

Research paper

Nitrogen-rich 5-(4-pyridyl)tetrazole-2-acetic acid and its alkaline earth metal coordination polymers for potential energetic materials



Gao Wen Yang, Yuan Ting Zhang, Qi Wu, Meng Jie Cao, Jiao Wu, Qiu Yan Yue, Qiao Yun Li*

Jiangsu Laboratory of Advanced Functional Material, Department of Chemistry and Material Engineering, Changshu Institute of Technology, Changshu 215500, Jiangsu, PR China

ARTICLE INFO

Article history:

Received 28 March 2016

Received in revised form 17 May 2016

Accepted 6 June 2016

Available online 15 June 2016

Keywords:

Hpytza

Alkaline earth metal

Energetic material

Thermal parameter

ABSTRACT

Tetrazole and its derivatives with rich nitrogen atoms may be potential candidates for energetic materials. Alkaline earth metal coordination compounds based on such ligands are relatively less investigated. Hpytza was prepared from 4-cyanopyridine and sodium azide, ethyl bromoacetate, where Hpytza = 5-(4-pyridyl)tetrazole-2-acetic acid. Hpytza and four alkaline earth metal coordination polymers [Mg(pytza)₂]_n (**1**), [Ca(pytza)₂(H₂O)₂]_n·3nH₂O (**2**), [Sr(pytza)₂(H₂O)₂]_n (**3**) and [Ba(pytza)₂(H₂O)₂]_n·nH₂O (**4**) were prepared under solvothermal conditions. The thermal behavior of these compounds were characterized by the differential scanning calorimetry (DSC) and thermogravimetric-differential thermogravimetric (TG-DTG) analyses. Furthermore, the critical temperature of thermal explosion and relevant thermal parameters ΔS, ΔH, ΔG of Hpytza and polymers **1–4** were calculated, as well, indicating that these compounds are potential energetic materials.

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1. Introduction

In recent years, the design and exploration of energetic materials has received increasing attention due to not only the energy shortage, but also the conventional materials are neither high energetic nor environmentally friendly. Typical of energetic materials, for instance, organic compounds [1], lead salts [2] as well as coordination compounds [3] have been widely. Recently, tetrazole and its derivatives with high nitrogen percentage are acknowledged as advanced materials, in the range of luminescence, magnetism, adsorption materials, etc [4]. Besides, coordination compounds consisting of metal center and ligands usually show relatively higher thermal stability, compared with the corresponding ligands. In our previous work, we reported the synthesis and characterization of 5-[N-acetato(4-pyridyl)]tetrazole and its alkaline earth metal coordination compounds [5]. To extend our previous work and explore the relationship of the thermal stability and energetic performance, 5-(4-pyridyl)tetrazole-2-acetato, the isomer of 5-[N-acetato(4-pyridyl)]tetrazole, was chosen to be reacted with alkaline earth metal salts yielded its four new polymers [Mg(pytza)₂]_n (**1**), [Ca(pytza)₂(H₂O)₂]_n·3nH₂O (**2**), [Sr(pytza)₂(H₂O)₂]_n (**3**) and [Ba(pytza)₂(H₂O)₂]_n·nH₂O (**4**). On one hand, the two isomers with abundant nitrogen and oxygen atoms tend to display various coordination modes, thus leading to structural variation.

On the other hand, the different position of the carboxylate group, however, may have a fundamental effect on the resulting structures. According to the latest literature, alkaline earth metal compounds based on tetrazole-carboxylate ligands are potential energetic materials but rarely investigated [6]. Therefore, investigations on such compounds will make sense both theoretically and practically. Furthermore, TGA and DSC tests demonstrate that the four polymers can be taken advantage of as potential explosive materials. And the relevant thermal parameters ΔS, ΔH and ΔG of polymers **1–4** are calculated, as well (see Scheme 1).

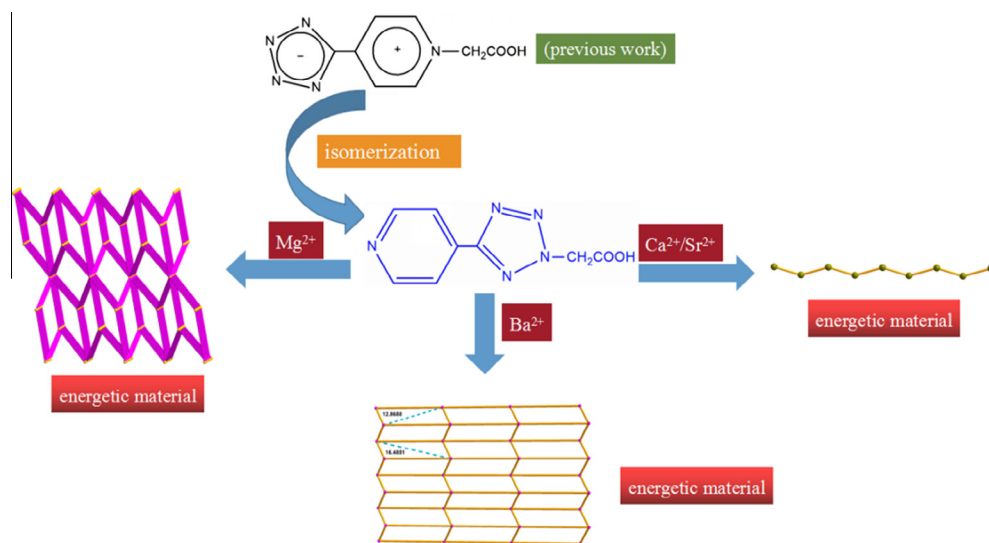
2. Results and discussions

2.1. General characterization of polymers **1–4**

In this work, one nitrogen rich ligand 5-(4-pyridyl)tetrazole-2-acetic acid and its alkaline earth metal coordination polymers were prepared. In the IR curve of Hpytza, the asymmetric vibration of the carboxylate group appears in the usual region (1730 cm⁻¹). Polymers **1–4**, however, show the similar peak at the region of 1640 to 1604 cm⁻¹ (1640 cm⁻¹ for **1**, 1635 cm⁻¹ for **2**, 1604 cm⁻¹ for **3** and 1625 cm⁻¹ for **4**), whose red shift may be explained by the coordination of the carboxylate group to the metal center (Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺). Peaks at 3424 cm⁻¹ for **2**, 3428 cm⁻¹ for **3** and 3417 cm⁻¹ for **4**, respectively, are ascribed to the O-H vibration of either coordinated water or guest water molecules. Polymer **1**, however, contains neither coordinated nor guest water molecules,

* Corresponding author. Tel./fax: +86 512 52251842.

E-mail address: liqiaoyun61@126.com (Q.Y. Li).



Scheme 1. Synthetic strategy for Hpytza and polymers **1–4**.

so it does not show a similar peak. The characteristic peaks of the C=N of both the pyridine and tetrazole rings are at 1562–1386 cm^{-1} for **1**, 1563–1403 cm^{-1} for **2**, 1462–1389 cm^{-1} for **3** and 1528–1385 cm^{-1} for **4**, respectively, which may overlap the peaks of the symmetric vibration of the carboxylate group.

2.2. Crystal structure of $[\text{Mg}(\text{pytza})_2]_n$ (**1**)

The X-ray diffraction reveals that polymer **1** crystallizes in monoclinic space group $C2/c$. As shown in Fig. 1a, each Mg(II) ion is in a distorted octahedral coordination arrangement surrounded by two nitrogen atoms from the tetrazolyl rings and four oxygen atoms from four carboxylate groups. The Mg–O bond lengths ranging from 2.068 to 2.070 Å are in excellent agreement with those of the previously reported Mg(II) compounds [5,7a–7e]. So are the Mg–N bond lengths (2.261 Å). Each pytza acts as a tridentate ligand to bridge three Mg(II) centers via one nitrogen atom of the pyridine ring and the carboxylate group in a $\mu_{1,3}$ -COO *syn-syn* mode. The structure can be simplified as a $(3^6, 4^{16}, 5^6)$ tsi network topology (Fig. 1b). Compared with $[\text{Mg}(\text{H}_2\text{O})_6](\text{a}4\text{-ptz})_2 \cdot 2\text{H}_2\text{O}$, where a4-ptz = 5-[N-acetato(4-pyridyl)]tetrazole, the isomer of 5-(4-pyridyl)tetrazole-2-acetato, the structure is substantially different since a4-ptz is uncoordinated to the Mg(II) center, instead, they are held together by hydrogen bonds. Therefore, the structure transforms a mononuclear to a three dimensional one. Two non-classic hydrogen bonds exist between the C–H group of the tetra-

zolyl ring and the oxygen atom of the carboxylate group [C(6)–H(6A)···O(2), O(7)–H(7A)···O(1)] to stabilize the supramolecular assembly (Table S2).

2.3. Crystal structure of $[\text{Ca}(\text{pytza})_2(\text{H}_2\text{O})_2]_n \cdot 3n\text{H}_2\text{O}$ (**2**)

Polymer **2** belongs to monoclinic space group $C2/c$ and the asymmetric unit contains half of the molecule. As shown in Fig. 2a, each Ca(II) center is octa-coordinated by three oxygen atoms from three water molecules and six ones from four carboxylate groups. The Ca–O bond lengths the range of 2.393–2.666 Å are in agreement with those of the previously reported Ca(II) compounds [5,7a,b,d], so the coordination arrangement can be described as an irregular square *anti*-prism. Compared with $[\text{Ca}(\text{a}4\text{-ptz})_2(\text{H}_2\text{O})_2]_n \cdot 2n\text{H}_2\text{O}$ whose 1D chain consists of the a4-ptz which acts as a monodentate ligand via one oxygen atom of the carboxylate group and the bridging water oxygen atom, there are two kinds of coordination modes of pytza: first, adjacent two Ca^{2+} are tetra-bridged by two oxygen atom of two water molecules and four oxygen atom of two carboxylate groups in a $\mu_{1,3}$ -COO *syn-syn* mode to form a binuclear unit; then neighboring binuclear units are doubly bridged by the carboxylate group in a $\mu_{1,1,3}$ -COO mode to generate a 1D zigzag chain extending along the *b* axis with Ca···Ca distance of 3.8845(15) Å and Ca···Ca···Ca angle of 143.945(31)° (Fig. 2b). Adjacent chains are held together by hydrogen bonds to form a 3D network structure (Table S2, Fig. S1).

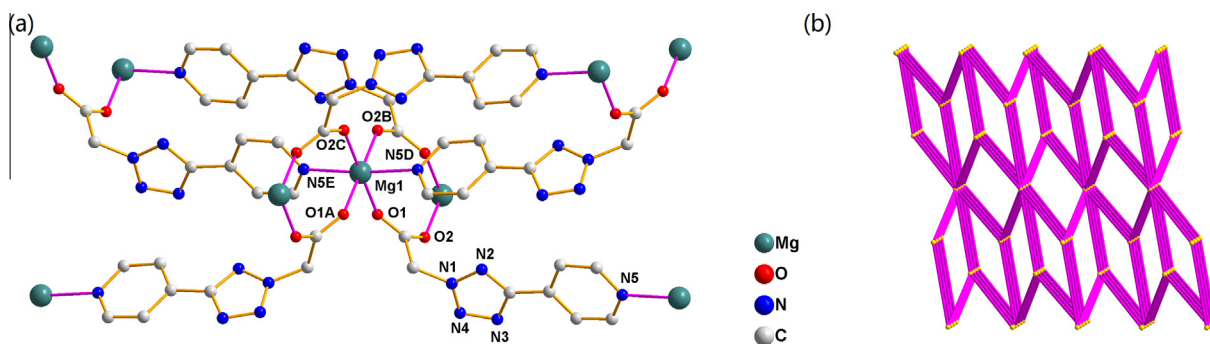


Fig. 1. (a) The coordination environment of Mg^{2+} in polymer **1**. Hydrogen atoms are omitted for clarity; (b) The 3D structure of polymer **1**.

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