



A novel 2D porous indium coordination polymer with tunable luminescent property



Xuejiao Li, Fangfang Wang, He Yang, Bo Xu^{*}, Cuncheng Li^{**}

Key Laboratory of Chemical Sensing & Analysis in Universities of Shandong (University of Jinan), School of Chemistry and Chemical Engineering, University of Jinan, Shandong, Jinan, 250022, China

ARTICLE INFO

Article history:

Received 12 January 2016

Received in revised form

30 March 2016

Accepted 31 March 2016

Available online 2 April 2016

Keywords:

Indium coordination polymer

Crystal structure

Luminescence

ABSTRACT

A new Indium coordination polymer $[\text{In}(\text{pda})_{1.5}(\text{phen})]_n$ **1** based on 1,4-phenylenediacetic acid (H_2pda) and phen = 1,10-phenanthroline was obtained under hydrothermal condition and further characterized by single crystal X-ray analysis and other physicochemical studies such as infrared spectrum (IR), elemental analysis, thermogravimetric analysis (TGA) and powder X-ray diffraction (PXRD). Structure analysis reveals that complex **1** exhibits 2D porous (6,3) connected layer structure. Luminescent property of **1** was investigated both in the solid state and in different solvents and the results indicated that complex **1** demonstrates distinct solvent dependent luminescent property.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Coordination polymers (CPs) have attracted increasing attention for various applications in the fields of luminescence, gas adsorption and separation, catalysis, chemical sensor and so on due to their unique properties and tailorability [1–4]. Designed synthesis of CPs with certain structures and properties can be achieved by rational selection and skilled assemble of organic ligand and salts under certain reaction condition [5–7]. Although a large number of CPs assembled from transition metals and rare earth elements have been reported, CPs based on main group metal elements is rarely studied [8–10]. On the other hand, we have noticed that CPs constructed from main group metals usually show wonderful properties in the fields of luminescence, optoelectronic devices, catalyst and so on [11–13]. However, because main group metals have obvious differences in electronic structures and coordination nature with transition metals or rare earth metals, it is still great challenge for chemists to design and prepare new CPs with novel topological architectures and fascinating properties based on main group metals. Bearing all this in mind, we have been engaged in the construction of CPs with main group metals and have reported Pb(II)-based CPs showing interesting luminescent properties

[14,15]. Now as an extension of our before work and inspired by prominent work of M. C. Hong, R. Q. Fan and their co-workers [16–18], we now focus our attention on the construction of CPs based on main group metal indium (III) salts. As known, the hydrolysis of In(III) salts is a great challenge for the synthesis of In-CPs. However, as In(III) complexes exhibit great potential applications in many fields as catalysis, photoluminescence, molecular recognition and so on, it is of great importance to further deepen the research. Now, in this work, we reported a novel indium CP constructed from indium nitrate, H_2pda and phen ligand under hydrothermal conditions formulated as $[\text{In}(\text{pda})_{1.5}(\text{phen})]_n$ **1**. X-ray crystal diffraction analysis reveals that complex **1** holds 2D porous (6,3) layer structure. The complex was further characterized by IR spectrum, PXRD, TG (see the [supporting information](#)) and elemental analysis. The photoluminescent properties of the complex have also been studied in detail and the results indicated that complex **1** shows tunable photoluminescence affected by different solvents.

2. Experimental details

2.1. Materials and general methods

All commercially available reagents and starting materials were of reagent-grade quality and used without further purification. Elemental analyses (C, H, N) were carried out on an Elementar Vario EL III analyzer. Infrared (IR) spectra were recorded on PerkinElmer

^{*} Corresponding author.

^{**} Corresponding author.

E-mail addresses: chm_xub@ujn.edu.cn (B. Xu), chm_licc@ujn.edu.cn (C. Li).

Spectrum One as KBr pellets in the range 4000–400 cm^{-1} . Thermogravimetric analysis was recorded with a NETZSCH STA 449C unit at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere. X-ray Powdered diffraction (XRPD) patterns of the samples were recorded by an X-ray diffractometer (Bruker D8 FOCUS). Luminescent spectra were carried out on an Edinburgh FLS920 phosphorimeter equipped with a continuous Xe-900 xenon lamp and an nF900 ns flash lamp.

2.2. Synthesis of complex 1

$[\text{In}(\text{pda})_{1.5}(\text{phen})_n]_n$ **1**: Complex **1** was isolated by mixing $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.2 mmol), phen (0.2 mmol), H_2pda (0.2 mmol), and NaOH (0.3 mmol) in 10 ml water and stirred for 30 min in air. Then the mixture was transferred to 25 ml stainless-steel reactors with Teflon liner and heated to 150 $^{\circ}\text{C}$ in 3 h. The temperature was kept at 150 $^{\circ}\text{C}$ for 4 days and cooled to room temperature during 24 h. Colorless block crystals of **1** was isolated by filtration, washed with distilled water, and dried in air (yield based on In: 32%). Anal. Calcd. for $\text{C}_{27}\text{H}_{20}\text{InN}_2\text{O}_6$ (583.27): C 55.60, H 3.46, N 4.80; found: C 55.52, H 3.21, N 4.77. IR (KBr, cm^{-1}): 3220 (m, br), 3063 (w), 1614 (vs), 1560 (s), 1432 (s), 1382 (s), 1187 (m), 1112 (w), 1047 (m), 852 (m), 756 (m), 690 (m).

2.3. Crystallographic details

Data collection was performed on a Xcalibur Eos Gemini diffractometer with graphite-monochromated Mo- $K\alpha$ ($\lambda = 0.71073$ Å) radiation at room temperature. The structures were solved by direct methods and refined by the full-matrix least-squares on F^2 using the *SHELXTL-97* program [19]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of hydrogen atoms attached to carbon atoms were generated geometrically (C–H bond fixed at 0.99 Å). Idealized positions of H atoms belonging to nitrogen atoms and water molecules were located from Fourier difference maps and refined isotropically. Crystallographic data and structure determination summaries are listed in Table 1. Selected bond lengths and angles of complex **1** are listed in Table 2.

Table 1
Crystal data and structure refinement parameters for compound **1**.

Complex	1
Empirical formula	$\text{C}_{27}\text{H}_{20}\text{InN}_2\text{O}_6$
Formula weight	583.27
Crystal system	monoclinic
Space group	$P2_1/n$
<i>a</i> (Å)	9.4054(3)
<i>b</i> (Å)	16.3729(6)
<i>c</i> (Å)	15.2367(7)
α (deg)	90.00
β (deg)	97.340(4)
γ (deg)	90.00
<i>V</i> (Å ³)	2327.13(16)
<i>Z</i>	4
<i>D</i> _{calc} (g/cm ³)	1.665
<i>F</i> (000)	1172
Reflns collected/unique	14368/4743
μ (mm ⁻¹)	1.063
GOF on F^2	1.048
<i>R</i> ₁ ^a (<i>I</i> > 2 σ (<i>I</i>))	0.0331
<i>wR</i> ₂ ^b (all data)	0.0828

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $wR(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

Table 2
Selected bond lengths (Å) and angles ($^{\circ}$) for complex **1**.

Complex 1			
In1–N1	2.285(2)	In1–O6 ¹	2.288(2)
In1–N2	2.286(3)	In1–O3	2.104(3)
In1–O2	2.327(3)	In1–O5 ¹	2.246(3)
In1–O1	2.239(2)	O1–In1–O5 ¹	136.58(9)
N1–In1–O2	86.53(9)	O6 ¹ –In1–O2	137.66(9)
N1–In1–O6 ¹	128.90(9)	O3–In1–N1	85.21(10)
N2–In1–N1	72.65(9)	O3–In1–N2	155.74(10)
N2–In1–O2	84.08(10)	O3–In1–O2	84.80(12)
N2–In1–O6 ¹	85.92(10)	O3–In1–O1	100.17(11)
O1–In1–N1	141.57(9)	O3–In1–O6 ¹	116.43(11)
O1–In1–N2	91.53(10)	O3–In1–O5 ¹	88.28(16)
O1–In1–O2	56.56(9)	O5 ¹ –In1–N1	81.16(10)
O1–In1–O6 ¹	82.78(9)	O1–In1–O5 ¹	136.58(9)
O5 ¹ –In1–N2	97.78(14)	O5 ¹ –In1–O6 ¹	55.96(10)
O5 ¹ –In1–O2	166.34(10)		

Symmetry transformations used to generate equivalent atoms: for **1** ¹ 5/2–*X*, –1/2 + *Y*, 1/2–*Z*.

3. Results and discussion

3.1. Structural analysis of compound 1

Single-crystal X-ray diffraction analysis reveals that complex **1** crystallizes in monoclinic $P2_1/n$ space group. The asymmetric unit contains one In(III) ion, one full (*pda-A*, marked by O1, O2, O5 and O6) and a half (*pda-B*, marked by O3 and O4) pda^{2-} ligand and one phen ligand. As illustrated in Fig. 1, the In(III) centre is seven-coordinated by five oxygen atoms from three carboxyl groups and two nitrogen atoms from one phen molecule in a distorted single-capped octahedral coordination geometry. The In–O bond distances range from 2.104(3) to 2.327(3) Å with an average bond length of 2.241(3) Å, while the two In–N bond lengths are 2.285(2) and 2.286(3) Å respectively, which are all comparable with that observed in other indium(III)-containing complexes [20,21]. In complex **1**, the *pda-A* ligand holds the η^2 – η^2 coordination mode with both the two carboxyl groups acting in chelating coordination mode, while the *pda-B* ligand displays η^1 – η^1 coordination mode with both the two carboxyl groups exhibiting a monodentate bridging mode. Further, central In(III) cations are 3-connected and are linked by these two kinds of pda^{2-} ligand into 2D (6, 3) layer structure as shown in Fig. 2. Pores in the 2D layers are almost rectangular with dimensions of 11.757 Å \times 19.989 Å and the vertex angles are 89.59 $^{\circ}$ and 90.41 $^{\circ}$. Packing of these layers results in a 3D supramolecular structure as shown in Fig. S1. There is no classic hydrogen bond in complex **1** as calculated by Platon, and only weak $\pi \cdots \pi$ interactions exist between layers and further stabilize the 3D supramolecular structure. Some other In(III) coordination polymers

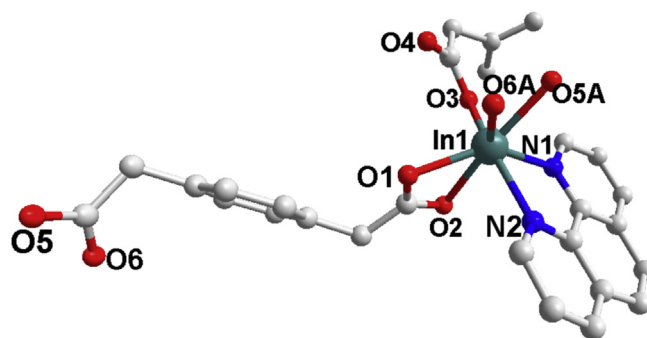


Fig. 1. The coordination environment of In(III) ions in **1**. Hydrogen atoms are omitted for clarity. Symmetry code: (A) 2.5–*x*, –0.5 + *y*, 0.5–*z*.

Download English Version:

<https://daneshyari.com/en/article/1408797>

Download Persian Version:

<https://daneshyari.com/article/1408797>

[Daneshyari.com](https://daneshyari.com)