Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Molecular Structure 783 (2006) 9–12

Journal of
MOLECULAR
STRUCTURE

www.elsevier.com/locate/molstruc

$[Zn(INO)_2(DMF)]\cdot DMF$: A new three-dimensional supramolecular open framework containing one-dimensional channels

Jun Hong*

Department of Chemistry, Jilin Normal University, Siping, 136000, People's Republic of China

Received 15 July 2005; revised 3 August 2005; accepted 5 August 2005
Available online 21 September 2005

Abstract

A three-dimensional supramolecular compound, $[Zn(INO)_2(DMF)]\cdot DMF$ (1) (INO = isonicotinic acid N-oxide), has been prepared in the DMF solution at room temperature, and characterized by elemental analysis, TG and single crystal X-ray diffraction. The three-dimensional supramolecular open framework of **1** contains rectangular channels with the dimensions of 9.02 × 10.15 Å, assembled from one-dimensional helical chains via hydrogen-bonding and π–π stacking interactions. Furthermore, compound **1** shows blue photoluminescence at room temperature.

Keywords: Crystal structure; Helical chain; Supramolecular network; Channel; Luminescence

1. Introduction

The rational design and synthesis of metal-directed supramolecular frameworks have received much attention in coordination chemistry because of their interesting molecular topologies and their tremendous potential applications in host–guest chemistry, catalysis, molecular selection, non-linear optics, ion exchange and microelectronics [1,2]. During the last decade, varieties of attractive networks with fascinating structural motifs, including honeycomb, brick wall, bilayer, ladder, herringbone, diamondiod, rectangular grid, and octahedral geometries, have been deliberately designed [3–8]. Generally, the construction of these metal-containing supramolecular frameworks can be achieved *via* two kinds of interactions, i.e. coordinate covalent bonds and weaker intermolecular forces including hydrogen bonding, π–π stacking and Coulombic interactions. It should be noted that these weaker intermolecular forces play an important role in the formation of high-dimensional frameworks [9–17]. One of the important targets in the formation of supramolecular assembly is to establish the possible links between units. In view of this, organic aromatic ligands are good candidates because they can not only act as hydrogen-bonding accepters or donors but also may provide recognition sites for π–π stacking interactions to form interesting supramolecular structures when coordinated with metal ions.

On the other hand, polynuclear d^{10} metal (Cu^{I}, Ag^{II}, Au^{I}, Zn^{II} or Cd^{II}) complexes have attracted extensive interest in recent years in that they not only exhibit appealing structures but also possess photoluminescent properties [18].

On the basis of the aforementioned points, we chose zinc nitrate and isonicotinic acid N-oxide [19] (INO) as building blocks and attempted to synthesize new suprmolecular compounds and study their luminescent property. In this paper we report a new three-dimensional supramolecular coordination polymer, $[Zn(INO)_2(DMF)]\cdot DMF$ (**1**). Interestingly, the compound consists of one-dimensional rectangular channels assembled by helical chains via hydrogen-bonding and aromatic π–π stacking interactions. Furthermore, compound **1** shows blue photoluminescence at room temperature.

2. Experimental section

2.1. Materials and methods

All chemicals purchased were of reagent grade and used without further purification. Elemental analyses (C, H

---

* Corresponding author. Tel.: +86 434 3292154.
E-mail address: junhong000@hotmail.com

0022-2860/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2005.08.013

and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. TG analysis was performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10°C min^{-1}. Excitation and emission spectra were obtained on a SPEX FL-2T2 spectrofluorometer equipped with a 450 W xenon lamp as the excitation source.

2.2. Synthesis

$Zn(NO_3)_2 \cdot 6H_2O$ (1 mmol, 0.2975 g) and isonicotinic acid N-oxide (2 mmol, 0.2800 g) were dissolved in DMF (10 mL). The solution was allowed to stand undisturbed for two weeks and colorless crystals grew at the bottom of beaker (yield 62% based on Zn). Elemental analysis (%) found: C 44.5, H 4.6, N 11.2. Calcd.: C 44.32, H 4.55, N 11.49.

2.3. X-ray crystallography

A colorless single crystal with dimensions $0.34 \times 0.26 \times 0.24$ mm^3 was glued on a glass fiber. Data were collected on a Rigaku *R*-axis RAPID IP diffractometer at 293 K using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and IP technique in the range $3.07° < \theta < 27.48°$. Empirical absorption correction was applied. The structure was solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXTL crystallographic software package [20]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. The hydrogen atoms of water molecule included at idealized positions. Further details of the X-ray structural analysis are given in Table 1. Selected bond lengths and angles are listed in Table 2. CCDC number: 277584.

Table 1
Crystal data and structure refinement for **1**

Experical formula	$C_{18}H_{22}N_4O_8Zn$
Formula weight	487.77
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	7.0453(14)
b (Å)	13.906(3)
c (Å)	22.344(5)
β°	91.64(3)
Volume ($Å^3$)	2188.2(8)
Z	4
P_{calc} ($mg\ m^{-3}$)	1.481
Absorption coefficient (mm^{-1})	1.173
F(000)	1008
Crystal size (mm)	$0.34 \times 0.26 \times 0.24$
θ range (°)	3.07–27.48
Reflections collected	20458
Independent reflections	4899
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4899/0/280
Goodness-of-fit on F^2	1.041
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0479$, $wR2 = 0.1215$
R indices (all data)	$R1 = 0.0785$, $wR2 = 0.1336$
Largest diff. peak and hole ($e\ Å^{-3}$)	0.515 and −0.424

3. Results and discussion

3.1. Structure description

The single-crystal X-ray structural analysis reveals that compound **1** exhibits an interesting three-dimensional supramolecular network containing one dimensional rectangular channel. The asymmetric unit contains one zinc atom, two INO groups, and two DMF molecules. The crystallographically unique zinc atom is coordinated by four oxygen atoms (Zn(1)–O(1A) = 2.013(2) Å; Zn(1)–O(3) = 2.242(2) Å; Zn (1)–O(4) = 2.088(2) Å, Zn(1)–O(5) = 1.997(2) Å) from three INO ligands, and one oxygen atom (Zn(1)–O(7) = 2.028(2) Å) from one DMF molecule, showing a distorted trigonal bipyramidal coordination geometry (Fig. 1). In addition, two types of INO ligands exist in 1: INO^A contains one monodentate bridging carboxylate group and one bridging N-oxide group, whereas INO^B contains only one chelating carboxylate group (see Scheme 1).

The adjacent Zn atoms are linked by INO^A ligands to form a chiral helical chain running along *b* axis (Fig. 2a). The helix is generated around the crystallographic 2_1 axis with a pitch of 13.906 Å, and decorated by INO^B ligands and coordinated DMF molecules bristling out at the two sides of the helix. The INO^B phenyl rings at each side of the helix are arranged in a parallel fashion with an inter-ring distance of 20.87(2) Å. This orientation plays a critical role in packing into a higher network through π–π stacking interactions. The adjacent helical chains with the same handedness are further connected into a chiral sheet through very significant C–H···O hydrogen bonds (C1–H1A···O2 3.088(4) Å, C7–H7A···O3 3.100(4)–Å) between aromatic carbon atoms (C1 and C7) and carboxyl oxygen atoms (O2 and O3) (see Fig. 2b). These chiral sheets are racemically packed through strong aromatic π-π stacking interactions

Table 2
Selected bond lengths (Å) and angles (°) for **1**

Bonds			
Zn(1)–O(5)	1.997(2)	Zn(1)–O(1A)	2.013(2)
Zn(1)–O(7)	2.028(2)	Zn(1)–O(4)	2.088(2)
Zn(1)–O(3)	2.242(2)		
Angles			
O(5)–Zn(1)–O(1A)	101.36(9)	O(5)–Zn(1)–O(7)	97.57(10)
O(1A)–Zn(1)–O(7)	101.15(10)	O(5)–Zn(1)–O(4)	108.65(10)
O(1A)–Zn(1)–O(4)	144.28(10)	O(7)–Zn(1)–O(4)	93.77(10)
O(5)–Zn(1)–O(3)	93.52(9)	O(1A)–Zn(1)–O(3)	99.42(9)
O(7)–Zn(1)–O(3)	154.16(9)	O(4)–Zn(1)–O(3)	60.51(8)
C(12)–O(3)–Zn(1)	85.86(18)	C(12)–O(4)–Zn(1)	92.65(18)
N(1)–O(5)–Zn(1)	119.00(17)	C(13)–O(7)–Zn(1)	122.6(2)

Symmetry transformations used to generate equivalent atoms: A: $-x, y+1/2, -z+1/2$.