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二维 Mn(Ⅱ)配位聚合物的水热合成、晶体结构和性质

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摘要:通过水热方法合成了一个二维配位聚合物[Mn(NIPA)(L)]$_n$ (**1**)(L=二(5,6-二甲基苯并咪唑基)-1,3-丙烷、H_2NIPA=5-硝基间苯二甲酸),并通过元素分析、IR、单晶 X-射线衍射对其进行了结构表征。结果表明化合物 **1**($MnC_{29}H_{27}N_5O_6$)属三斜晶系:$P\bar{1}$,a=1.029 41(10),b=1.057 10(10),c=1.324 91(12) nm,Z=2,V=1.395 5(2) nm^3,M_r=596.50,D_c=1.420 g·cm^{-3},F(000)=618,μ=0.525 mm^{-1},S=1.027,R=0.041 7,wR=0.097 5。结构分析表明每个 Mn(Ⅱ)与 2 个 L 配体上的 2 个氮原子、来自 3 个不同 NIPA 上的 2 个螯合氧原子以及 2 个单齿氧原子形成六配位模式。相邻的由 2 个羧基连接成的双核 Mn(Ⅱ)簇通过成对的 NIPA 连接成一维双链结构,进而通过成对的 L 配体拓展成二维(4,4)网络。此外,还研究了该化合物的热稳定性和荧光性质。

关键词:水热合成;晶体结构;锰(Ⅱ)配合物;光致发光性质
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Hydrothermal Synthesis, Crystal Structure and Property of a 2D Mn(Ⅱ) Coordination Polymer

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Abstract: A 2D coordination polymer [Mn(NIPA)(L)]$_n$ (**1**) (L=1,1′-(1,3-propanediyl)bis(5,6-dimethylbenzimidazole), H_2NIPA=5-nitroisophthalic acid) has been hydrothermally synthesized and structurally characterized by elemental analysis, IR and single crystal X-ray diffraction analysis. Compound **1** ($MnC_{29}H_{27}N_5O_6$): triclinic system, space group $P\bar{1}$, a=1.029 41(10) nm, b=1.057 10(10) nm, c=1.324 91(12) nm, Z=2, V=1.395 5(2) nm^3, M_r=596.50, D_c=1.420 g·cm^{-3}, F(000)=618, μ=0.525 mm^{-1}, S=1.027, the final R=0.041 7 and wR=0.097 5. The crystal structure analysis indicates that the Mn(Ⅱ) cation is six-coordinated by two nitrogen atoms from two L ligands, two chelating oxygen atoms and two monodentate oxygen atoms from three carboxylic groups of different NIPA anions. The adjacent bimetallic Mn(Ⅱ) clusters linked by carboxylic groups are connected by pairs of NIPA anions to form a 1D double chain and the chains are further extended through pairs of L ligands into 2D (4,4) network. Moreover, the thermal stability and photoluminescence property of the title compound were investigated. CCDC: 850309.

Key words: hydrothermal synthesis; crystal structure; manganese(Ⅱ) complex; photoluminescence property

0 Introduction

In the past decades, using transition metal and organic multidentate ligands to construct metal-organic coordination polymers has attracted a great deal of interest, not only because of their structural diversities, but also owing to their promising applications in luminescence, magnetism material and catalysis[1-3]. The rational design of prospective structures with specific properties can be obtained by careful selection of metal

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cations and the properties of the ligands, such as flexibility and substituent group[4-6]. Among the large numbers of multidentate N-donor ligands, flexible multi-benzimidazole derivatives seem to be excellent building block with versatile coordination modes as well as the remarkable coordination ability and stability, and have been widely used in constructing novel functional transition metal coordination polymers by Ma, Lang and our group[7-9]. On the other hand, V-shaped aromatic dicarboxylates [isophthalic acid, 5-hydroxyisophthalic acid, 5-tert-butylisophthalic acid and 5-nitroisophthalic acid (H_2NIPA)] with an ideal 120° coordination angles are convenient bridging units for linking the adjacent metallic centers to form various architectures[10-14]. As the expansion of our previous work[15-16], we select 1,1′-(1,3-propanediyl)bis (5,6-dimethylbenzimidazole) (L) and H_2NIPA to investigate the coordination behaviors of flexible double benzimidazole derivative and 5-substituent aromatic dicarboxylate with transition metal. A new 2D 4-connected Mn(Ⅱ) coordination polymer $[Mn(NIPA)(L)]_n$ (**1**) has been obtained by hydrothermal method. So far, although some coordination polymers constructed by flexible benzimdazolyl-based ligands have been documented, the coordination polymers based on flexible 5,6-dimethylbenzimidazole derivative are rarely obtained[15-16].

1　Experimental

1.1　General procedures

All chemicals purchased were of reagent grade and used without further purification. L was synthesized by the method of the literature[17] and characterized by FTIR spectra. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240C analyzer and FTIR spectra were taken on a Magna FTIR 560 spectrometer (500~4 000 cm^{-1}) with KBr pellets. Fluorescence spectra were performed on an F-4500 fluorescence/phosphorescence spectrophotometer at room temperature.

1.2　Synthesis of $[Mn(NIPA)(L)]_n$

A mixture of $MnCl_2$ (0.1 mmol), L (0.1 mmol), H_2NIPA (0.1 mmol), NaOH (0.2 mmol), H_2O (10 mL), stirred for 20 min, was sealed to a Teflon-lined stainless steel autoclave (25 mL) and kept at 150 ℃ for 3 d. After the mixture was slowly cooled to room temperature, pale yellow block crystals of **1** suitable for X-ray diffraction were obtained in 22% yield (based on Mn). Anal. Calcd. for $MnC_{29}H_{27}N_5O_6$(%): C, 58.39; H, 4.56; N, 11.74; Found(%): C, 58.42; H, 4.58; N, 11.72. IR (KBr, cm^{-1}): 3 104s, 1 621s, 1 586m, 1 564s, 1 525m, 1 453s, 1 375s, 1 342s, 1 270m, 1 080m, 846s, 730s.

1.3　X-ray crystallography

The data were collected on a Bruker Smart Apex Ⅱ CCD diffractometer with Mo $K\alpha$ (λ 0.071 073 nm) at 295 K ($-12 \leqslant h \leqslant 12, -12 \leqslant k \leqslant 12, -15 \leqslant l \leqslant 15$) in the range of $2.52° \leqslant \theta \leqslant 25.03°$ by using an ω-2θ scan mode. A total of 10 007 reflections were collected, of which 4 791 were independent (R_{int}=0.030 5) and 3 630 reflections were used in the succeeding refinement. The structures were solved by the direct method and refined by the Full-matrix least-squares on F^2 using the SHELX-97 software [18-19]. All H atoms were positioned geometrically (C-H 0.093 nm) and refined as riding mode and all the non-hydrogen atoms were refined anisotropically. The final R=0.041 7 and wR=0.097 5 ($w=1/[\sigma^2(F_o^2)+(0.040\,7P)^2+0.342\,3P]$, where $P=(F_o^2+2F_c^2)/3$. S=1.027. The highest peak and deepest hole in the final difference Fourier map are 234 and −265 e·nm^{-3}. The crystal data and structure refinement details for **1** are listed in Table 1. Selected bond lengths and angles are given in Table 2.

CCDC: 850309.

Table 1　Crystal data and structure refinement for 1

Empirical formula	$C_{29}H_{27}MnN_5O_6$	b / nm	1.057 10(10)
Crystal size / mm	0.20×0.16×0.14	c / nm	1.324 91(10)
Formula weight	596.50	α / (°)	76.052 0(10)
Crystal system	Triclinic	β / (°)	89.710 0(10)
Space group	$P\bar{1}$	γ / (°)	85.871 0(10)
a / nm	1.029 41(10)	V / nm^3	1.395 5(2)

Continued Table 1

Z	2	Unique reflections (R_{int})	4 791 (0.030 5)
D_c / (g·cm^{-3})	1.420	Data / restraints / parameters	4 791 / 0 / 374
μ / mm^{-1}	0.525	Goodness-of-fit on F^2	1.027
F(000)	618	Final R indices ($I>2\sigma(I)$)	R_1=0.041 7, wR_2=0.088 7
θ range / (°)	2.52~25.03	R indices (all data)	R_1=0.061 8, wR_2=0.097 5
Reflections collected	9 989	Largest diff. peak and hole / (e·nm^{-3})	234/−265

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

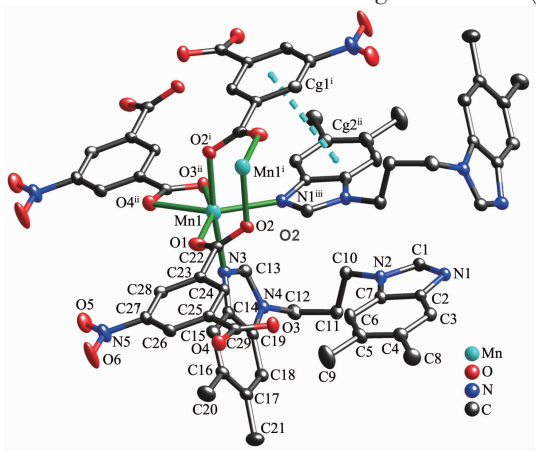
Mn(1)-O(1)	0.210 03(18)	Mn(1)-O(3)^{ii}	0.223 52(18)	Mn(1)-N(3)	0.228 7(2)
Mn(1)-O(2)^{i}	0.219 74(18)	Mn(1)-N(1)^{iii}	0.226 9(2)	Mn(1)-O(4)^{ii}	0.229 74(18)
O(1)-Mn(1)-O(2)^{i}	93.58(7)	O(3)^{ii}-Mn(1)-N(1)^{iii}	92.92(7)	O(1)-Mn(1)-O(4)^{ii}	98.45(7)
O(1)-Mn(1)-O(3)^{ii}	155.57(7)	O(1)-Mn(1)-N(3)	89.17(8)	O(2)^{i}-Mn(1)-O(4)^{ii}	90.18(7)
O(2)^{i}-Mn(1)-O(3)^{ii}	93.12(7)	O(2)^{i}-Mn(1)-N(3)	174.44(7)	O(3)^{ii}-Mn(1)-O(4)^{ii}	58.06(7)
O(1)-Mn(1)-N(1)^{iii}	110.91(8)	O(3)^{ii}-Mn(1)-N(3)	86.31(8)	N(1)^{iii}-Mn(1)-O(4)^{ii}	150.60(7)
O(2)^{i}-Mn(1)-N(1)^{iii}	86.60(7)	N(1)^{iii}-Mn(1)-N(3)	87.90(8)	N(3)-Mn(1)-O(4)^{ii}	94.19(7)

Symmetry codes: ^{i} −x+1, −y, −z+1; ^{ii} x+1, y, z; ^{iii} −x+1, −y+1, −z+1

2 Results and discussion

2.1 Description of the structure

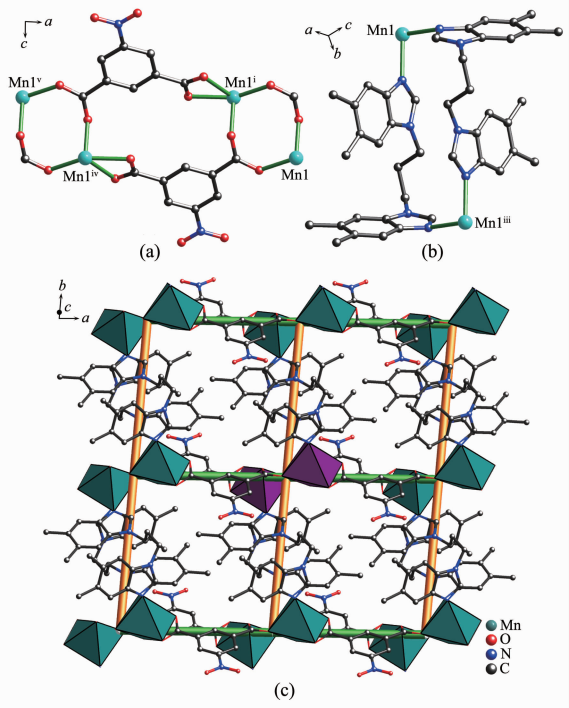
Single crystal X-ray analysis reveals that compound **1** is a 2D coordination polymer possessing two kinds of double linkers. As shown in Fig.1, each Mn(Ⅱ) cation is six-coordinated by two nitrogen from two L ligands in trans positions[15], two oxygen atoms of a chelating group and two monodentate oxygen atoms of two bridging carboxylic groups from three different NIPA anions to form an octahedron coordination geometry. In the coordination octahedron, the distances of Mn-N and Mn-O are in the range of 0.226 9(2)~0.228 7(2) nm, 0.210 03(18)~0.229 74(18) nm, respectively. The bond angles around Mn (Ⅱ) vary from 58.06(7)° (O(3)^{ii}-Mn(1)-O(4)^{ii} (^{ii} x+1, y, z)) to 174.44(7)° (O(2)^{i}-Mn(1)-N(3)) (^{i} −x+1, −y, −z+1), indicating the octahedron is slightly distorted, which may be induced by the steric effect of the ligands. Two Mn(Ⅱ) cations related by a center of inversion are bridged by two μ_2-carboxylic groups of different NIPA ligands generating a bimetallic cluster [$Mn_2N_2O_4$] with a Mn⋯Mn^{i} separation of 0.449 7(7) nm. The binuclear units are connected by pairs of NIPA anions forming a 1D infinite double chain extended along a direction (Fig.2a). The distance between the cores of bimetallic units is 1.029 41(10) nm. The 1D double-chains are extended by pairs of L ligands with TG′ conformation (the torsion angle of aromatic rings from L ligand is 73.21° and the N1⋯N3 distance is 0.725 1(27) nm) to form a 2D network and the distance between the cores of binuclear units is 1.057 1 nm (Fig.2b and 2c). Considering the bimetallic unit as a node, keeping the $(L)_2$ and $(NIPA)_2$ as the double spacers, compound **1** exhibits an interesting (4,4) network (Fig.2c)[20]. Moreover, the 2D layers are stabilized through intra-layer π-π stacking interactions between phenyl rings of NIPA and L ligands. The distance of center to center, Cg1^{i}⋯Cg2^{iii}, is 0.367 13(2) nm and the dihedral angle is 8.58° (Cg1 is the aromatic



Symmetry codes: ^{i} −x+1, −y, −z+1; ^{ii} x+1, y, z; ^{iii} −x+1, −y+1, −z+1

Fig.1 Coordination environment in **1** with thermal ellipsoids

ring C(23)^{i}/C(24)^{i}/C(25)^{i}/C(26)^{i}/C(27)^{i}/C(28)^{i} from NIPA, Cg2 is the aromatic ring C(2)^{iii}/C(3)^{iii}/C(4)^{iii}/C(5)^{iii}/C(6)^{iii}/C (7)^{iii} of L ligand (^{iii} $-x+1, -y+1, -z+1$)). The perpendicular distance of Cg1^{i} on Cg2^{iii} is 0.332 65(11) nm. In our previous work, we adopted Cl^-, NO_3^- and monocarboxylates as anion ligands, which can not extend the discrete metal centers into high dimensional network[16]. In this paper, a V-shaped aromatic dicarboxylate (NIPA) was successfully selected to link the bimetallic units into 2D coordination polymer, which demonstrate that careful selection of the ligands is a good way to obtain prospective structures.



Symmetry codes: ^{iv} $-1+x, y, z$; ^{v} $-x, -y, 1-z$

Fig.2　(a) View of the $(NIPA)_2$; (b) $(L)_2$ double linkers; (c) 2D (4,4) network through two kinds of double linkers

2.2　IR spectrum, thermal stability and photoluminescent characterizations

The main features in the IR spectrum of **1** mainly concern the L ligand, carboxylate and nitro groups. The bands at 848, 1 456 and 1 523 cm^{-1} can be attributed to ν(C-N) of N-heterocyclic rings of L ligand and the bands at 3 103 cm^{-1} are assigned to ν(C-H) of $-CH_3$ and $-CH_2-$ of L ligand[15-16]. The absorptions at 1 579 and 1 390 cm^{-1} are attributed to the asymmetric stretching vibration $\nu_{asym}(COO^-)$ and the symmetric $\nu_{sym}(COO^-)$, and the bands at 1 344 cm^{-1} can be attributed to vibration of $-NO_2$ groups from NIPA[13,15]. The TG curve of **1** exhibits two continuous weight loss stages in the range of 50~625 ℃, as shown in Fig.3. The first weight loss of 55.75% around 310~425 ℃ corresponds to the release of the L ligand (calcd. 55.73%). The second weight loss in the range of 425~550 ℃ can be attributed to the further decomposition of the framework to form MnO as a final product (obsd. 11.86, calcd. 11.89%). As shown in Fig.4, the photoluminescence spectra of **1** and free L ligand were investigated in solid state at room temperature. The free L ligand displays the only photoluminescence emission peak at 465 nm upon excitation at 380 nm. Compound **1** exhibits blue photoluminescence with an emission maximum at ca. 468 nm upon excitation at 300 nm. Compared with the emission of L, slight red shift of *ca.* 3 nm has been observed. Compared with the $\pi^* \rightarrow \pi$ transitions of L ligand, the carboxylate ligands show very weak $\pi^* \rightarrow n$ transitions and contribute a little to the photoluminescence of the title compound[21]. Therefore, the solid state photoluminescence of compound **1** may be attributed to

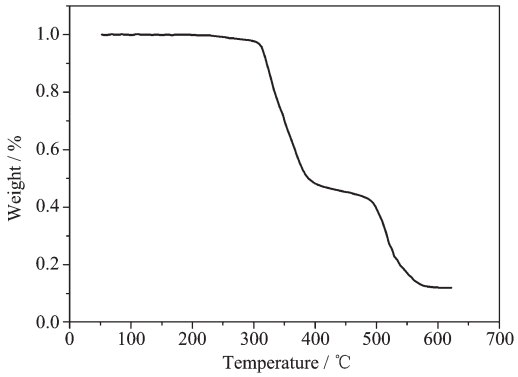


Fig.3　Thermogravimetric analysis of **1**

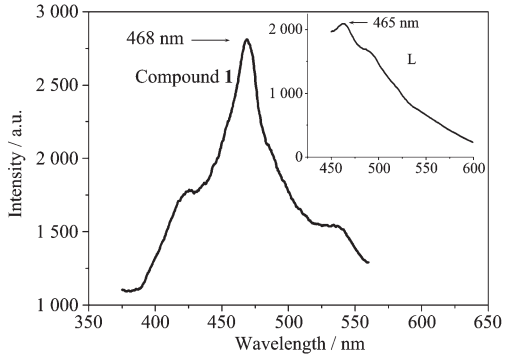


Fig.4　Solid-state emission spectra of compound **1** and L at room temperature

$\pi^*\rightarrow\pi$ transitions of coordinated L ligand[15-16].

References:

[1] Tabellion F M, Seidel S R, Arif A M, et al. *J. Am. Chem. Soc.*, **2001**,**123**:11982-11990

[2] Bi Y F, Wang X T, Liao W P, et al. *J. Am. Chem. Soc.*, **2009**, **131**(33):11650-11651

[3] YANG Ying-Qun (杨颖群), CHEN Man-Sheng (陈满生), CHEN Zhi-Min (陈志敏), et al. *Chinese J. Inorg. Chem.*(*Wuji Huaxue Xuebao*), **2011**,**27**(9):1847-1851

[4] Xu X X, Lu Y, Wang E B, et al. *Cryst. Growth Des.*, **2006**,**9**: 2029-2035

[5] Wang X L, Chen Y Q, Gao Q, et al. *Cryst. Growth Des.*, **2010**, **10**:2174-2184

[6] Yang H X, Meng X R, Liu Y, et al. *J. Solid State Chem.*, **2008**, **181**:2178-2184

[7] Li S L, Lan J Q, Ma J C, et al. *Cryst. Growth Des.*, **2010**,**10**(3): 1161-1170

[8] Li L L, Yuan R X, Liu L L, et al. *Cryst. Growth Des.*, **2010**,**10** (4):1929-1938

[9] Wang X L, Zhang J X, Liu G C, et al. *Inorg. Chim. Acta*, **2011**, **368**:207-215

[10]Chen X M, Liu G F. *Chem. Eur. J.*, **2002**,**8**:4811-4817

[11]Wang X L, Bi Y F, Lin H Y, et al. *Cryst. Growth Des.*, **2007**,**7**: 1086-1091

[12]Wang X L, Liu G C, Zhang J X, et al. *Dalton Trans.*, **2009**,**36**: 7347-7349

[13]Wang X L, Zhang J X, Liu G C, et al. *Russ. J. Coord. Chem.*, **2010**,**36**(9):668-679

[14]Zhou D S, Wang F K, Yang S Y, et al. *CrystEngComm*, **2009**, **11**:2548-2554

[15]Liu G C, Zhang J X , Wang X L, et al. *Z. Naturforsch.*, **2011**, **66b**:125-132

[16]Wang X L, Yang Song, Liu G C, et al. *Inorg. Chim. Acta*, **2011**,**375**:70-76

[17]Lan Y Q, Li S L, Qin J S, et al. *Inorg. Chem.*, **2008**,**47**(22): 10600-10610

[18]Sheldrick G M. *SHELXS*-97, *Program for Crystal Structure Solution*, University of Göttingen, Germany, **1997**.

[19]Sheldrick G M. *SHELXL*-97, *Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1997**.

[20]Batten S R, Robson R. *Angew. Chem. Int. Ed.*, **1998**,**37**:1460-1494

[21]Wang X L, Bi Y F, Liu G C, et al. *CrystEngComm*, **2008**,**10**: 349-356