

一个由 5-硝基间苯二甲酸和 1,10-啉啡咯啉构筑的 锰配位聚合物的水热合成和晶体结构

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摘要: 通过水热法合成了 1 个新的金属-有机配位聚合物 $[\text{Mn}(\text{NIPH})(\text{phen})_2] \cdot 4\text{H}_2\text{O}$ (H_2NIPH =5-硝基间苯二甲酸, phen=1,10-邻菲咯啉)。并对其进行了元素分析、热重、红外光谱和 X-射线单晶衍射测定。该配合物属于单斜晶系, $P2_1/n$ 空间群。晶体学数据: $a=1.082\ 2(2)\ \text{nm}$, $b=2.288\ 3(5)\ \text{nm}$, $c=1.289\ 6(3)\ \text{nm}$, $\beta=105.11(3)^\circ$, $V=3.083\ 2(11)\ \text{nm}^3$, $\text{C}_{32}\text{H}_{27}\text{MnN}_5\text{O}_{10}$, $M_r=696.53$, $D_c=1.501\ \text{g} \cdot \text{cm}^{-3}$, $\mu(\text{Mo } K\alpha)=0.497\ \text{mm}^{-1}$, $F(000)=1\ 436$, $Z=4$, 最终 $R=0.059\ 2$, $wR=0.134\ 5$ 用于 4 079 个可观测点。在晶体结构中, 锰原子为六配位与来自 2 个不同的 NIPH 配体上的 2 个羧基氧原子和来自 2 个 phen 配体上的 4 个氮原子配位, 呈现畸变的八面体几何构型。而且该配合物通过氢键和 π - π 堆积作用扩展成三维超分子网状结构。

关键词: 水热合成; 晶体结构; 配位聚合物

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Hydrothermal Synthesis and Crystal Structure of a Mn(II) Coordination Polymer Assembled by 5-Nitroisophthalic Acid and 1,10-Phenanthroline

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Abstract: A new metal-organic coordination polymer $[\text{Mn}(\text{NIPH})(\text{phen})_2] \cdot 4\text{H}_2\text{O}$ (**1**, H_2NIPH =5-nitroisophthalic acid, phen=1,10-phenanthroline) has been hydrothermally synthesized and structurally characterized by elemental analyses, TG, IR spectroscopy and single-crystal X-ray diffraction. The complex crystallizes in monoclinic, space group $P2_1/n$ with $a=1.082\ 2(2)\ \text{nm}$, $b=2.288\ 3(5)\ \text{nm}$, $c=1.289\ 6(3)\ \text{nm}$, $\beta=105.11(3)^\circ$, $V=3.083\ 2(11)\ \text{nm}^3$, $\text{C}_{32}\text{H}_{27}\text{MnN}_5\text{O}_{10}$, $M_r=696.53$, $D_c=1.501\ \text{g} \cdot \text{cm}^{-3}$, $\mu(\text{Mo } K\alpha)=0.497\ \text{mm}^{-1}$, $F(000)=1\ 436$, $Z=4$, the final $R=0.059\ 2$ and $wR=0.134\ 5$ for 4 079 observed reflections ($I>2\sigma(I)$). In the crystal structure, the manganese atom is six-coordinated with two carboxylate oxygen atoms from two different NIPH ligands and four nitrogen atoms from two phen ligands, showing a distorted octahedral geometry. Furthermore, it exhibits a 3D supramolecular network through hydrogen bonding and π - π stacking interactions. CCDC: 818823.

Key words: hydrothermal synthesis; crystal structure; coordination polymer

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The design and synthesis of metal-organic polymeric frameworks have attracted great attention due to their potential applications and fascinating structures^[1-4]. Great interests have been focused on self-assembly in the supramolecular architectures by exploiting coordinative bonding, hydrogen bonding, π - π stacking interaction and other weak intermolecular interactions^[5-8]. Among the frameworks reported so far, polycarboxylate ligands such as terephthalate, isophthalate, 1,3,5-benzenetricarboxylate and 1,2,4,5-benzenetetracarboxylate have been proved particularly effective for the constructions of 1D, 2D and 3D coordination polymers^[9-11]. Moreover, polycarboxylic acids with various functional groups such as amine, hydroxyl, sulfonate and nitro groups have formed many novel inorganic-organic hybrid materials^[12-13]. In an effort of establishing strategies aiming at designing novel metal coordination polymers, we utilized the 5-nitroisophthalic acid (H_2NIPH) and polycyclic aromatic bidentate ligands, phen, to generate coordination polymers. The 5-nitroisophthalate(NIPH) is known as a versatile ligand, in which the two carboxylate groups can form covalent bonds with metal centers, while the nitro group can also act as a hydrogen-bond acceptor constructing strong hydrogen bonds in the assembly of coordination polymers. To our knowledge, metal coordination polymers with 5-nitroisophthalate have been reported^[14-17].

Presented here are the synthesis and structure of a novel manganese(II) coordination polymer $[\text{Mn}(\text{NIPH})(\text{phen})_2] \cdot 4\text{H}_2\text{O}$ with infinite one-dimensional chains. The chain packing in **1** gives rise to three-dimensional structure based on weak coordination bond, hydrogen bonding and π - π stacking interactions.

1 Experimental

1.1 General procedures

All materials were commercially purchased and used without further purification. Infrared spectra (KBr pellets) were taken on a Perkin-Elmer 2400LS II spectrometer and elemental analyses for C, H and N

were performed on a Perkin-Elmer 240C analyzer. The TG studies were performed on a Perkin-Elmer TGA7 analyzer

1.2 Synthesis

The title compound was prepared from a mixture of $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.12 g, 0.5 mmol), H_2NIPH (0.11 g, 0.5 mmol), phen (0.10 g, 0.5 mmol) and H_2O (18 mL) in a 30 mL Teflon-lined autoclave under autogenous pressure at 170 °C for five days. After cooling to room temperature, yellow block crystals were collected by filtration and washed with distilled water in 30% yield (based on Mn). Anal. Calcd. for $\text{C}_{32}\text{H}_{27}\text{MnN}_5\text{O}_{10}$ (%): C, 55.18; H, 3.91; N, 10.05. Found(%): C, 55.16; H, 3.88; N, 10.04. IR (KBr, cm^{-1}): 3 425m, 3 091w, 1 831w, 1 620 m, 1 528s, 1 447w, 1 425m, 1 344s, 1 225w, 1 196w, 1 103m, 1 088w, 1 048w, 1 014w, 964w, 931w, 920w, 865w, 850s, 806w, 790m, 773w, 730m, 687w, 639w, 537w, 452w.

1.3 Structure determination

A single crystal of the title compound with dimensions of 0.20 mm×0.20 mm×0.20 mm was mounted on a Bruker Smart Apex II CCD diffractometer equipped with a graphite-monochromatic $\text{Mo K}\alpha$ ($\lambda=0.071\ 073$ nm) radiation using an φ - ω scan mode at 292(2) K. In the range of $5.28^\circ < 2\theta < 50.70^\circ$, a total of 14 178 reflections were collected and 5 566 were independent of $R_{\text{int}}=0.054\ 2$, of which 4 079 were observed with $I > 2\sigma(I)$. The correction for Lp factors was applied. The structure was solved by direct methods with SHELXS-97 program^[18] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97^[19]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. All H atoms were placed in calculated positions and refined as riding with $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})$. The final $R=0.059\ 2$ and $wR=0.134\ 5$ ($w=1/[\sigma^2(F_o^2)+(0.120\ 0P)^2+1.404\ 8P]$, where $P=(F_o^2+2F_c^2)/3$). $S=1.124$, $(\Delta\rho)_{\text{max}}=1\ 395$, $(\Delta\rho)_{\text{min}}=-540\ \text{e}\cdot\text{nm}^{-3}$ and $(\Delta/\sigma)_{\text{max}}=0.000$. The selected important bond parameters are given in Table 1.

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

Mn(1)-N(1)	0.230 0(4)	Mn(1)-N(2)	0.227 3(4)	Mn(1)-N(3)	0.228 5(4)
Mn(1)-N(4)	0.226 7(4)	Mn(1)-O(1)	0.214 0(4)	Mn(1)-O(4A)	0.207 7(4)

Continued Table 1

O(4A)-Mn(1)-O(1)	98.12(15)	N(4)-Mn(1)-N(2)	165.34(15)	O(4A)-Mn(1)-N(1)	167.38(16)
O(4A)-Mn(1)-N(4)	93.15(15)	O(4A)-Mn(1)-N(3)	88.92(14)	O(1)-Mn(1)-N(1)	89.61(14)
O(1)-Mn(1)-N(4)	92.91(14)	O(1)-Mn(1)-N(3)	164.40(14)	N(4)-Mn(1)-N(1)	96.41(15)
O(4A)-Mn(1)-N(2)	96.32(15)	N(4)-Mn(1)-N(3)	72.72(14)	N(2)-Mn(1)-N(1)	72.76(15)
O(1)-Mn(1)-N(2)	96.78(14)	N(2)-Mn(1)-N(3)	96.25(14)	N(3)-Mn(1)-N(1)	86.10(14)

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

2 Results and discussion

2.1 IR spectrum

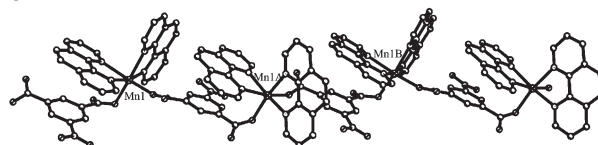
The COO^- is coordinated with its asymmetric and symmetric stretching appearing at 1620 cm^{-1} ($\nu(\text{OCO})_{\text{asym}}$) and 1344 cm^{-1} ($\nu(\text{OCO})_{\text{sym}}$)^[20], respectively. The $\Delta\nu(\nu(\text{OCO})_{\text{asym}} - \nu(\text{OCO})_{\text{sym}})$ is 276 cm^{-1} (>200), showing the presence of monodentate linkage of carboxylates in the dianions. Thus the carboxylates coordinate to the metal as monodentate ligands via the carboxylate groups^[21]. The absence of the characteristic bands at around 1700 cm^{-1} in compound **1** attributed to the protonated carboxylic group indicates the complete deprotonation of cbba ligand upon reaction with Mn ions^[22]. In addition, X-ray diffraction analysis further indicates the existence of monodentate coordination manners of the carboxylate groups and prence deprotonation of NIPH ligands.

2.2 Description of the structure

An asymmetric unit diffraction analysis reveals that **1** contains a Mn atom, an NIPH ligand, two chelating phen ligands and four crystal water molecules (Fig.1). In complex molecular center, Mn(II) atom is six-coordinated in a distorted octahedral geometry, *i.e.* each Mn atom is bonded by four nitrogen atoms of two phen ligands with the bond distance ($\text{Mn(1)-N(1)}=$

$0.230\,0(4)\text{ nm}$, $\text{Mn(1)-N(2)}=0.227\,4(4)\text{ nm}$, $\text{Mn(1)-N(3)}=0.228\,6(4)\text{ nm}$, $\text{Mn(1)-N(4)}=0.227\,1(4)\text{ nm}$) and two carboxylate-oxygen atoms of two different NIPH ligands with bond distances ($\text{Mn(1)-O(1)}=0.214\,1(4)\text{ nm}$, $\text{Mn(1)-O(4A)}=0.207\,4(4)\text{ nm}$). One carboxylate oxygen atom and three nitrogen atoms (O(1), N(2), N(3), N(4)) define an equatorial plane, while the axial coordination sites are occupied by one nitrogen atom [N(1)] and one carboxylate oxygen atom (O(4A)). The N(O)-Mn-O(N) angles range from $72.60(16)^\circ$ to $167.39(17)^\circ$.

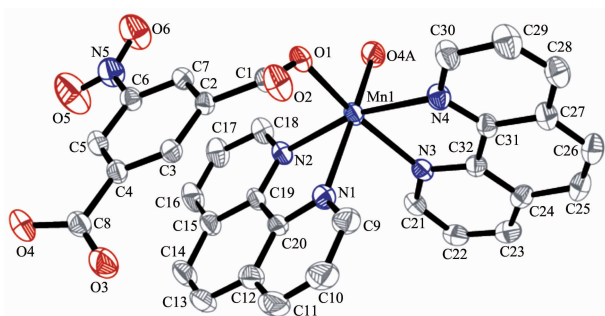
Each NIPH ligand adopts a μ_2 -bridging mode to connect with two Mn atoms leading to a 1D chain (Fig.2) in the structure of compound **1**. The distance of neighboring Mn \cdots Mn bridged by NIPH ligands is $0.984\,3\text{ nm}$, while each phen ligand acts as a terminal ligand.



Symmetry code: A: $x-1/2, -y+1/2, z+1/2$; B: $x-1, y, z+1$

Fig.2 A view of the one-dimensional architecture

Hydrogen bonding interactions are usually important in the synthesis of supramolecular architecture^[23]. There are persistent O-H \cdots O hydrogen bonding interactions in the complex (Table 2), which play an important role in stabilizing the network structure and controlling the orientation of NIPH ligands (Fig.3). Moreover, there are π - π interactions in compound **1** between phen ligands from adjacent chains and phen and NIPH ligands in the same chain (Fig.4). The centroid-to-centroid distances between adjacent aromatic rings are $0.368\,7\text{ nm}$ for C24C25C26C27C31C32 and C24'C25'C26'C27'C31'C32' (symmetry code: $1-x, 1-y, 1-z$) and $0.362\,0\text{ nm}$ for C24C25C26C27C31C32 and C12C13C14C15C19C20 aromatic rings. The



Symmetry code: A: $x-1/2, -y+1/2, z+1/2$; Hydrogen atoms and crystal water molecules are omitted for clarity

Fig.1 Molecular structure of the title compound

Table 2 Hydrogen bonds for complex 1

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H...A}) / \text{nm}$	$d(\text{D...A}) / \text{nm}$	$\angle(\text{DHA}) / (^\circ)$
O(7)-H(7B)...O(3)D	0.097 4	0.244 1	0.296 3	113.14
O(7)-H(7C)...O(1)C	0.096 2	0.217 3	0.305 5	151.86
O(8)-H(8A)...O(8)C	0.085	0.250 9	0.304 5	121.98
O(8)-H(8B)...O(2)C	0.095 8	0.185 0	0.279 0	166.46
O(9)-H(9B)...O(2)	0.090 8	0.231 8	0.293 2	124.67
O(9)-H(9C)...O(10)	0.087 9	0.203 1	0.278 8	143.74
O(10)-H(10B)...O(8)	0.092 1	0.177 4	0.264 6	156.90
O(10)-H(10C)...O(3)	0.087 1	0.193 0	0.276 9	161.41

Symmetry code: C: $-x+2, -y, -z+1$; D: $x-1, y, z$.

perpendicular distances are 0.349 0 nm for C24C25 C26C27C31C32 and C24' C25' C26' C27' C31' C32' (symmetry code: $1-x, 1-y, 1-z$) and 0.345 1 nm for C24C25C26C27C31C32 and C12C13C14C15C19C20 aromatic rings. Therefore, through hydrogen bonds and π - π interactions, the one-dimensional chains are further extended into a three-dimensional supramolecular framework.

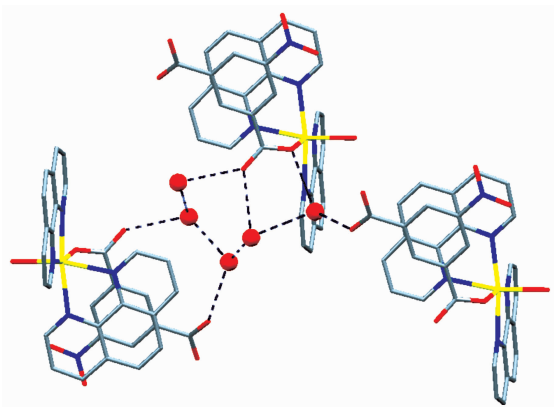
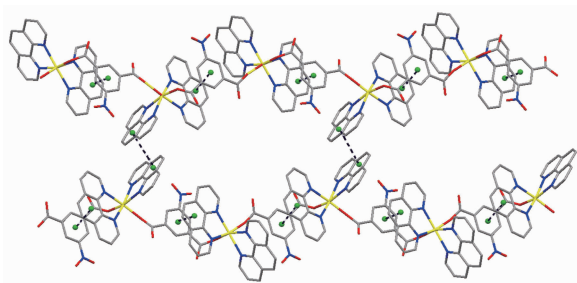


Fig.3 A view of hydrogen bonds in complex 1



Dotted lines show the π - π interactions

Fig.4 A view of π - π stacking interactions in complex 1

2.3 Thermal analysis

TG curve of **1** shows that the first weight loss of 39.1% from 22 to 338 $^\circ\text{C}$ corresponds to the removal of crystal water molecules and NIPH ligand (calcd.

40.3%). Upon further heating, an obvious weight loss (47.6%) occurs in the temperature range of 338~451 $^\circ\text{C}$, corresponding to the release of cbba and bipy ligand (calcd.: 47.7%). After 451 $^\circ\text{C}$ no weight loss is observed, which means the complete decomposition of **1**. The residual weight should be MnO.

References:

- [1] Rao C N R, Natarajan S, Vaidhyanathan R. *Angew. Chem. Int. Ed.*, **2004**,**43**(12):1466-1496
- [2] Moulton B, Zaworotko M J. *Chem. Rev.*, **2001**,**101**(6):1629-1658
- [3] Li H, Eddaoudi M, Yaghi O M, et al. *Nature*, **1999**,**402**(6759): 276-279
- [4] Hargman P J, Hargman D, Zubieta J. *Angew. Chem. Int. Ed.*, **1999**,**38**(18):2638-2684
- [5] Yaghi O M, Li H, Davis C, et al. *Acc. Chem. Res.*, **1998**,**31**(8): 474-484
- [6] Humphrey S M, Mole R A, Wood P T, et al. *J. Chem. Soc. Dalton Trans.*, **2004**,**11**:1670-1678.
- [7] Xu J Q, Xu D Q, Tang A Q, et al. *Sci. China Ser. B: Chem.*, **2004**,**47**(1):10-16
- [8] Ye K Q, Wu Y, Wang Z, et al. *Chin. Sci. Bull.*, **2005**,**50**(5): 417-420
- [9] Li X M, Niu Y L, Wang Q W, et al. *Chinese J. Struct. Chem.*, **2010**,**29**(7):1122-1126
- [10] Zarracino R G, Quinones J R, Hopfl H T. *Inorg. Chem.*, **2003**,**42**(12):3835-3845
- [11] Murugavel R, Krishnamurthy D, Sathiyendiran M. *J. Chem. Soc. Dalton Trans.*, **2002**,**1**:34-39
- [12] Sun D F, Cao R, Sun Y, et al. *Chem. Comm.*, **2003**,**13**:1528-1529
- [13] Tao J, Yin X, Jiang Y B, et al. *Inorg. Chem. Comm.*, **2003**,**6** (9):1171-1174

- [14]Tao J, Yin X, Wei Z B, et al. *Eur. J. Inorg. Chem.*, **2004**,**1**: 125-133
- [15]Luo J H, Hong M C, Wang R, et al. *Inorg. Chem.*, **2003**,**42** (15):4486-4488
- [16]Luo J H, Hong M C, Wang R, et al. *Eur. J. Inorg. Chem.*, **2003**,**14**:2705-2710
- [17]Abourahma H, Moulton B, Zaworotko M J, et al. *J. Am. Chem. Soc.*, **2002**,**124**(34):9990-9991
- [18]Sheldrick G M. *SHELXS 97, Program for the Solution of Crystal Structure*, University of Göttingen, Germany, **1997**.
- [19]Sheldrick G M. *SHELXS 97, Program for the Refinement of Crystal Structure*, University of Göttingen, Germany, **1997**.
- [20]Devereux M, Shea D O, Kellett A, et al. *Inorg. Biochem.*, **2007**,**101**:881-892
- [21]Farrugia L J, Wing X A. *Windows Program for Crystal Structure Analysis*, University of Glasgow, Glasgow, UK, **1988**.
- [22]Bellamy L J. *The Infrared Spectra of Complex Molecules*. New York: Wiley, **1958**.
- [23]Krische M J, Lehn J M. *Struct. Bonding*, **2000**,**96**:3-29