

Novel heteroleptic lanthanide organic frameworks containing pyridine-2,5-dicarboxylic acid and *in situ* generated piperazine-2,5-dicarboxylic acid from piperazine: Hydrothermal synthesis and luminescent properties

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ABSTRACT

Two novel 3D lanthanide metal-organic frameworks [Ln(pydc)(pip)_{1/2}(H₂O)] (Ln=Ce (**1**) and Pr (**2**), H₂pydc=2,5-pyridinedicarboxylic acid, H₂pip=2,5-piperazinedicarboxylic acid) have been synthesized under hydrothermal conditions and characterized by elemental analysis, IR spectroscopy, thermogravimetric analysis (TGA), powder X-ray diffractions (PXRD), and single-crystal X-ray diffractions. Field emission scanning electron microscopy (FESEM) was used for morphological analysis. Complexes are isostructural and feature interesting 3D frameworks. Both compounds crystallize in the monoclinic system, space group P2₁/c. Structural analyses of **1** and **2** show that Ln³⁺ ions connect with each other through H₂pydc and H₂pip. To the best of our knowledge, they are the first heteroleptic lanthanide polymers obtained through *in situ* 2,5-piperazinedicarboxylic acid syntheses. Moreover, thermal and luminescent properties of the compounds have been investigated.

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1. Introduction

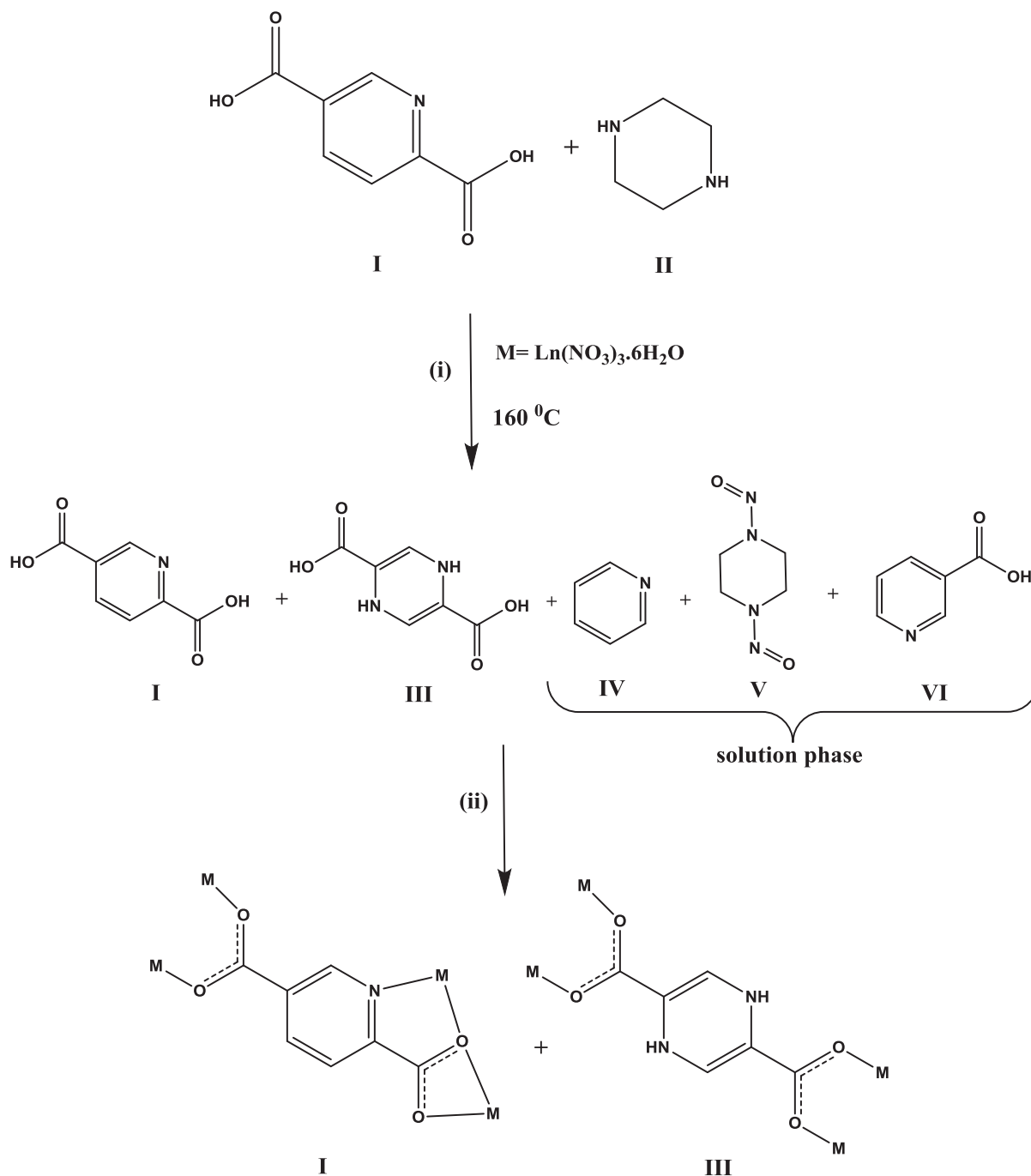
Metal-organic frameworks (MOFs) containing lanthanides and multifunctional carboxylic acid ligands have recently received more attention due not only to their intriguing structure, but also to their enormous range of applications. In particular, they can potentially be applied in catalysis, luminescence, hydrogen storage, optoelectronic devices, sensors, ion exchange, magnetism, and material science [1–6]. As mixed ligands, lanthanides, multi-dentate carboxylates and N,O are widely used together for generating MOFs [7–10]. Lanthanides have higher and different coordination numbers and more flexible coordination geometries than transition metals [11,12]. Although these properties make it difficult to control the synthesis of MOFs, they are good candidates to provide unusual molecular architectures. To prepare lanthanide-based MOFs, the rigid and multifunctional pyridinedicarboxylic acid ligands such as 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-pyridinedicarboxylic have been extensively used [13–16]. They have N- and O-donor atoms that can bridge different metal centers coordinated to metal atoms by two carboxylic groups and nitrogen atom as multidentate ligands. In addition, they are the “ligand

star” in coordination chemistry of such MOFs at all times [17]. H₂pydc was chosen as a ligand star in this work because it can easily coordinate with metal atoms to form an infinite structure. Having two carboxyl groups with a 180° angle may be helpful to reduce the space hindrance and form rigid frameworks in the hydrothermal conditions [18].

Hydrothermal *in situ* ligand synthesis, such as decarboxylation or hydroxylation of carboxyl groups, has become a powerful method in engineering coordination and organic chemistry and for preparing unexpected organic ligands and their complexes. This technique has proved to be an effective method in the MOFs that are difficult to synthesize by conventional means. Although many coordination polymers have been reported by *in situ* decarboxylation ligand synthesis [19–23], formation of the ligand synthesis is rare and there have been only a few reports in the literature [24,25]. In this study, we observed the formation of a new ligand by employing high temperature under hydrothermal conditions. Here, we report the first example of both *in situ* decarboxylation and ligand formation in the presence of piperazine and H₂pydc. The ligand H₂pydc lost two carboxyl groups and these groups linked 2- and 5- positions of the piperazine and produced H₂pip, as shown in Scheme 1. In this study, 2,5-pyridinedicarboxylic acid and 2,5-piperazinedicarboxylic acid were used as donor ligands and two new lanthanide coordination polymers were prepared: [Ln(pydc)(pip)_{1/2}(H₂O)] (Ln=Ce (**1**) and Pr (**2**), H₂pydc=2,5-

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I- H₂pydc, **II-** Piperazine, **III-** H₂pip, **IV-** Pyridine, **V-** N-N'-dinitrosopiperazine, **VI-** 3-pyridinecarboxylic acid.

Scheme 1. Schematic representation of *in situ* rearrangement from piperazine to piperazine-2,5-dicarboxylic acid ligand under the hydrothermal conditions (i) and coordination modes of the ligands with metal (ii). **I-** H₂pydc, **II-** piperazine, **III-** H₂pip, **IV-** pyridine, **V-** N-N'-dinitrosopiperazine, **VI-** 3-pyridinecarboxylic acid.

pyridinedicarboxylic acid, H₂pip=2,5-piperazinedicarboxylic acid). The thermal stabilities and luminescence properties of the compounds were presented. Also, possible mechanism of *in situ* decarboxylation and new formation were discussed. To the best of our knowledge, the synthesized MOFs exhibited the first both *in situ* decarboxylation and rearrangement reactions by Ln(NO₃)₃·6H₂O (Ln=Ce and Pr), H₂pydc and piperazine reactants under hydrothermal conditions.

2. Experimental

2.1. Materials and methods

Ce(NO₃)₃·6H₂O, Pr(NO₃)₃·6H₂O, 2,5-pyridinedicarboxylic acid, and piperazine were purchased from commercial sources and used as received. Hydrothermal syntheses were carried out in 23-mL PTFE-lined stainless-steel containers under autogenous pressure. IR spectra were measured with Thermo Scientific Nicolet IS10

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