Inorganic Chemistry Communications 35 (2013) 321–325

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

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

A new (3,3,6)-connected achiral 3D supramolecular network containing unique helical chains based on 1*H*-benzimidazole-5,6-dicarboxylato and Pb(II)

Yang Liu, Ping Liu *, Qing Liu, Ling-Yan Pang, Chun-Yan Ren, Yao-Yu Wang

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of the Ministry of Education, Shaanxi Key Laboratory of Physico-Inorganic Chemistry, College of Chemistry & Materials Science, Northwest University, Xi'an 710069, PR China

ARTICLE INFO

Article history:
Received 4 June 2013
Accepted 20 July 2013
Available online 26 July 2013

Keywords:
Coordination polymer
Helical chain
Hydrogen bond
Fluorescence

ABSTRACT

A new 1D Pb(II) coordination polymer, $\{[Pb(Hbidc)(phen)]\cdot H_2O\}_n$ (**1**), has been synthesized by a solvothermal method based on 1*H*-benzimidazole-5,6-dicarboxylato (H_3bidc) and 1,10-phenanthroline (phen). Complex **1** features two types of helical chains, a 1D left- and right-handed double-stranded helical chain and a supramolecular helical chain, which interweave into a new (3,3,6)-connected achiral 3D supramolecular network. Notably, the supramolecular helical chains are induced by the different spatial orientations of the 1D double-stranded helical chains. The structure and properties of **1** have been determined by single crystal X-ray diffraction, powder X-ray diffraction (PXRD), elemental analysis (EA), thermogravimetric (TG) analysis and solid state fluorescence spectra.

The rational design and synthesis of supramolecular coordination polymers which contain chiral information have received increasing attentions not only for the fascinating esthetics, but also for their realistic and potential applications as functional materials in catalysis, molecular recognition, separation, nonlinear optics and luminescence [1–3]. It is well known that several aspects, including the nature of metal ions, solvents, ligands, pH, temperatures, templates, counterions, and so on, might play important roles in determining the final structures of coordination polymers. Among the multiple factors mentioned above, the most important ones are the geometrical and electronic properties of ligands and metal ions [4].

The multidentate and rigid 1*H*-benzimidazole-5,6-dicarboxylic acid (H_3bidc) features V-shaped characteristics which could induce asymmetric units and improve the helicity of polymeric chains [5]. In addition, it possesses a relatively large conjugated system which might contribute to the desirable fluorescence property [6,7]. Employing H_3bidc, some coordination polymers involving helical structures have been documented [8–10]. For example, Sun and co-workers have synthesized one lanthanide-based complex ($\{[Dy_2(Hbidc)_2(H_2O)(SO_4)]\cdot H_2O\}_n$), in which the H_3bidc ligands exhibited V-shaped characteristics and formed an infinite Dy1–O2–C9–O3–Dy1 helical chain [9]. Though, many single-, double-, meso- and multi-helical complexes have been reported, the rational construction of supramolecular helical structure is still obstructed by the limited understanding of the structural constraints [11,12]. Moreover, chirality transfer through covalent bond and noncovalent interactions is a significant topic in material and biology science [13,14].

Until now, much of the efforts have been focused on the research of transition- and lanthanide-metal ions, however, the heavy metal ions of main group were not profoundly developed despite their important applications in electroluminescent devices or organic light-emitting diode (OELD) technology [15]. As a main group component, Pb(II) has a large radius, showing variable coordination numbers from 2 to 10 and exhibiting the possible occurrence of a stereochemically active or inactive lone pair electrons, which could be beneficial to construct novel coordination polymers [16–18]. Moreover, the 1,10-phenanthroline (phen) was employed as a co-ligand for its excellent coordinating ability and large conjugated system [19]. In the earlier research, we have synthesized a series of Er(III) complexes using H_3bidc [5]. For proceeding the research on H_3bidc, a 1D coordination polymer $\{[Pb(Hbidc)(phen)]\cdot H_2O\}_n$ (**1**) has been obtained by solvothermal method [20]. The structure and properties of **1** have been studied by single crystal X-ray diffraction, elemental analysis, powder X-ray diffraction, thermogravimetric analysis and solid state fluorescence spectra.

X-ray diffraction analysis reveals that 1D complex **1** crystallizes in the monoclinic system with space group $P2_1/c$ (Table S1) and the asymmetric unit contains one Pb(II) ion, one $Hbidc^{2-}$ and one phen ligand (Fig. 1a). The Pb(II) ion is eight-coordinated by two N atoms (N1 and N2) from one phen ligand and six O atoms (O1, O2, O2A, O3A, O3B and O4B) from three different $Hbidc^{2-}$ ligands and shows a distorted bicapped trigonal prism coordination geometry (Fig. S1a). As listed in Table S2, there are six Pb–O bond distances, including three relatively shorter Pb–O bonds (Pb1–O1 = 2.627 Å, Pb1–O3A = 2.631 Å and Pb1–O4A = 2.504 Å) and three longer ones (Pb1–O2 = 2.833 Å,

---

* Corresponding author. Tel./fax: +86 29 88302604.
E-mail address: liuping@nwu.edu.cn (P. Liu).

1387-7003/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.inoche.2013.07.013

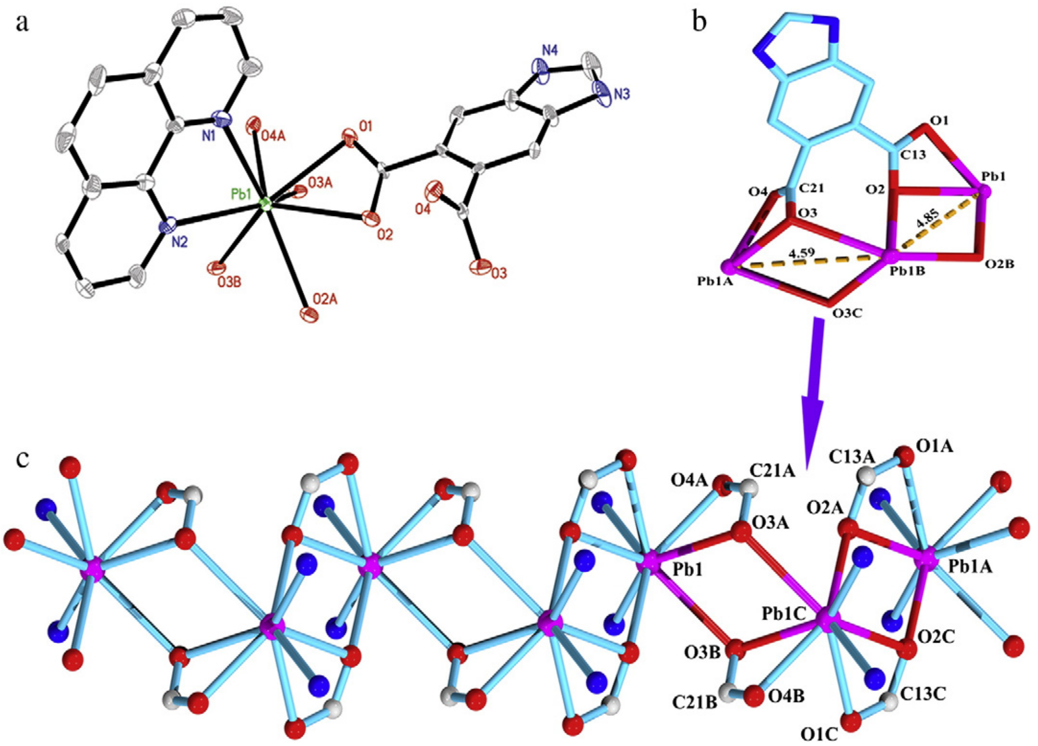

Fig. 1. (a) Coordination environment of Pb(II) in **1**, all H atoms and lattice H_2O molecules are omitted for clarity. (b) The μ_3-coordination mode of $Hbidc^{2-}$ ligand and two Pb···Pb separations. (c) 1D chain viewed in *b* axis. Atom coloring scheme: Pb, pink; O, red; N, blue; C, gray. Symmetry codes: (A) $x+1, y, z$; (B) $1-x, 2-y, 2-z$; (C) $2-x, 2-y, 2-z$.

Pb1 – O2B = 2.854 Å and Pb1 – O3B = 2.815 Å), are within the range of Pb – O covalent bond length (ranging from 2.46 to 2.96 Å) [18,21,22]. Meanwhile, the Pb – N distances are 2.707 and 2.779 Å, which are similar with the reported values [18]. The O – Pb – O/O – Pb – N angles vary from 47.7(5) to 139.0(4)°/59.5(4) to 144.5(3)°, respectively.

Notably, all the N atoms of the $Hbidc^{2-}$ ligands were uncoordinated. The reasons maybe that, on the one hand, the strong steric hindrance of rigid benzimidazole groups and *p*–*π* conjugation between imidazolyl N atoms and benzene rings decrease the coordination activity of N atoms. On the other hand, Pb(II) ion is a hard acid, thus it is more easily to coordinate with hard base O atom than to softer base N atom [5]. As shown in Fig. 1b, two carboxylic groups of one $Hbidc^{2-}$ ligand link three Pb(II) ions in μ_3–η^1:η^2:η^2:η^1 coordination mode and two carboxylic groups from two different $Hbidc^{2-}$ ligands bridge two Pb(II) ions forming a four-membered (Pb_2O_2) subring (Fig. S1b). The dihedral angle between the adjacent (Pb_2O_2) subring planes (R_a: Pb1B – O2 – Pb1 – O2A and R_b: Pb1 – O3A – Pb1C – O3B) is 88.84°. The Pb···Pb separations in R_a and R_b are 4.59 Å and 4.85 Å, respectively. The dihedral angles between the two carboxylic group planes (P_a: O4 – C21 – O3 – Pb1A and P_b: O1 – C13 – O2 – Pb1), between the imidazole plane and the carboxylic group plane (P_a or P_b) are 79.19°, 75.04° and 30.74°, respectively. The two (Pb_2O_2) subrings arrange alternately to form a 1D $(Pb_2O_2)_n$ chain (Fig. 1c) with $bmdc^{2-}$ and phen ligands arranged orderly (Fig. S1c). On the other hand, the 1D chain can also be viewed as being constructed by two different eight-membered ($Pb_2C_2O_4$) subrings (Pb1B – O2 – C13 – O1 – Pb1 – O2A – C13A – O1A and Pb1 – O3A – C21A – O4A – Pb1C – O3B – C121B – O14B) (Fig. S1d). With further structural analysis, a unique double-stranded helical chain is observed. As shown in Fig. 2, the smaller right-handed helical chain is constructed from the Pb – O bridges and the larger left-handed helical chain is comprised of the Pb – O – C – O bridges. Both of them share the same axis with the same pitch of 7.057(7) Å.

Furthermore, the adjacent double-stranded chiral chains construct a 3D supramolecular framework through the intermolecular hydrogen bonds and *π*–*π* stacking interactions (Fig. S2). In order to minimize the big void cavities and stabilize the framework, the potential voids are full of phen ligands which display staggered arrangement with ring centroid separation of 3.726 Å, indicating a weak *π*–*π* stacking interactions (Fig. S3) [23,24]. The intermolecular hydrogen bond distances between the lattice water molecules, uncoordinated imidazolyl N atoms and uncoordinated carboxylic O atoms, N(4) – H(4)···O(5), O(5) – H(5A)···O(1) and O(5) – H(5B)···N(3), are 2.78, 2.82 and 2.83 Å, respectively. The details of the hydrogen bonds are listed in Table S3.

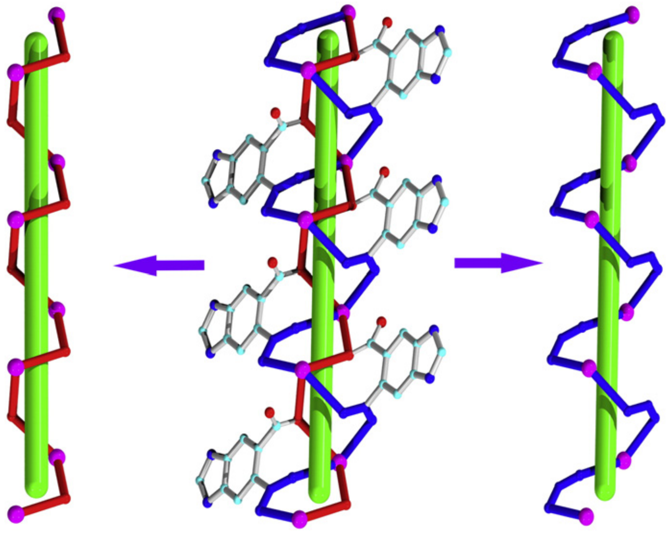

Fig. 2. The double-stranded helical chains which share the same axis; the red chain is the left-helical and the blue one is the right-helical. Atom coloring scheme: Pb, pink; O, red; N, blue; C, green.