

Construction of six new coordination complexes with 5-(3-pyridyl) tetrazole-2-acetato



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ABSTRACT

Six new complexes with 3-pytza ligand (3-pytza = 5-(3-pyridyl) tetrazole-2-acetato), $[\text{Sr}(3\text{-pytza})_2(\text{H}_2\text{O})_2]_n \cdot n\text{H}_2\text{O}$ (**1**), $[\text{Zn}(3\text{-pytza})_2(\text{H}_2\text{O})_2]_n \cdot 2n\text{H}_2\text{O}$ (**2**), $[\text{Cu}(3\text{-pytza})_2(\text{H}_2\text{O})_2]_n \cdot 2n\text{H}_2\text{O}$ (**3**), $[\text{Pb}(3\text{-pytza})_2]_n$ (**4**), $[\text{Eu}(3\text{-pytza})_2\text{Cl}(\text{H}_2\text{O})_2]_n$ (**5**), $[\text{Tb}(3\text{-pytza})_2\text{Cl}(\text{H}_2\text{O})_2]_n$ (**6**) have been synthesized. These compounds were characterized by elemental analysis, IR spectroscopy and single-crystal X-ray diffraction. The X-ray analysis reveals that these compounds display 1D or 2D structures. Furthermore, the luminescent properties of **1–6** were investigated at room temperature in the solid state.

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1. Introduction

The design and construction of coordination compounds with unique structural motifs and unique chemical as well as physical properties has been given considerable attention in either coordination chemistry or material chemistry [1]. On the one hand, from the point view of crystal engineering, ligands are often designed in order to form specific lattice structures, that is to say, the shapes and symmetry of the organic ligands are vital to form the unique structures of the coordination topologies. One of the important characteristics of an organic compound used as a ligand is its diverse coordination modes, molecular rigidity and flexibility which may determine the orientation of the binding sites [2]. On the other hand, many objective factors, such as the ligand-to-metal ratio, the solvent system, the pH values and the temperature can inevitably influence the final structures of our targeted molecules. As versatile building blocks, carboxylate–tetrazole organic ligands, for instance, tetrazolate-5-acetic acid (H_2tza) [3], tetrazolate-5-formic acid (Htzf) [4], tetrazole-1-acetic acid (Htza) [5], 5-aminotetrazole-1-acetic acid (Hatza) [6], 5-(2-pyrazinyl) tetrazole-2-acetic acid (Hpztza) [7], 5-(2-pyridyl) tetrazole-2-acetic acid (Hpytza) [8], 5-[N-acetato(3-pyridyl)] tetrazole (a3-ptz) [9], 5-[N-acetato(4-pyridyl)] tetrazole (a4-ptz) [10], 5-[(4-nitryl)phenyl] tetrazole-1-acetato (nptza) [11], etc. have proven to be good

candidates for the construction of new coordination compounds. However, the compounds based on 5-(3-pyridyl) tetrazole-2-acetato potassium salt ligand (K3-pytza), a new tetrazole-containing carboxylate ligand, to the best of our knowledge, has only been reported with Sm [12]. In this paper, we have further our investigation to treat 3-pytza potassium salt with several metal ions, ranging from the s-block element Sr(II), the ds-block ones Zn(II), Cu(II), the p-block one Pb(II) to the f-block ones, Eu(III), Tb(III). Six new coordination compounds, namely, $[\text{Sr}(3\text{-pytza})_2(\text{H}_2\text{O})_2]_n \cdot n\text{H}_2\text{O}$ (**1**), $[\text{Zn}(3\text{-pytza})_2(\text{H}_2\text{O})_2]_n \cdot 2n\text{H}_2\text{O}$ (**2**), $[\text{Cu}(3\text{-pytza})_2(\text{H}_2\text{O})_2]_n \cdot 2n\text{H}_2\text{O}$ (**3**), $[\text{Pb}(3\text{-pytza})_2]_n$ (**4**), $[\text{Eu}(3\text{-pytza})_2\text{Cl}(\text{H}_2\text{O})_2]_n$ (**5**), $[\text{Tb}(3\text{-pytza})_2\text{Cl}(\text{H}_2\text{O})_2]_n$ (**6**) were obtained. The 3-pytza ligand in **1–6** shows four different coordination modes (Scheme 1). Herein we report their synthesis, crystal structures and luminescent properties along with the synthetic conditions on the formation of such complexes.

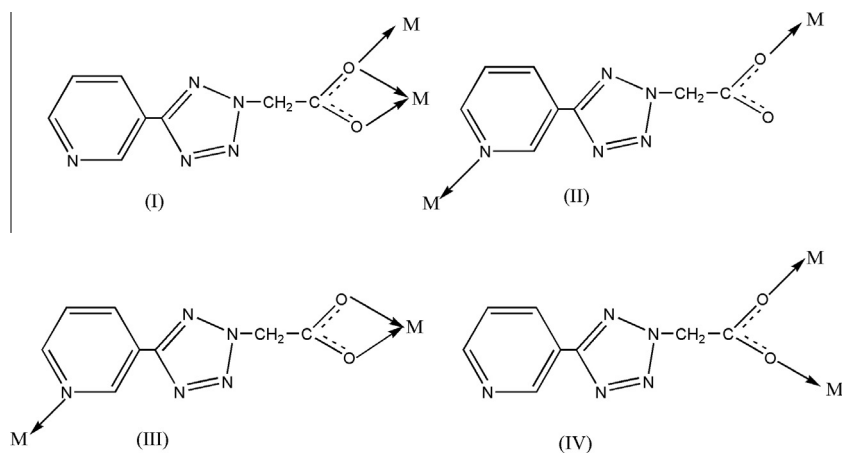
2. Experimental

2.1. Materials and instruments

5-(3-pyridyl) tetrazole (designated as H3-pytz) was prepared by [2+3] cycloaddition reactions, by treating 3-cyanopyridine with NaN_3 in toluene in the presence of triethylammonium chloride. The reaction of H3-pytz with ethyl bromoacetate in methanolic potassium hydroxide solution gave mostly H(tetrazole)-substituted products 5-(3-pyridyl) tetrazole-2-acetato potassium salt (K3-pytza) [13]. All chemicals were obtained from commercial

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Scheme 1. The coordination modes of the 3-pytza ligand in **1–6**.

sources and used without further purification. The elemental analyses for C, H and N were performed with a PE2400 elemental analyzer. The IR spectra were obtained on a NICOLET380 spectrometer using KBr disks in the range 4000–400 cm^{-1} . Photoluminescent analyses were performed on an F-4600 fluorescence spectrometer. Single crystal X-ray diffraction was carried out by a Rigaku SCX-mini-CCD diffractometer.

2.2. Synthesis of $[\text{Sr}(3\text{-pytza})_2(\text{H}_2\text{O})_2]_n \cdot n\text{H}_2\text{O}$ (**1**) and $[\text{Zn}(3\text{-pytza})_2(\text{H}_2\text{O})_2]_n \cdot 2n\text{H}_2\text{O}$ (**2**)

A mixture of $\text{Sr}(\text{NO}_3)_2$ (0.0211 g, 0.1 mmol) or $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.0298 g, 0.1 mmol) and K3-pytza (0.0486 g, 0.2 mmol) in mixture of EtOH (3 mL) and water (6 mL) was heated at 80 °C for 4 h with stirring, then cooled to the room temperature and filtered, the colorless block crystals **1** or **2** was obtained. For **1**, yield: 55% based on Sr. *Anal.* Calc. for $\text{C}_{16}\text{H}_{18}\text{N}_{10}\text{O}_7\text{Sr}$: C, 34.94; H, 3.30; N, 25.47. Found: C, 35.22; H, 3.42; N, 25.64%. IR (KBr, cm^{-1}): 3491(s), 3334(m), 1639(s), 1600(s), 1530(m), 1438(s), 1400(s), 1378(m), 1310(m), 1155(w), 1025(w), 825(m), 752(w), 732(w), 631(w), 585(w). For **2**, yield: 58% based on Zn. *Anal.* Calc. for $\text{C}_{16}\text{H}_{18}\text{N}_{10}\text{O}_8\text{Zn}$: C, 35.21; H, 3.69; N, 25.66. Found: C, 35.47; H, 3.77; N, 25.89%. IR (KBr, cm^{-1}): 3456(s), 3298(m), 1635(s), 1619(m), 1538(m), 1443(m), 1379(s), 1302(s), 1204(m), 1155(m), 1104(m), 1064(m), 1047(m), 824(w), 755(w), 673(w), 640(w), 522(w).

2.3. Synthesis of $[\text{Cu}(3\text{-pytza})_2(\text{H}_2\text{O})]_n \cdot 2n\text{H}_2\text{O}$ (**3**) and $[\text{Pb}(3\text{-pytza})_2]_n$ (**4**)

A mixture of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.0370 g, 0.1 mmol) or $\text{Pb}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.0514 g, 0.1 mmol) and K3-pytza (0.0486 g, 0.2 mmol) in water (9 mL) was heated at 90 °C for 8 h with stirring, then cooled to the room temperature and filtered, the block crystals **3** (blue) or **4** (colorless) was obtained. For **3**, yield: 45% based on Cu. *Anal.* Calc. for $\text{C}_{16}\text{H}_{18}\text{CuN}_{10}\text{O}_7$: C, 36.54; H, 3.45; N, 26.63. Found: C, 36.28; H, 3.51; N, 26.73%. IR (KBr, cm^{-1}): 3353(s), 3255(m), 1609(s), 1567(s), 1473(m), 1440(s), 1418(s), 1378(m), 1306(m), 1196(m), 1036(m), 823(m), 730(w), 679(w), 637(w), 577(w). For **4**, yield: 61% based on Pb. *Anal.* Calc. for $\text{C}_{16}\text{H}_{12}\text{N}_{10}\text{O}_4\text{Pb}$: C, 31.22; H, 1.97; N, 22.76. Found: C, 31.48; H, 2.10; N, 22.59%. IR (KBr, cm^{-1}): 1607(s), 1440(s), 1420(s), 1390(s), 1296(m), 1204(m), 1152(m), 1057(m), 1005(m), 924(w), 821(m), 731(w), 678(w), 588(w).

2.4. Synthesis of $[\text{Eu}(3\text{-pytza})_2\text{Cl}(\text{H}_2\text{O})_2]_n$ (**5**) and $[\text{Tb}(3\text{-pytza})_2\text{Cl}(\text{H}_2\text{O})_2]_n$ (**6**)

A mixture of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (0.0366 g, 0.1 mmol) or $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ (0.0373 g, 0.1 mmol) and K3-pytza (0.0486 g, 0.2 mmol) in mixture of EtOH (5 mL) and water (2 mL) was sealed in a 25 mL teflon-lined stainless steel container, which was heated at 120 °C for 48 h. After the sample was cooled to room temperature, the colorless block crystals **5** or **6** was obtained. For **5**, yield: 34% based on Eu. *Anal.* Calc. for $\text{C}_{16}\text{H}_{16}\text{ClEuN}_{10}\text{O}_6$: C, 30.42; H, 2.55; N, 22.17. Found: C, 30.24; H, 2.59; N, 22.33%. IR (KBr, cm^{-1}): 3343(s), 1611(s), 1573(s), 1449(s), 1419(s), 1393(m), 1377(m), 1313(w), 1197(w), 1037(m), 827(w), 752(w), 731(w), 637(m), 581(w). For **6**, yield: 38% based on Tb. *Anal.* Calc. for $\text{C}_{16}\text{H}_{16}\text{ClTbN}_{10}\text{O}_6$: C, 30.09; H, 2.52; N, 21.93. Found: C, 29.80; H, 2.62; N, 21.67%. IR (KBr, cm^{-1}): 3343(s), 3280(s), 1613(s), 1574(s), 1450(s), 1419(s), 1394(m), 1378(m), 1313(w), 1198(w), 1038(m), 827(w), 752(w), 732(w), 638(m), 582(w).

2.5. Single crystal structures determination

Suitable single crystals of complexes **1–6** were mounted on a Rigaku SCXmini-CCD diffractometer equipped with a graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 291 K. All absorption corrections were performed using the CrystalClear programs. The crystal structures of **1–6** were solved by direct methods and refined on F^2 by full-matrix least-squares using anisotropic displacement parameters for all non-hydrogen atoms [14a]. For **1–6**, important crystal data and collection and refinement parameters are summarized in Table 1S, and selected bond lengths and angles are given in Table 1. Hydrogen-bonding parameters are given in Table 2S.

3. Results and discussions

3.1. Syntheses consideration and general characterizations

In this work, we selected 3-pytza ligand with both flexible carboxylate group and rigid tetrazolyl and pyridyl rings to construct metal coordination architectures in order to explore the influence of metal ions and the synthesis conditions in forming such complexes. Besides, s-block element Sr(II), p-block one Pb(II), ds-block ones Zn(II), Cu(II) and especially the f-block ones, Eu(III), Tb(III) which are more likely to display different coordination numbers and geometries when coordinated to the same ligand due to their different ionic radii and coordination abilities, therefore,

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