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Construction of three low dimensional Zn(II) complexes based on different organic-carboxylic acids

Xiu-Xia Zhou, Mao-Sheng Liu, Xiao-Ming Lin, Hua-Cai Fang, Jian-Qiao Chen, Ding-Qiao Yang, Yue-Peng Cai *

Key Lab of Technology on Electrochemical Energy Storage and Power Generation in Guangdong Universities, School of Chemistry and Environment, South China Normal University, Guangzhou 510006, PR China

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ABSTRACT

Three new Zn(II) complexes based on different organic-carboxylic acids, $[Zn(mba)_2(2,2'\text{-bipy})]$ (**1**), $[Zn(mpdaH)_2(H_2O)_4]\cdot 4H_2O$ (**2**) and $[Zn(cda)_2(H_2O)_2]_n$ (**3**) (Hmba = 4-methylbenzoic acid, H_2mpda = 2,6-dimethylpyridine-3,5-dicarboxylic acid and H_2cda = chelidonic acid) have been synthesized successfully under hydrothermal conditions. X-ray single crystal diffractions show that compounds **1** and **2** are the mononuclear and **3** is one-dimensional chain, in which the Zn(II) centers have different coordination geometries with octahedron for **1** and **2** and tetrahedron for **3**. Through π–π stacking and/or hydrogen bonding (O–H···O and O–H···N) interactions, different supramolecular structures are assembled, namely, 2D supramolecular layer for **1** and 3D supramolecular networks for **2** and **3**. Furthermore, the IR, TGA and luminescent properties are also investigated in this work.

1. Introduction

The rational design and synthesis of metal-organic frameworks (MOFs) with carboxylic acids using various secondary building units (SBUs) connected through coordination bonds, supramolecular contacts (hydrogen bonding, π···π stacking, etc.), or their combination, continue to be interesting and attractive due to not only their potential properties in catalysis, magnetic behavior, optical material and adsorption, but also their intriguing network architectures [1–5]. A large number of different dimensional coordination polymers have been prepared and characterized using a variety of carboxylic acids. Of the many such kinds of compounds investigated, those containing benzene-core carboxylic acids constitute an important family as they have proven to be good candidates for the rich coordination modes, such as terminal monodentate, chelating to one metal center and various modes of bridging coordination of two, three, four or even five metal centers [6], and also function as hydrogen-bond acceptors as well as donors in assembling supramolecular complexes [7–8]. In recent years, the scope of the investigations on benzene-core carboxylic acids has been enhanced enormously by using N- or O-heterocyclic dicarboxylic acids such as pyridine-, pyran-dicarboxylic acids which can use their carboxylate oxygens and nitrogen or oxygen atoms on the heterocycle to approach metal ions, to form interesting frameworks [9–10]. Although quite a number of compounds have been prepared and explored by the use of such heterocyclic dicarboxylic acids, there are still a great deal of uncharacterized compounds with novel crystal structures emerged under various reaction conditions, and these new compounds mostly are serendipitous, especially the emergence of fancy and intricate supramolecular architectures assembled by small building blocks through hydrogen bonding and π···π stacking interactions, which greatly attract chemists' attention.

In the past years, we have prepared a series of new metal-organic frameworks in the presence of heterocyclic multi-carboxylic acids via the hydrothermal synthesis, and their supramolecular architectures have also been investigated [11]. In order to continue and extend our work, we have recently synthesized three new Zn(II) complexes with 4-methylbenzoic acid, pyridine- and pyran-dicarboxylic acids, that is, $[Zn(mba)_2(2,2'\text{-bipy})]$ (**1**), $[Zn(mpdaH)_2(H_2O)_4]\cdot 4H_2O$ (**2**) and $[Zn(cda)_2(H_2O)_2]_n$ (**3**). Compounds **1** and **2** are prepared from 4-methylbenzoic acid (Hmba) and 2,6-dimethylpyridine-3,5-dicarboxylic acid (H_2mpdc), respectively, and they are both zero-dimensional structures, while compound **3** is synthesized from chelidonic acid (H_2cda) and it possesses a one-dimensional linear structure. Through π···π stacking or hydrogen bonding (O–H···O) interactions, compounds **1** and **3** are further assembled into 2D layer and 3D network supramolecular structures, respectively. However, compound **2** is connected into three-dimensional supramolecular structure through hydrogen bonding (O–H···O and O–H···N) and π···π stacking interactions. To the best of our knowledge, these three carboxylic acids (Hmba, H_2mpdc and H_2cda) and their supramolecular coordination

* Corresponding author. Tel.: +86 020 33033475; fax: +86 20 85215865.
E-mail address: ypcai8@yahoo.com (Y.-P. Cai).

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chemistry have been less explored up to now [9]. Thus, it is interesting to study the hydrothermal synthesis and coordination chemistry of these ligands and explore the photoluminescence of the resulted coordination frameworks. In this work, we describe the synthesis, characteristic and properties of the three new complexes.

2. Experimental

2.1. Materials and measurements

All materials were reagent grade, obtained from commercial sources and used without further purification. Elemental analyses were performed on a Perkin–Elmer 240C analytical instrument. The metal analysis was performed on an ICP AES Liberty Series II Varian apparatus. IR spectra in the 4000–400 cm^{-1} range were measured with a Thermo Nicolet 320 FT-IR spectrometer using KBr discs. Thermal analyses (under nitrogenated atmosphere, heating rate of 5 °C/min) were carried out in a Labsys NETZSCH TG 209 Setaram apparatus. The luminescent spectra for the solid-state were recorded at room temperature on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width is 5.0 nm.

2.2. Preparation of complex [Zn(mba)$_2$(2,2′bipy)] (**1**)

A mixture of Hmba (0.135 g, 1.0 mmol), $Zn(ClO_4)_2 \cdot 6H_2O$(0.186 g, 0.50 mmol), 2,2′-bipy (0.078 g, 0.50 mmol) and H_2O (10 cm^3) was placed in a 20 cm^3 Teflon reactor and kept under autogenous pressure at 160 °C for 3 days, and then slowly cooled to room temperature at a rate of 0.5 °C min^{-1}. Colourless block crystals of **1** suited for single crystal X-ray diffraction analyses were formed with a yield of approximately 22% (based on Zn). *Anal.* calc. for $C_{26}H_{22}N_2O_4Zn$: C, 63.49; H, 4.51; N, 5.70. Found: C, 63.46; H, 4.55; N, 5.63; Zn, 13.32%. Zn, 13.29%. Selected IR data (KBr, cm^{-1}): 3035(w), 2937(m), 1632(s), 1553(s), 1472(w), 1435(m), 1401(m), 1376(m), 1313(s), 1276(m), 1192(m), 1160(w), 1121(w), 1089(s), 1017(vs), 926(s), 793(w), 768(s), 661(m).

2.3. Preparation of complex [Zn(mpdcH)$_2$(H_2O)$_4$] · 4H_2O (**2**)

Similar to the preparation of **1**, the hydrothermal reaction of H_2mpdc (0.181 g, 1.0 mmol), $Zn(ClO_4)_2 \cdot 6H_2O$ (0.186 g, 0.50 mmol), 2,2′-bipy (0.078 g, 0.50 mmol) and H_2O (10 cm^3) in a 20 cm^3 Teflon reactor under autogenous pressure was performed at 160 °C for 72 h and then was cooled to room temperature at a rate of ca. 0.5 °C min^{-1} to give colorless prism crystals of **2** (yield: 31% based on Zn). Zn, 11.02. *Anal.* calc. for $C_{18}H_{32}N_2O_{16}Zn$: C, 36.16; H, 5.40; N, 4.69; Zn, 10.94. Found: C, 36.09; H, 5.49; N, 4.72%. Selected IR data (KBr, cm^{-1}): 3439(br), 1645(s), 1595(s), 1434(m), 1385(s), 1359(s), 1196(m), 1124(w), 1060(w), 1029(w), 932(w), 794(w), 746(m).

2.4. Preparation of complex [Zn(cda)$_2$(H_2O)$_2$]$_n$ (**3**)

Compound **3** was obtained using the same reaction procedure as described for compound **2** taking H_2cda in place of H_2mpdc. The colorless block crystals of **3** were isolated in about 38% yield (based on Zn). *Anal.* calc. for $C_7H_6O_8Zn$: C, 29.66; H, 2.13; Zn, 23.06. Found: C, 29.62; H, 2.25; Zn, 23.12%. Selected IR data (KBr, cm^{-1}): 3419(br), 1625(s), 1575(m), 1520(m), 1429(s), 1387(s), 1337(m), 1202(w), 1190(m), 1120(m), 1060(m), 856(m), 748(m), 726(m).

2.5. X-ray crystallography

The three complexes **1**–**3** were determined by single crystal X-ray diffraction. Suitable single crystals were mounted on a glass fiber and the intensity data were collected on a Bruker APEX II diffractometer at 298 K using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Absorption corrections were performed using the SADABS program [12]. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 of data using SHELXTL software [13]. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically, the aqua hydrogen atoms were located from difference maps and refined with isotropic temperature factors. A summary of parameters for the data collection and refinements for three complexes are given in Table 1. Selected bond lengths and angles for complexes **1–3** are listed in Table 2. Hydrogen-bonding data of complexes **1–3** are listed in Table 3.

Table 1
Crystal data and structure refinement for compounds **1**–**3**

Complex	**1**	**2**	**3**
Empirical formula	$C_{26}H_{22}N_2O_4Zn$	$C_{18}H_{32}N_2O_{16}Zn$	C_7H6O_8Zn
Formula weight	491.83	597.83	283.49
Temperature (K)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions			
a (Å)	7.6208(4)	7.6312(4)	5.1098(2)
b (Å)	9.8140(6)	8.6555(4)	9.3271(4)
c (Å)	15.7439(9)	10.7260(5)	9.8661(4)
α (°)	79.148(3)	69.635(2)	104.937(2)
β (°)	83.929(3)	69.686(2	95.279(2)
γ (°)	79.936(3)	83.593(2)	93.442(2)
V (Å^3)	1135.4(1)	622.9(1)	450.7(1)
Z	2	1	2
$\rho_{calc.}$ (mg m^{-3})	1.439	1.594	2.089
μ (m^{-1})	1.117	1.067	2.753
F(000)	508	312	284
Crystal size (mm)	0.26 × 0.22 × 0.17	0.22 × 0.20 × 0.17	0.28 × 0.26 × 0.22
θ Range for data collection (°)	2.70–25.50	2.71–25.50	2.15–27.50
$h/k/l$ (maximum, minimum)	−9,9/−11,7/−19,18	−9,9/−10,10/−12,12	−6,6/−12,11/−12,12
Reflections collected	5245	3767	5675
Unique (R_{int})	3766 (0.0227)	2284 (0.0207)	2033 (0.0178)
Completeness to q = 27.13 (%)	99.10	98.10	98.10
Absorption correction	empirical	empirical	empirical
Maximum and minimum transmission	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	3766/0/300	2284/12/196	2033/6/158
Goodness-of-fit on F^2	1.046	1.081	1.028
Final R_1[a], wR_2[b] indices [$I > 2\sigma(I)$]	0.0424, 0.0975	0.0274, 0.0753	0.0203, 0.0534
R_1, wR_2 indices (all data)	0.0596, 0.1072	0.0276, 0.0756	0.0211, 0.0538
Largest difference in peak and hole (e Å^{-3})	0.341/−0.306	0.354/−0.334	0.366/−0. 502

[a] $R = \sum|F_o| - |F_c|/S|F_o|$.

[b] $wR = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(F_o^2)2]1/2$. $w = 1/[\sigma^2(F_o^2) + (0.0472P)^2 + 0.3107P]$ for **1**, $w = 1/[\sigma^2(F_o^2) + (0.0389P)^2 + 0.2999P]$ for **2**, $w = 1/[\sigma^2(F_o^2) + (0.0282P)^2 + 0.2805P]$ for **3**, $P = (F_o^2 + 2F_c^2)/3$.