(2) and 2.796 Å for O(6)···O(2)). The third kind of hydrogen bonds is between the coordinated water molecules and the oxygen atoms from the HODA ligands, in which the O(6)···O(5) bond is relatively longer (3.190 Å) (Table 3). Thus the units of I are linked as a 3D supramolecular structure by the intermolecular H-bonds.

In compound **II** (Fig. 1b), Cd(II) atom is seven-coordinated in a distorted pentagonal bipyramid geometry, in which the equatorial sites are occupied by five oxygen atoms (O(1), O(1*A*), O(2), O(2*A*), and O(4)). The four in five oxygen atoms mentioned are from two HODA ligands, while the last one is from the coordinated water molecule. The bond lengths range from 2.234(5) to 2.431(3) Å. The axial site is formed by the two coordinated water molecules (O(3), O(3*A*)), while the length of those bonds are all 2.349(3) Å. In compound II, the bond angles of OCdO do not significantly deviate from orthogonal (Table 2).

As shown in Fig. 2b, hydrogen bonds of N–H···O type in **II** have been observed between the hydrogen atoms from the HODA ligands and the coordinated

Table 2. Selected bond distances (Å) and angles (deg) for the two compounds*

Bond	d, Å	Bond	d, Å
I			
Cu(1)–O(3)	1.933(2)	Cu(1)–O(5)	1.984(2)
II			
Cd(1)–O(1)	2.431(3)	Cd(1)–O(3)	2.349(3)
Cd(1)–O(2)	2.350(3)		2.234(5)
Angle	ω, deg	Angle	ω, deg
II			
O(1)Cd(1)O(1*A*)	167.20(13)	O(2)Cd(1)O(1)	54.37(10)
O(2)Cd(1)O(1*A*)	138.35(10)	O(3*A*)Cd(1)O(1*A*)	84.35(11)
O(2)Cd(1)O(2)	84.70(14)	O(3*A*)Cd(1)O(2)	89.55(12)
O(3)Cd(1)O(1)	84.35(11)	O(3*A*)Cd(1)O(2*A*)	91.00(13)
O(3)Cd(1)O(1*A*)	95.57(11)	O(4)Cd(1)O(1)	83.60(7)
O(3)Cd(1)O(2)	91.00(13)	O(4)Cd(1)O(2)	137.65(7)
O(3)Cd(1)O(2*A*)	89.55(12)	O(4)Cd(1)O(3)	89.63(9)
O(3*A*)Cd(1)O(3)	179.25(18)		

* Symmetry transformations used to generate equivalent atoms: (*A*) $-x + 2$, $-y$, z.

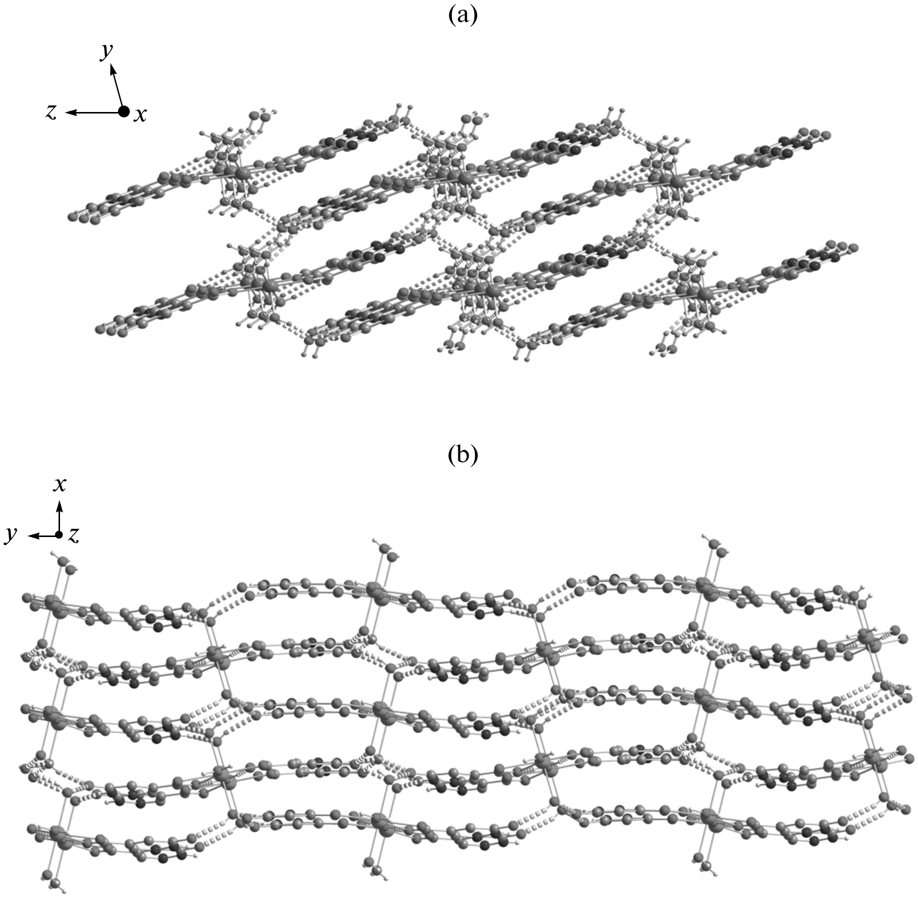

Fig. 2. 3D supramolecular structure constructed via H-bond interactions in structures **I** (a) and **II** (b).

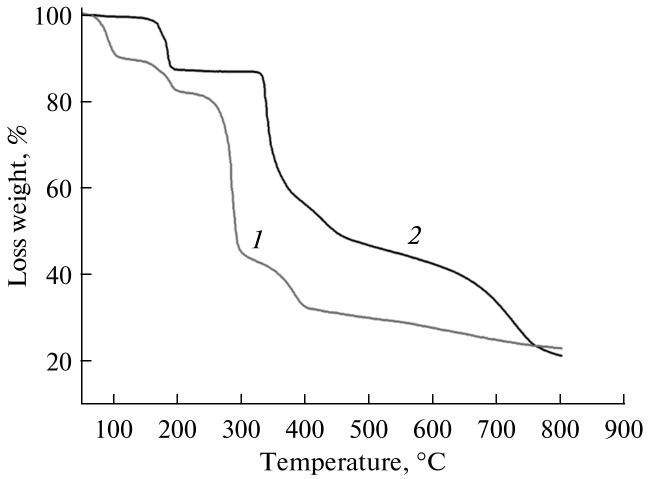

Fig. 3. TG of the compounds **I** (*1*) and **II** (*2*).

water molecules (2.847 for N(2)···O(3)). Meanwhile the other kind of hydrogen bonds has been found, existing between the hydrogen atoms from the coordinated water molecules and the oxygen atoms from the HODA ligands. The data for such hydrogen bonds are as follows: 2.696 Å for O(3)···O(5), 2.724 Å for O(4)···O(2). Every oxygen atoms of the coordinated water molecules are all in part connecting adjacent two units of $[Cd(HODA)_2(H_2O)_3]$ (Table 3). Thus 3D supramolecular structure of compound **II** is formed.

TGA was carried out to characterize the thermal stability of the compound **I** and **II** under a nitrogen atmosphere with a heating rate of 10°C/min (Fig. 3). The thermal decomposition of the compound **I** can be mainly formed by three stages. The first step occurred at 67–124°C, in which the lattice water molecules were lost (calcd.: 12.02%, found: 11.05%). At around 153 to 206°C, the coordination water molecules lost (calcd.: 8.17%, found: 8.70%) and the anhydrous product was stable upon to 235°C and then the third step occurred. The left residue of 17.99% can be attributed to CuO (calcd.: 16.41%). As for the compound II, there was no obvious weight loss until the decomposition of the framework occurred at about 157°C, which belong to the loss of the coordination water molecules (calcd.: 12.16%, found: 12.77%). At around 327°C, its second weight loss started. At that time, CdO was continuously formed. The weight of

Table 3. Hydrogen bond interactions for the two compounds

D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
I				
N(2)–H(2)···O(2)	0.86	1.98	2.823(4)	165
O(2)–H(2*A*)···O(1)	0.94	1.86	2.730(4)	152
O(2)–H(2*B*)···O(6)	0.85(3)	2.02(4)	2.796(4)	151(4)
O(5)–H(5*A*)···O(2)	0.82	1.91	2.727(3)	171
O(5)–H(5*B*)···O(1)	0.89	1.85	2.716(3)	165
O(6)–H(6*A*)···O(4)	0.73	2.02	2.709(5)	159
O(6)–H(6*B*)···O(5)	0.91(3)	2.29(12)	3.190(5)	167(14)
C(1)–H(1)···O(3)	0.93	2.47	2.780(4)	100
C(1)–H(1)···O(4)	0.93	2.59	3.325(5)	136
C(5)–H(5)···N(1)	0.93	2.56	3.486(4)	171
II				
N(2)–H(2)···O(3)	0.86(4)	2.01(5)	2.847(4)	165(4)
O(3)–H(3*A*)···O(5)	0.71(5)	1.99(5)	2.697(5)	179(7)
O(3)–H(3*B*)···O(5)	0.72(4)	2.00(4)	2.701(4)	164(4)
O(4)–H(4*A*)···O(2)	1.02(10)	1.75(11)	2.724(5)	157(8)

residue of compound **II** is 27.65% at 800°C which corresponding to the calculation of 29.37%.

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