A Three-dimensional Tm(III)-Zn(II) Heteronuclear Metal-organic Framework Based on Imidazoledicarboxylate Ligand: Synthesis, Crystal Structure and Luminescence Property Postprint

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Abstract

A d-f heteronuclear metal-organic framework (MOF), {[Tm3Zn6(bipy2)2(mimda)7 (H2O)3] · (H2O)5}n (1, H3mimda = 2-methyl-1-H-imidazole-4,5-dicarboxylic acid, and bipy = 4,4 -bipyridine), has been synthesized under solvothermal conditions, and structurally characterized by elemental analysis, IR spectra and X-ray single-crystal diffraction. It crystallizes in orthorhombic system, space group Pnma with a = 16.1102(9), b = 33.5805(19), c = 16.8593(10) Å, = 97.344(11)°, V = 9120.7(9) Å3, Z = 4, F(000) = 5184, the final R = 0.0530 and wR = 0.1306. In complex 1, the Tm(III) ions adopt two types of coordination fashions. Complex 1 shows one-dimensional (1-D) Tm-Zn heteronuclear zigzag chains, and these chains are further linked by H3mimda ligands into Tm-Zn heteronuclear 2-D lattice-like arrays. The 2-D heteronuclear units were connected through [Zn6(mimda)6] rings to give rise to the Tm-Zn heteronuclear cages. Finally, H3mimda ligands connected the cages into a 3-D heterometallic framework by the combination of [TmO7]n and Tm-Zn heteronuclear cages. In addition, the thermal stability and luminescent property have been investigated.

Full Text

A Three-Dimensional Tm(III)-Zn(II) Heteronuclear Metal-Organic Framework Based on Imidazole-dicarboxylate Ligand: Synthesis, Crystal Structure and Luminescence Property

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ABSTRACT

A d-f heteronuclear metal-organic framework (MOF), {[Tm Zn (bipy) (mimda) (H O)]· (H O) } (1, H mimda = 2-methyl-1-H-imidazole-4,5-dicarboxylic acid, and bipy = 4,4 -bipyridine), has been synthesized under solvothermal conditions and structurally characterized by elemental analysis, IR spectroscopy, and single-crystal X-ray diffraction. The compound crystallizes in the orthorhombic system, space group *Pnma*, with unit cell parameters a = 16.1102(9), b = 33.5805(19), c = 16.8593(10) Å, = 97.344(11)°, V = 9120.7(9) Å^3, Z = 4, $F(000)$ = 5184, and final R = 0.0530 and wR = 0.1306. In complex 1, the Tm(III) ions adopt two distinct coordination geometries. The structure features one-dimensional (1-D) Tm-Zn heteronuclear zigzag chains that are further linked by H mimda ligands into two-dimensional (2-D) lattice-like arrays. These 2-D heteronuclear units are connected through [Zn (mimda)] rings to generate Tm-Zn heteronuclear cages, which are ultimately connected into a three-dimensional heterometallic framework via H mimda ligands bridging the combination of [TmO] units and Tm-Zn heteronuclear cages. Additionally, the thermal stability and luminescent properties of the complex have been investigated.

Keywords: d-f heteronuclear metal-organic frameworks; Tm(III) complex; 2-methyl-1-H-imidazole-4,5-dicarboxylic acid; luminescence

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1. INTRODUCTION

In recent years, lanthanide-based metal-organic frameworks (MOFs) have attracted considerable attention due to their intriguing structural topologies and potential applications in gas storage, luminescence, and magnetism [**?**]. Lanthanide metal ions possess high coordination numbers and exhibit emission

wavelengths ranging from the visible to the near-infrared region. However, their absorption coefficients are typically very low with slow emissive rates due to Laporte-forbidden f-f transitions [**?**, **?**]. To mitigate this limitation, our strategy employs imidazole dicarboxylate ligands as chromophores in combination with transition metals that can enhance energy transfer [**?**]. Imidazole dicarboxylate ligands containing N and O donors are particularly attractive because they can adopt a variety of coordination modes, proving to be excellent building blocks for constructing MOFs with fascinating structures and useful properties. Numerous imidazole dicarboxylate-based MOFs incorporating transition metal ions have been reported [**?**, **?**]. Additionally, introducing pillared rigid ligands containing N atoms such as 4,4 -bipyridine into these frameworks represents another effective strategy for generating diversified structures and enhancing the performance of the resulting MOFs [**?**]. Nevertheless, designing and constructing d-f heteronuclear MOFs [**?**] with dicarboxylate ligands remains challenging due to varying reaction conditions such as pH values, metal-to-ligand ratios, solvents, and reaction temperatures. In this contribution, we report a new complex, {[Tm Zn (bipy) (mimda) (H O)] · (H O) } (1), synthesized using the H mimda ligand and bipy, and we investigate its IR spectroscopy, photoluminescence, and thermal stability.

2. EXPERIMENTAL

2.1 Materials and Physical Measurements

All chemicals and solvents purchased were of reagent grade and used without further purification. Elemental analyses for carbon, hydrogen, and nitrogen were performed on a Model 240 Perkin-Elmer elemental analyzer. The infrared spectrum was recorded on an IRAffinity-1S spectrometer in the range of 3500–500 cm ^{1}. The X-ray powder diffraction (XRPD) pattern of 1 was recorded at 293 K on a Bruker D8 Advance diffractometer (Cu K , = 1.54056 Å) operated at 40 kV and 30 mA, using a Cu-target tube and a graphite monochromator. Thermogravimetric analysis (TGA) experiments were conducted on a Perkin-Elmer Diamond SII thermal analyzer from room temperature to 1200 °C under a nitrogen atmosphere at a heating rate of 10 °C · min ^{1}. Emission and excitation spectra were recorded on an F-7000 (HITACHI) spectrophotometer at room temperature.

2.2 Synthesis of Complex 1

A mixture of Tm O (0.05 mmol, 0.0192 g), Zn(NO) ·6H O (0.0370 g, 0.1 mmol), H mimda (0.15 mmol, 0.0270 g), and bipy (0.1 mmol, 0.0170 g) was dissolved in a DMF-water solution (10 mL). The mixture was transferred to a Teflon-lined autoclave and heated at 162 °C for 5400 minutes, then cooled to room temperature. Colorless crystals of 1 were obtained in 0.0048 g yield (48%, based on lanthanide element). Elemental analysis: Calcd. (%) for C H N O Tm Zn : C, 27.91; H, 1.92; N, 9.45. Found: C, 27.95; H, 1.90; N, 9.47. IR (cm ^{1}): 3340w, 2974m, 2897w, 2367m, 1716w, 1539m, 1388m, 1049m, 887m, 771m.

2.3 Crystal Structure Determination

A colorless block crystal of complex 1 (0.26 mm × 0.21 mm × 0.18 mm) was mounted on a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromatized Mo K radiation (= 0.71073 Å) using a / scan mode at room temperature. A total of 99936 reflections were collected, of which 10650 independent reflections (R = 0.0837) in the range of 1.75 27.50° with index ranges of -20 h 20, -43 k 43, and -21 l 21 were used for the structure determination at 293(2) K. All non-hydrogen atoms were refined with anisotropic thermal parameters. The structure was solved by direct methods using SHELXS-97 [**?**], and hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement using geometrical restraints. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [**?**]. For complex 1, disordered methyl carbon atoms of H mimda ligands were restrained to obtain reasonable thermal parameters [**?**]. The final refinement converged to $R = 0.0530$ and $wR = 0.1306$ ($w = 1/[\ ^2(F^2)$ + $(0.0406P)^2$ + $146.3998P]$, where $P = (F^2 + 2F^2)/3$), $S = 1.093$, (Δ) = 2.776 and (Δ) = -1.150 e•Å ^{3}. Selected bond lengths and angles and hydrogen bond parameters are listed in Tables 1 and 2, respectively.

3. RESULTS AND DISCUSSION

3.1 Crystal Structure of Complex 1

Single-crystal X-ray analysis reveals that 1 crystallizes in the orthorhombic system, space group *Pnma*. As shown in Fig. 1 [Figure 1: see original paper], the asymmetric unit of 1 contains three Zn(II) ions, two Tm(III) ions, four H mimda ligands, one bipy ligand, three coordinated water molecules, and five lattice water molecules. The Zn(II) centers exhibit three distinct coordination modes, with Zn(1) and Zn(3) sharing the same coordination number. Zn(1) is coordinated by nitrogen atom N(2) and oxygen atom O(4) from one Hmimda^2 ligand, nitrogen atom N(5#3) and oxygen atom O(10#3) from another Hmimda^2 ligand, and one oxygen atom O(4W) from a coordinated water molecule. Zn(3) is coordinated by two nitrogen atoms N(4) and N(7) and two oxygen atoms O(8) and O(14) from two different H mimda ligands, plus one nitrogen atom (N8) from a bipy ligand. Zn(2) is six-coordinated by nitrogen atoms N(1), N(3), N(6) and oxygen atoms O(2), O(6), O(12) from three different H mimda ligands.

The asymmetric unit contains two crystallographically unique Tm(III) centers with different coordination environments. Tm(1) is seven-coordinated by six carboxylate oxygen atoms O(1), O(1#1), O(3), O(3#1), O(5), O(5#1) from three H mimda ligands and one oxygen atom O(1W) from a coordinated water molecule, adopting a pentagonal bipyramidal geometry (TmO). The Tm(1)-Ocarboxyl bond lengths range from 2.212(7) to 2.256(7) Å, while the Tm(1)-Owater bond length is 2.361(10) Å. Tm(2) is eight-coordinated by five oxygen atoms O(7), O(9), O(11), O(13), O(13#1), O(14) from three H mimda ligands and two additional oxygen atoms O(2W), O(3W) from coordinated water

molecules, forming an octahedral coordination geometry. The Tm(2)–O bond distances range from 2.193(6) to 2.486(5) Å, and the bond angles around each Tm(III) center vary from 64.2(2)° to 159.4(2)°. Detailed hydrogen bonding parameters for 1 are presented in Table 2, all of which fall within the normal range for such weak interactions [**?**].

As illustrated in Scheme 1, the mimda^{3} anions adopt both - N,O: O,O : N ,O and - N,O: N ,O O,O : O ,O coordination modes to connect adjacent Tm(III) and Zn(II) ions. Each TmO unit connects two neighboring Zn(II) chelate units through two H mimda ligands in different coordination modes to generate a 1D zigzag chain, which further extends into a unique 2D Tm-Zn heteronuclear metal-organic network structure (Fig. 2b [Figure 2: see original paper]). Additionally, six H mimda ligands link neighboring Zn(II) ions via N,O-chelating to form a [Zn (mimda)] ring, with bipy acting as a terminal ligand that leaves a free N atom. These [Zn (mimda)] rings are connected by one H mimda ligand to afford a 1D six-membered ring chain along the *b*-axis, as shown in Fig. 2c [Figure 2: see original paper]. The resulting 3D framework of 1 can be described as [Tm Zn (minda) (bipy)] heteronuclear cages linked by (TmO) units through H mimda ligands in modes a and b (Fig. 3 [Figure 3: see original paper]), similar to other recently reported Ln compounds [**?**]. In the Tm-Zn heteronuclear cage, [Zn (mimda)] and [Tm (mimda)] subunits are connected by H mimda ligands, creating an "interlock" structural motif. After hypothetical removal of guest water molecules, the total potential solvent-accessible void volume for this 3D framework is 2025.8 Å^{3} per unit cell (accounting for 22.2% of the total unit cell volume), as calculated using the PLATON program [**?**].

3.2 Powder X-Ray Diffraction Patterns and Thermal Stability

As shown in Fig. 4 [Figure 4: see original paper], the powder X-ray diffraction (PXRD) pattern of complex 1 exhibits characteristic peaks at 2 positions of 9.8°, 12.2°, 16.4°, 18.3°, and 28.2°. The experimental pattern matches well with the simulated one, indicating the phase purity of the bulk synthesized samples. Thermogravimetric analysis (TGA) was performed on a sample consisting of numerous single crystals from 30 to 1200 °C under N atmosphere at a heating rate of 10 °C $\cdot$ min ^{1}, with the TG and DTA curves shown in Fig. 5 [Figure 5: see original paper]. Complex 1 first undergoes a weight loss of 5.1% at approximately 175 °C, corresponding to the release of eight water molecules (calcd. 5.4%). The framework decomposes at about 260 °C, attributed to the departure of bipy moieties (11.7%, calcd. 10.6%). Upon further heating, complex 1 continues to break down, showing an obvious weight loss of H mimda ligands above 700 °C.

3.3 Luminescence Property

The luminescence properties of complex 1, bipy, and the free H mimda ligand were investigated in the solid state at room temperature. As illustrated in Fig. 6 [Figure 6: see original paper], complex 1 exhibits an emission band with a

maximum at 476 nm upon excitation at 325 nm. In contrast, the maximum emission wavelengths of the H mimda ligand and bipy are 416 nm (= 315 nm) and 363 nm (= 270 nm), respectively. Compared with the free ligands, the luminescence of complex 1 likely originates from ligand-based emission, with enhancement and significant red-shift probably resulting from coordination between the free ligands and metal ions during framework formation [**?**].

[Figure 1: see original paper]

[Figure 2: see original paper]

[Figure 3: see original paper]

[Figure 4: see original paper]

[Figure 5: see original paper]

[Figure 6: see original paper]

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