

一维链状铁(II)配位聚合物的合成与晶体结构

车广波^{*,1,2,3} 李秀颖¹ 徐占林^{1,2,3} 刘春波^{1,2,3} 王庆伟^{1,2,3}

(¹ 吉林师范大学化学学院, 四平 136000)

(² 吉林师范大学应用化学研究所, 四平 136000)

(³ 医药中间体吉林省高等学校工程研究中心, 四平 136000)

关键词: 铁(II)配位聚合物; 二吡啶[3,2-a:2',3'-c]并吩嗪; 2,6-吡啶二甲酸; 晶体结构

中图分类号: O614.81^{†1}

文献标识码: A

文章编号: 1001-4861(2009)03-0556-04

Synthesis and Crystal Structure of Iron(II) Coordination Polymer Composed of 1D Chains

CHE Guang-Bo^{*,1,2,3} LI Xiu-Ying¹ XU Zhan-Lin^{1,2,3} LIU Chun-Bo^{1,2,3} WANG Qing-Wei^{1,2,3}

(¹Department of Chemistry, Jilin Normal University, Siping, Jilin 136000)

(²Institute of Applied Chemistry, Jilin Normal University, Siping, Jilin 136000)

(³College of Jilin Province, Engineering Research Center of Medicine Intermediate, Siping, Jilin 136000)

Abstract: A coordination polymer, namely $[\text{Fe}(\text{DPPZ})(\text{dipic})]_n$ (**1**) (DPPZ=dipyrido[3,2-a:2',3'-c]phenazine and H_2dipic =pyridine-2,6-dicarboxylic acid), has been obtained by using hydrothermal synthesis method. The crystal structure was determined by X-ray single crystal structure analysis with the following data: Monoclinic, $P2_1/c$, $a=0.794\,95(16)$ nm, $b=3.601\,1(7)$ nm, $c=0.734\,32(15)$ nm, $\beta=106.07(3)^\circ$, $V=2.020\,0(7)$ nm³, $Z=4$, $M_r=503.25$, $D_c=1.655$ g·cm⁻³, $F(000)=1\,024$, $\mu(\text{Mo } K\alpha)=0.795$ mm⁻¹, $R=0.038\,5$ and $wR=0.081\,0$. Complex **1** has octahedral coordination geometry and forms 1D zigzag coordination chains that organize into an unusual 3D supramolecular motif through noncovalent bonds, such as π - π stacking interactions and C-H \cdots O hydrogen bonds. The result of TG analysis indicates that the title complex is stable till 290 °C. CCDC: 716602.

Key words: iron(II) coordination polymer; dipyrido[3,2-a:2',3'-c]phenazine; pyridine-2,6-dicarboxylic acid; crystal structure

0 Introduction

Coordination polymers have attracted much interest from chemists by their intriguing structural diversities and molecular topologies, and also their potential applications as functional materials in magnetism, luminescence, molecular recognition, catalysis and chirality etc^[1~6]. Much attention in this area has been

focused on the design and construction of novel topological structure and the relationships between their frameworks and properties^[7]. Building blocks derived from the appropriate modification of 1,10-phenanthroline (phen) have hitherto been extensively explored, as ligands in different transition metal complexes^[8~10]. Dipyrido[3,2-a:2',3'-c]phenazine (DPPZ) as an important derivative of phen has been widely used to

收稿日期: 2008-10-07。收修改稿日期: 2008-12-18。

吉林省自然科学基金项目(No.20060516); 吉林师范大学博士启动基金项目(No.2006006, 2007009); 吉林师范大学学科基地建设基金项目(No.2006041)和研创新(学)(No.2006066)。

*通讯联系人。E-mail: guangbochejl@yahoo.com

第一作者: 车广波, 男, 35 岁, 博士, 副教授; 研究方向: 无机-有机杂化材料的合成及光电特性研究。

construct metal-organic complexes due to its excellent coordinating ability and further capacity to provide potential supramolecular recognition sites for π - π aromatic stacking interactions^[11]. Furthermore, coordination polymers based on DPPZ in combination with nitrogen-containing heteroaryldicarboxylate ligand, such as pyridine-2,6-dicarboxylic acid (H_2dipic) have not been studied. As an extension of our study, we adopt hydrothermal techniques and successfully synthesize a new 1D coordination polymer: $[Fe(DPPZ)(dipic)]_n$ (**1**), building from iron(II) ion and the mixed ligands. Herein, we present the synthesis, structural and thermal property of complex **1** and supramolecular interactions such as π - π stackings and C-H \cdots O hydrogen bonds responsible for the extended networks are also discussed.

1 Experimental

1.1 Materials and general methods

With the exception of the ligand DPPZ, which was synthesized by the method of the literature^[12], all chemicals purchased were of reagent grade and used without further purification. FTIR spectra (KBr pellets) were taken on a Perkin-Elmer 2400LSII spectrometer. The C, H, N elemental analysis was carried out with a Perkin-Elmer 240C element analyzer, whereas thermogravimetric analysis (TG) was conducted on a NETZSCH STA 449C analyzer.

1.2 Synthesis of the title compound

A mixture of $FeSO_4 \cdot 4H_2O$ (0.112 0 g, 0.5 mmol),

DPPZ (0.141 0 g, 0.5 mmol), H_2dipic (0.083 0 g, 0.5 mmol), NaOH (0.008 0 g, 0.2 mmol) and H_2O (15 mL) were placed in a 25 mL Teflon-lined stainless steel vessel and then heated to 160 $^{\circ}C$ for three days and the reactant was cooled at a rate of 5 $^{\circ}C \cdot h^{-1}$. The brown crystals were obtained with a yield of 70.2% based on Fe. Elemental analysis: calcd. for **1**(%): C, 59.67; H, 2.60; N, 13.92. Found(%): C, 59.64; H, 2.62; N, 13.93. Main IR bands (cm^{-1}): 3 109s, 1 625s, 1 570s, 1 447w, 1 408w, 1 365m, 1 123m, 737s.

1.3 Crystal structure determination

Single crystal X-ray diffraction data of complex **1** was collected on a Bruker Smart Apex CCD diffractometer at 292(2) K with Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm). A total of 17 260 reflections were collected in the range of $2.26^{\circ} \leq \theta \leq 26.05^{\circ}$, of which 3 979 were unique with $R_{int}=0.053\ 9$ and 2 843 with $I>2\sigma(I)$ were considered as observed. Empirical absorption corrections were applied using SADABS^[13]. The structure was solved by direct methods with SHELXS-97 program^[14] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97^[15]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. The final $R=0.038\ 5$ and $wR=0.081\ 0$ ($w=1/[\sigma^2(F_o^2)(0.034\ 5 P)^2+0.856\ 6 P]$, where $P=(F_o^2+2F_c^2)/3$). $S=1.030$, $(\Delta\rho)_{max}=464$ and $(\Delta\rho)_{min}=-389\ e \cdot nm^{-3}$ and $(\Delta/\sigma)_{max}=0.001$. Further details for crystallographic data and refinement conditions are summarized in Table 1. Selected bond distances and angles are listed in Table 2.

CCDC: 716602.

Table 1 Crystal data and structure parameters for the title complex

Empirical formula	$C_{25}H_{13}N_5O_4Fe$	Absorption coefficient / mm^{-1}	0.795
Formula weight	503.25	$F(000)$	1 024
Temperature / K	292(2)	Crystal size / mm	0.332 \times 0.272 \times 0.238
Crystal system	Monoclinic	$\theta / (^{\circ})$	2.26~26.05
Space group	$P2_1/c$	Limiting indices	$-9 \leq h \leq 9, -42 \leq k \leq 44, -9 \leq l \leq 9$
a / nm	0.794 95(16)	Reflections collected / unique (R_{int})	17 260 / 3 979 (0.053 9)
b / nm	3.601 1(7)	Refinement method	Full-matrix least-squares on F^2
c / nm	0.734 32(15)	Data / restraints / parameters	3 979 / 0 / 316
$\beta / (^{\circ})$	106.07(3)	Goodness of fit on F^2	1.03
V / nm^3	2.020 0(7)	Final R indices [$I>2\sigma(I)$]	$R_1=0.038\ 5, wR_2=0.081\ 0$
D_c / ($g \cdot cm^{-3}$)	1.655	Largest diff. peak and hole / ($e \cdot nm^{-3}$)	464, -389
Z	4		

Table 2 Selected bond lengths (nm) and bond angles ($^{\circ}$) for compound **1**

Fe-N(1)	0.214 6(2)	Fe-N(2)	0.217 9(2)	Fe-N(5)	0.207 4(2)
Fe-O(4) ⁱ	0.213 71(19)	Fe-O(1)	0.213 15(19)	Fe-O(3)	0.216 86(18)
N(5)-Fe-O(4) ⁱ	97.39(8)	O(1)-Fe-O(4) ⁱ	97.02(8)	O(1)-Fe-N(2)	85.08(8)
N(5)-Fe-N(1)	172.16(8)	O(1)-Fe-N(1)	99.01(8)	N(1)-Fe-N(2)	76.40(8)
O(4) ⁱ -Fe-N(1)	88.63(8)	N(5)-Fe-O(3)	74.48(8)	O(4) ⁱ -Fe-N(2)	165.02(8)
O(1)-Fe-O(3)	149.75(7)	O(4B)-Fe-O(3)	89.09(8)	O(3)-Fe-N(2)	96.55(8)
N(1)-Fe-O(3)	110.78(8)	N(5)-Fe-N(2)	97.48(8)	N(5)-Fe-O(1)	75.35(8)

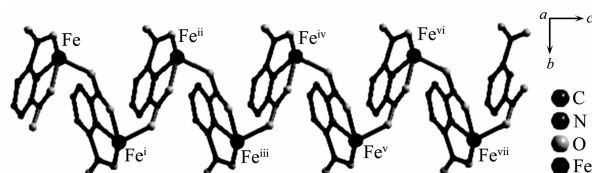
Symmetry transformations used to generate equivalent atoms: ⁱ $x, y, z+1/2$.

2 Results and discussion

2.1 Crystal structure of the title complex

The crystal structure reveals that complex **1** exhibits a unique zigzag chain structure consisting of [Fe(DPPZ)(dipic)] entities. As shown in Fig.1, each Fe(II) atom is coordinated by three N atoms [Fe-N(1)=0.214 6(2) nm, Fe-N(2)=0.217 9(2) nm, Fe-N(5)=0.207 4(2) nm] from one chelating DPPZ ligand and one dipic²⁻ ligand, three O atoms [Fe-O(1)=0.213 15(19) nm, Fe-O(3)=0.216 86(18) nm, Fe-O(4)ⁱ=0.213 71(19) nm] from two dipic²⁻ ligands, residing in a distorted octahedral environment. In **1**, each dipic ligand adopts tridentate coordination mode, the pyridine nitrogen atom and two oxygen atoms of two carboxylic groups chelates a Fe(II) ion, while the others two oxygen atoms adopt the monodentate and noncoordinated mode, respectively. On the basis of these connection modes, the Fe ions are linked by bridging dipic ligands to form a distinctive zigzag chain running along the [001] direction, with the shortest Fe...Fe distance of 0.596 2 nm across the single dipic²⁻ bridge. Here, the chains are decorated with DPPZ ligands alternately at two sides (Fig.2). The predominant face-to-face π - π stacking interactions between the DPPZ ligands of adjacent

chains occur in two different directions with the shortest centroid-centroid distance being 0.348 1 nm, so a 3D framework structure is formed. In addition, the C-H...O hydrogen bonds involving the hydrogen of aromatic rings and the carboxylic groups of dipic²⁻ ligands further stabilize the structure [C(1)-H(1)...O(4): 0.093, 0.256, and 0.309 7(4) nm, 117 $^{\circ}$, symmetry code: $x, 1/2-y, 1/2+z$; C(2)-H(2)...O(2): 0.093, 0.244, and 0.326 6(4) nm, 149 $^{\circ}$, symmetry code: $1+x, y, 1+z$; C(15)-H(15)...O(1): 0.093, 0.247, and 0.335 1(4) nm, 159 $^{\circ}$, symmetry code: $x, y, -1+z$; C(21)-H(21)...O(3): 0.093, 0.259, and 0.330 0 (4) nm, 134 $^{\circ}$, symmetry code: $-1+x, 1/2-y, -1/2+z$).



The symmetry code: ⁱ $x, -y+1/2, z+1/2$; ⁱⁱ $x, y, z+1$; ⁱⁱⁱ $x, -y+1/2, z+3/2$; ^{iv} $x, y, z+2$; ^v $x, -y+1/2, z+5/2$; ^{vi} $x, y, z+3$; ^{vii} $x, -y+1/2, z+7/2$

Fig.2 One dimensional chain of **1** viewed from c axis, the DPPZ were omitted for clarity

2.2 Thermal analysis

Thermogravimetric experiment of complex **1** was performed to explore its thermal stability. Complex **1** exhibits two steps of weight losses: the first weight loss of 33.01% from 290 to 370 $^{\circ}\text{C}$ displays the loss of dipic²⁻ ligands (calcd 32.80%); the second weight loss of 55.93% from 390 to 470 $^{\circ}\text{C}$ is ascribed to the loss of DPPZ (calcd 56.06%). The final product may be FeO. The analysis result indicates that complex **1** is stable at ambient conditions.

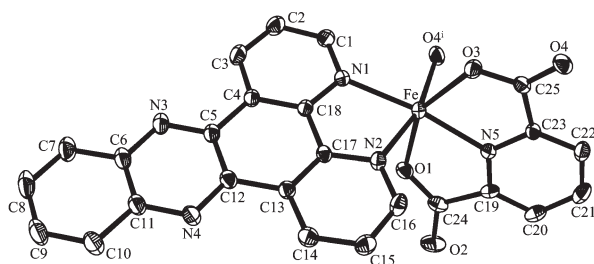


Fig.1 Crystal structure of compound **1**

References:

- [1] Wen D L, Liu S X, Lin M. *Journal of Molecular Structure*, **2008**,**876**:154~161
- [2] Zhuang W J, Jin L P. *Appl. Organometal. Chem.*, **2007**,**21**:76~82
- [3] Moulton B, Zaworotko M J. *Chem. Rev.*, **2001**,**101**:1629~1658
- [4] Eddaoudi M, Moler D B, Li H, et al. *Acc. Chem. Res.*, **2001**, **34**:319~330
- [5] Janiak C. *Dalton Trans*, **2003**:2781~2804
- [6] Bradshaw D, Claridge J B, Cussen E J, et al. *Acc. Chem. Res.*, **2005**,**38**:273~282
- [7] Cui G H, Li J R, Tian J L, et al. *Cryst. Growth & Des.*, **2005**,**5**: 1775~1780
- [8] Che G B, Xu Z L, Liu C B. *Acta Cryst.*, **2006**,**E62**:m1370~m1372
- [9] Che G B, Liu C B, Liu B, et al. *Cryst. Eng. Comm.*, **2008**,**10**: 184~191
- [10] LIU Chun-Bo(刘春波), CHE Guang-Bo(车广波), WANG Qing-Wei(王庆伟), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2008**,**24**:835~838
- [11] XU Zhan-Lin(徐占林), LI Xiu-Ying(李秀颖), CHE Guang-Bo (车广波), et al. *Chinese J. Struct. Chem. (Jiegou Huaxue)*, **2008**,**27**:593~597
- [12] Che G B, Li W L, Kong Z G, et al. *Synth. Commun.*, **2006**,**36**: 2519~2524
- [13] Sheldrick G M. *SADABS: Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany, **1996**.
- [14] Sheldrick G M. *SHELXS-97, Program for the Solution of Crystal Structure*, University of Göttingen, **1997**.
- [15] Sheldrick G M. *SHELXS-97, Program for the Refinement of Crystal Structure*, University of Göttingen, **1997**.