Inorganic Chemistry Communications 19 (2012) 15–18

Contents lists available at SciVerse ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Construction of lanthanide/zinc coordination polymers: In situ ligand reactions and templated synthesis

Yan Liu, Lingling Gao, Xuyan Lv, Jianfeng Liu, Tuoping Hu *

Department of Chemistry, North University of China, Taiyuan, Shanxi 030051, PR China

ARTICLE INFO

Article history:
Received 11 November 2011
Accepted 21 January 2012
Available online 1 February 2012

Keywords:
N ligands
Metal organic frameworks
Lanthanide
In situ reaction

ABSTRACT

Two lanthanide/zinc coordination polymers, $[Zn_2Pr(H_2O)_4(OH)(bipy)(IMDC)_2]\cdot bipy\cdot 2H_2O$ (**1**), and $[Pr(phen)(HDTIM)(NO_3)(H_2O)]\cdot H_2O$ (**2**), based on 2H-imidazole-4,5-dicarboxylic acid (H_3IMDC) and 4,5-di(1H-tetrazol-5-yl)-2H-imidazole (H_3DTIM) ligands have been synthesized. Both ligands were in situ generated from the same precursor, 2H-imidazole-4,5-dicarbonitrile (HIMDN), by control of the reaction condition.

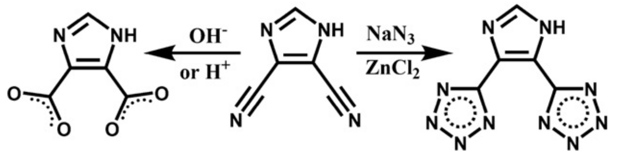
Construction of new types of coordination polymers based on various multi-functional organic ligands is still an attractive field in supramolecular chemistry and crystal engineering [1–3]. In the past decade, the rapidly developing in situ ligand reaction, which was considered as a bridge between coordination chemistry and organic synthetic chemistry, provides a new strategy in the construction of novel functional coordination polymers [4]. By use of the advantage of in situ ligand reaction, new types of coordination polymers, which cannot be obtained from the target ligands, can be rationally synthesized. For example, Xiong and coworkers have synthesized a series of MOFs based on tetrazole ligands in situ generated from CN-containing precursor [5]. Lin et al. reported a series of acentric MOFs of metal-carboxylate based on in situ ligand reaction [6], which may not be obtained from their corresponding carboxylate ligands. Recently, we reported two transition-metal coordination polymers with novel $\{Zn_8O_{13}\}$ SBU or chiral channels through in situ ligand reaction [7]. Our research results reveal that by control of the reaction condition, different types of organic ligands can be generated from the same precursor [2H-imidazole-4,5-dicarbonitrile (HIMDN)]. Continuing our previous work, in this communication, we describe two novel lanthanide coordination polymers with 1D chain and 2D bilayer framework based on in situ ligand reaction (Scheme 1).

The lanthanide coordination polymers, $[Zn_2Pr(H_2O)_4(OH)(bipy)(IMDC)_2]\cdot bipy\cdot 2H_2O$ (**1**), and $[Pr(phen)(HDTIM)(NO_3)(H_2O)]\cdot H_2O$ (**2**), (H_3IMDC = 2H-imidazole-4,5-dicarboxylic acid, H_3DTIM = 4,5-di(1H-tetrazol-5-yl)-2H-imidazole) were synthesized by hydrothermal reaction of 2H-imidazole-4,5-dicarbonitrile (HIMDN) and metal ions [8]. The crystals of complexes **1** and **2** are structurally characterized by single crystal X-ray diffraction [9]. The formula of complexes **1** and **2** was further confirmed by elemental analysis and thermal gravimetric analysis (TGA).

It is well known that the in situ ligand reaction of CN-containing ligand and NaN_3 in the presence of $ZnCl_2$ can generate tetrazole ligand. By control of the reaction conditions, two different organic ligands were in situ generated from the same precursor.

Thus, the hydrothermal reaction of HIMDN, NaN_3, $ZnCl_2$, and $Pr(NO_3)_3\cdot 6H_2O$ resulted in the formation of a large amount of green crystals of **2**.

Single-crystal X-ray diffraction reveals that complex **1** crystallizes in orthorhombic *Cmca* space group. The asymmetric unit consists of one zinc ion, half praseodymium ion, one IMDC ligand, half coordinated bipy ligand, half coordinated OH group, half uncoordinated bipy ligand and five uncoordinated water molecules. Complex **1** is a 2D bilayer framework templated by 4,4-bipy molecules. 2H-imidazole-4,5-dicarbonitrile (HIMDN) was hydrolyzed to 2H-imidazole-4,5-dicarboxylic acid (H_3IMDC) during the hydrothermal reaction, as found in our previous result. Both carboxylate groups of IMDC are deprotonated and the coordination modes of the ligand is shown in Scheme 2.

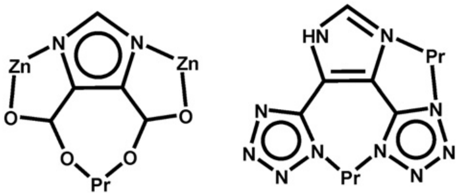


Scheme 1. The different types of organic ligands generated from the same precursor.

---

* Corresponding author. Tel.: +86 351 3923197; fax: +86 351 3923197.
E-mail address: hutuopingsx@yahoo.com.cn (T. Hu).

1387-7003/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.inoche.2012.01.019



Scheme 2. The coordination modes of the ligand.

The zinc ion is coordinated by two oxygen atoms, two nitrogen atoms from different IMDC ligands, and one coordinated bipy molecule, in a square pyramidal geometry (Fig. 1). The IMDC ligands adopt bis-chelating mode through nitrogen atom and one of carboxyl oxygen atom to link zinc ions, giving rise to a 1D infinite chain with the nearest Zn···Zn distance of 6.017(2) Å. The Pr ion is coordinated by four oxygen atoms from two IMDC ligands, four coordinated water molecules, and one OH group, with the average Pr–O distance of 2.473(2) Å. The 1D zinc chains are further connected by sharing Pr ions through the coordination of the remaining carboxyl oxygen atoms, to generate a 2D layer containing large 24-membered metallamacrocycles. Two such layers are further connected by 4,4′-bipy ligands through coordinating to zinc ions to give rise to a bilayer framework with the nearest Zn···Zn distance of 11.216(3) Å. In the 2D bilayer, eight zinc ions and four Pr ions are engaged by IMDC and 4,4′-bipy to form a large $\{Zn_8Pr_4\}$ box, in which the uncoordinated 4,4′-bipy reside. Each $\{Zn_8Pr_4\}$ box trapped two uncoordinated 4,4′-bipy molecules. The pyridine rings are parallel to each other. There are weak interactions between the pyridine rings themselves based on π···π stacking as the pyridyl Cg–Cg distance is nearly 3.908(3) Å (Fig. 2).

The uncoordinated 4,4′-bipy molecules may play template role in the formation of the 2D bilayer, as found in other zeolite, phosphate, and sulfate systems [10]. In our previous work, we reported a 2D layered lanthanide–organic framework templated by 4,4′-bipy molecules [11]. Although several 3D lanthanide coordination polymers templated by 4,4′-bipy molecules have been reported [12], the templated synthesis of 2D lanthanide transition-metal bilayer remains unexplored prior to this work.

It is interesting to point out that there exist strong hydrogen bonding interactions between the coordinated water molecules in one bilayer and the coordinated carboxyl oxygen atoms in the adjacent bilayer (O···O distance: 2.700(3) Å). These hydrogen bonding interactions further connect the 2D bilayers into a 3D porous framework with 1D channels. The channels' region of the framework is host to 4,4′-bipy molecules. These 4,4′-bipy molecules serve as guest-templates. This was realized in that the 4,4′-bipy molecules in complex **1** remain neutral and uncoordinated to the Pr^{3+} and formed strong hydrogen bonding interactions with the coordinated water molecules (O···N distance: 2.706(5) Å). All these hydrogen bonds contribute to stability of the framework.

Complex **2** crystallizes in monoclinic $P2_1/c$ space group and the asymmetric unit consists of one praseodymium ion, one HDTIM, one phen, one coordinated NO_3^- group, one coordinated water molecule, and one uncoordinated water molecule. The HDTIM ligand was in situ generated from HIMDN and partly deprotonated during the reaction. The $ZnCl_2$ plays the role of catalyst and does not take part in coordination, which is quite different from our previous result [7]. The Pr ion is coordinated by four nitrogen atoms from two different HDTIM ligands, two nitrogen atoms from one coordinated phen ligand, two oxygen atom from one coordinated NO_3^- group, and one coordinated water molecule. The average Pr–O and Pr–N distances are 2.553(3) and 2.616(3) Å, respectively. Thus, the HDTIM ligand adopts chelating–bridging mode to infinitely connect Pr ions to generate a 1D chain, with the nearest Pr···Pr distance of 7.074(2) Å. All

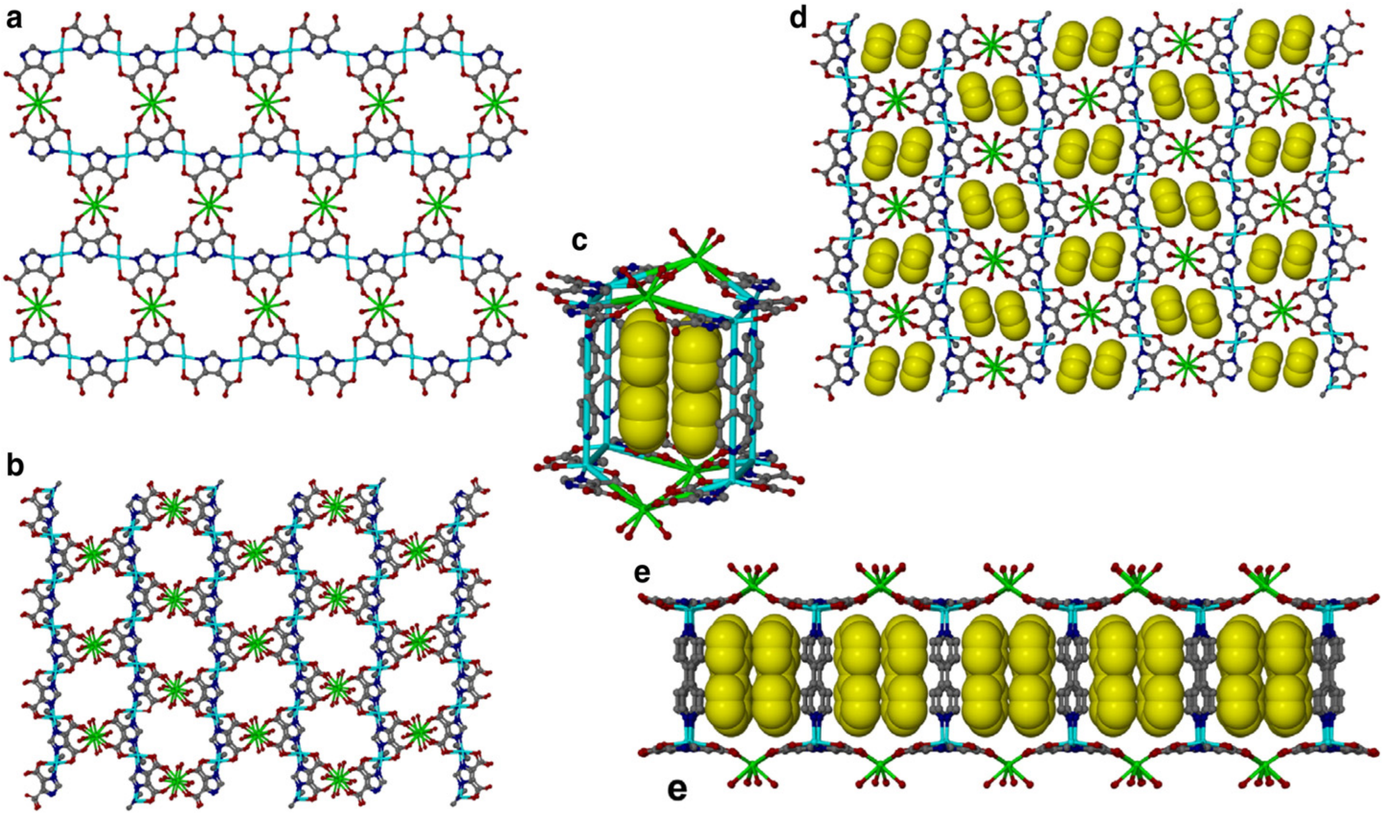


Fig. 1. a) the 2D layer formed by IMDC connecting Zn and Pr ions; b) the bilayer structure of **1** along a axis; c) the $\{Zn_8Pr_4\}$ box trapped two uncoordinated 4,4′-bipy molecules; d) and e) the 2D bilayer trapped 4,4′-bipy molecules along a and c axes, respectively. The uncoordinated 4,4′-bipy molecules were shown in yellow color. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)