



Three complexes based on ligands 1-hydroxybenzotriazole and 1,4-benzenedicarboxylic acid: Synthesis, structures and luminescence properties

Zhong-Qiang Zhang^{a,b}, Ru-Dan Huang^{a,*}, Yan-Qing Xu^a, Li-Qiong Yu^a, Zhi-Wei Jiao^a, Qin-Lei Zhu^a, Chang-Wen Hu^{a,*}

^a Department of Chemistry, School of Science, Beijing Institute of Technology, Beijing 100081, PR China

^b Department of Chemistry, HengShui University, HengShui City, HeBei Province 053000, PR China

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ABSTRACT

Three new complexes, $[\text{Mn}(\text{OBt})_2(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$ (**1**) (OBt = 1-hydroxybenzotriazole ion), $[\text{Zn}_2(\text{OBt})_2(\text{BDC})(\text{H}_2\text{O}) \cdot \text{H}_2\text{O}]_n$ (**2**) (H_2BDC = 1,4-benzenedicarboxylic acid), and $[\text{Cu}_3(\text{OBt})_2(\text{BDC})(\mu_3\text{-OH})_2(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ (**3**) were synthesized by hydrothermal method and were characterized by elemental analysis, IR spectroscopy, TGA, XRPD, and single-crystal X-ray diffraction. The results from single-crystal X-ray diffraction indicate that **1**, **2** and **3** are zero-dimensional (0D), two-dimensional (2D) and two-dimensional (2D) frameworks, respectively. In particular, there are all two crystallographically unique metal ions in the structures of complexes **2** and **3**. Complex **2** possesses two helical chains in its structure. In the structure of **3**, the chains that are built from tri-copper clusters and $\mu_3\text{-O}$ atoms are connected with BDC^{2-} to construct 2D grid structure. The luminescence properties of the three complexes were investigated.

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1. Introduction

The current increasing interest of experts in metal–organic frameworks not only stems from their potential applications in areas such as optoelectronics, magnetism, ion exchange, catalysis, nonlinear optics, fluorescent materials, and porous materials, but also from their intriguing variety of topologies and motifs [1–5]. The compounds that with one or several azole rings in molecule have various types of coordination modes and strong linking ability through bridging with proper metal ions, such as monodentate, bidentate, tridentate, and chelating [6–17].

Benzotriazolates (HBt) and its derivatives are very important compounds which have an azole ring in molecule [18–27]. One of HBt derivatives, HOBt, is a well-known peptide-coupling additive [28,29]. It exhibits corrosion inhibitive properties toward Cu [30,31] and Fe [32,33]. However, there are few relative literatures reported about complexes based on HOBt [29–39]. In the molecule structure of HOBt, one hydroxide substitutes H that connected N(1) of the azole ring (Scheme 1), thus the O atom of hydroxide and two N atoms of azole ring in HOBt can be coordinated to metal ions. In addition, when it coordinates to metal ions, the steric influence of exocyclic O atom on hydroxide is weaker than the influence of N on azole ring. Therefore, HOBt provides more coordination modes and choices than HBt does while HOBt is coordinating to metal ions.

The motivation for this study was the expectation that HOBt could potentially provide various coordination motifs to form either discrete or consecutive complexes under appropriate synthesis condition, and could build a variety of types for complexes with various novel and attractive topologies.

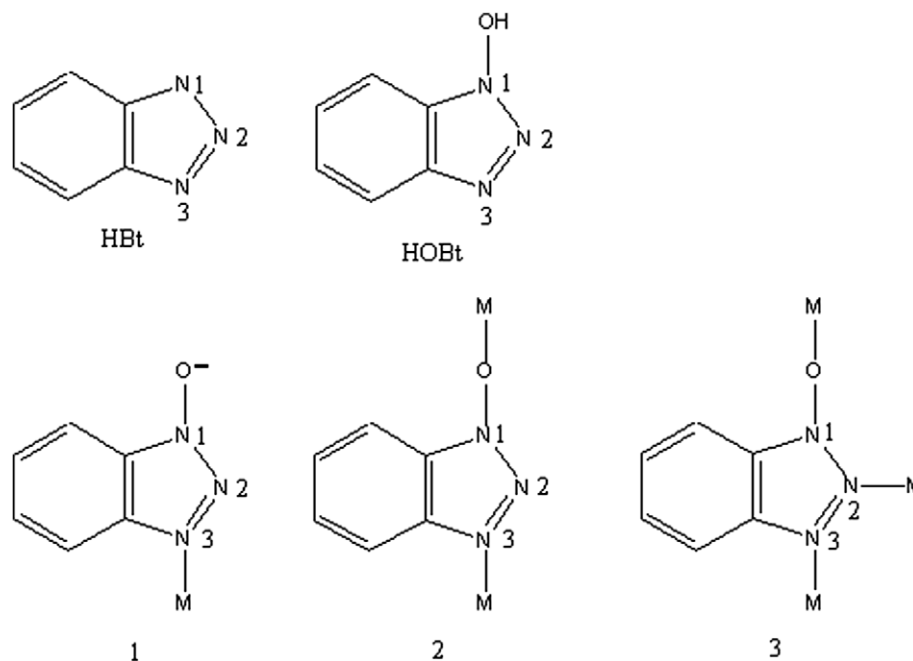
The three coordination modes between HOBt and metal ions are shown in Scheme 1. As a structural building block, HOBt may link metal centers through N(2), N(3) on azole ring or O atoms on hydroxide to provide secondary building units (SBUs). These building blocks can then be linked through the three coordination sites to expand to high-dimensional materials. Otherwise, $\pi\text{-}\pi$ conjugation including six-member ring and five-member ring that exists in the molecule of HOBt, and the new complexes based on HOBt may exhibit interesting luminescence properties.

H_2BDC is an important ligand [40–45]. There are a lot of relative literatures illustrating complexes based on H_2BDC [40–45]. The two coordination modes between H_2BDC and metal ions are shown in Scheme 2. H_2BDC is usually employed in the architectures for metal ions coordination polymers [46]. We aimed to explore promising synthetic routes for the construction of metal–organic complexes via combination of HOBt and H_2BDC and metal cations. The synthetic strategy is to construct 1D framework using HOBt and metal cations, then achieve new high-dimensional MOFs by BDC^{2-} ions as bridging ligand.

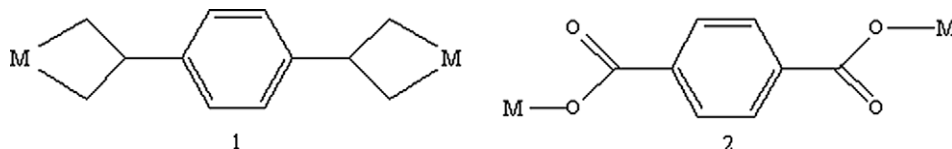
In this paper, three novel complexes, $[\text{Mn}(\text{OBt})_2(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$, $[\text{Zn}_2(\text{OBt})_2(\text{BDC})(\text{H}_2\text{O}) \cdot \text{H}_2\text{O}]_n$ and $[\text{Cu}_3(\text{OBt})_2(\text{BDC})(\mu_3\text{-OH})_2(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$, were synthesized and were characterized by elemental

* Corresponding authors. Tel.: +86 10 68912668.

E-mail address: huangrd@bit.edu.cn (R.-D. Huang).



Scheme 1. Three coordinated modes of HOBt in the text.



Scheme 2. Two coordinated modes of H₂BDC in the text.

analysis, IR spectroscopy, TGA, XRPD, and single-crystal X-ray. The luminescence properties of the three complexes were investigated as well.

2. Experimental section

2.1. Materials and methods

All chemicals and reagents were used as received from commercial sources without further purification. Elemental analyses (C, H and N) were performed on a Perkin–Elmer 2400 Elemental Analyzer. The solid infrared spectra (IR) were obtained from a FT-IR-670 spectrophotometer (Thermo Nicolet USA) in the range of 400–4000 cm^{-1} by using KBr pellets. XRPD were performed with a Rigaku D/max γ A (Japan, $\lambda = 0.154060$ nm). Thermo-gravimetric analyses (TGA) were performed with a NETSCHZ STA-499C thermoanalyzer under N₂ (20–600 °C range) at a heating rate of 10 °C/min.

Data collections of X-ray diffraction intensities for the three compounds were performed on Bruker SMART APEX-CCD diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Intensity data were collected at 273 K for **1**, 173 K for **2** and **3**, respectively. Empirical absorption corrections were applied using the SADABS program. The three structures were solved by direct methods using SHELXTL-97 [47] package of crystallographic software and refined by full-matrix least-squares technique on F^2 . All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to C, N and O atoms were located at geometrically calculated positions and refined with isotropic thermal parameters included in the final stage of the refine-

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

Complex	1	2	3
Formula	C ₁₂ H ₂₂ N ₆ OgMn	C ₂₀ H ₁₆ N ₆ O ₈ Zn ₂	C ₂₀ H ₂₂ N ₆ O ₁₂ Cu ₃
Formula weight	449.3	599.13	729.07
Temperature (K)	273(2)	173(2)	173(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P21/c	P21/c	C2/c
<i>a</i> (Å)	6.875(2)	18.483(3)	26.223(18)
<i>b</i> (Å)	9.811(3)	5.3787(9)	5.928(4)
<i>c</i> (Å)	28.102(9)	28.182(4)	16.115(10)
α (°)	90	90	90
β (°)	94.159(5)	129.600(7)	97.152(15)
γ (°)	90	90	90
<i>V</i> (Å ³)	1890.6(11)	2158.7(6)	2486(3)
<i>Z</i>	4	4	4
<i>D</i> _{calcd} (Mg m ⁻³)	1.579	1.843	1.943
<i>F</i> (0 0 0)	932	1208	1460
Reflections collected	11378	12652	7439
Goodness-of-fit on F^2	1.001	0.982	0.991
<i>R</i> ₁ , w <i>R</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0699, 0.1828	0.0459, 0.0845	0.0482, 0.1017
<i>R</i> ₁ , w <i>R</i> ₂ (all data)	0.1027, 0.2010	0.0852, 0.0980	0.0819, 0.1188

ment on calculated positions bonded to their carrier atoms. The crystal data and structure refinements for compounds **1–3** are shown in Table 1.

2.2. Synthesis of [Mn(OBt)₂(H₂O)₄] \cdot 3H₂O (**1**)

A mixture of 1-hydroxybenzotriazole 0.0675 g (0.5 mmol) and Mn(CH₃COO)₂ \cdot 4H₂O 0.1225 g (0.5 mmol), was stirred in water

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