

苯并咪唑-5,6-二甲酸-锰配合物的合成,晶体结构和磁性质

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摘要: 采用水热法将 MnCl_2 与苯并咪唑-5,6-二甲酸混合反应合成出一个新的具有二维层状结构的锰金属配位聚合物 $[\text{Mn}(\text{Hbim})(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})_2$ (**1**), 并分别用元素分析, 红外谱图, 差热分析和 X-射线单晶衍射表征该结构。X-射线单晶衍射分析表明, 晶体属于正交晶系, $Pbca$ 空间群, 晶胞参数 $a=0.728\,2(14)\text{ nm}$, $b=1.804\,5(4)\text{ nm}$, $c=1.915\,5(4)\text{ nm}$, $V=2.429\,3(8)\text{ nm}^3$, $Z=8$, $\text{C}_{10}\text{H}_{12}\text{MnN}_2\text{O}_8$, $M_r=331.15$, $D_c=1.811\text{ g}\cdot\text{cm}^{-3}$, $F(000)=1\,352$, $\mu(\text{Mo K}\alpha)=1.130\text{ mm}^{-1}$, 最终 $R=0.037\,1$, $wR=0.085\,8$ 。在配位聚合物中, 锰-羧基 Z 字形链相互连接成具有尺寸为 $0.57\text{ nm}\times 0.75\text{ nm}$ 一维通道的二维网络结构, 并进一步被分子间的氢键作用构筑成三维超分子结构。磁性质测试表明该化合物为反铁磁。

关键词: 锰配合物; 晶体结构; 水热合成; 磁性质

中图分类号: O614.71+1

文献标识码: A

文章编号: 1001-4861(2011)07-1446-05

Synthesis, Crystal Structure and Magnetic Properties of Mn(II) Benzimidazole-5,6-dicarboxylate Complex

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Abstract: A new manganese coordination polymer $[\text{Mn}(\text{Hbim})(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})_2$ (**1**) (where Hbim=1H-benzimidazole-5,6-dicarboxylate) has been synthesized by hydrothermal method and characterized by elemental analysis, IR, TGA and single-crystal X-ray diffraction. It crystallizes in orthorhombic, space group $Pbca$ with $a=0.728\,2(14)\text{ nm}$, $b=1.804\,5(4)\text{ nm}$, $c=1.915\,5(4)\text{ nm}$, $V=2.429\,3(8)\text{ nm}^3$, $Z=8$, $\text{C}_{10}\text{H}_{12}\text{MnN}_2\text{O}_8$, $M_r=331.15$, $D_c=1.811\text{ g}\cdot\text{cm}^{-3}$, $F(000)=1\,352$, $\mu(\text{Mo K}\alpha)=1.130\text{ mm}^{-1}$, the final $R=0.037\,1$ and $wR=0.085\,8$ for observed reflections with $I>2\sigma(I)$. Compound **1** is a 2D coordination polymer including 1D channels of $0.57\text{ nm}\times 0.75\text{ nm}$ (excluding van der Waals radii) along the c axis made up of interconnected Mn-carboxylate zigzag chains, and displays a three-dimensional (3D) supramolecular network via multiple intermolecular hydrogen bonds. Furthermore, the temperature dependent magnetic susceptibility has been evaluated under $1\,000\text{ Oe}$, and reveals the antiferromagnetic coupling. CCDC: 805737.

Key words: manganese coordination polymer; crystal structure; hydrothermal synthesis; magnetic properties

Coordination polymers materials are receiving growing attention due to their potential applications in magnetism, ion exchange, catalysis, gas separation, sensor, and many other areas^[1-5]. The rational selection of organic ligands is crucial to design and

synthesize the target coordination polymers, which not only determine their structure and dimensionality, but also influence their potential properties and applications^[6-7]. Among these organic ligands, 1H-benzimidazole-5,6-dicarboxylate (H_2bim) is an excellent

收稿日期: 2010-12-28。收修改稿日期: 2011-04-17。

广东省科技计划项目(No.2006B13501006)资助。

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candidate for the construction of supramolecular complexes because it possesses two nitrogen atoms of the imidazole ring and four oxygen atoms of carboxylate groups. Although H₂bim has diverse coordination capabilities upon reacting with transition metal ions^[8-10], alkaline-earth metal ions^[11] and lanthanide ions^[10]. To the best of our knowledge, the 2D Mn^{II} coordination polymers with H₂bim including 1D channels have been no reported to date.

In this paper, we present the synthesis, crystal structure, and variable temperature magnetic susceptibility of this new 2D Mn^{II} carboxylate coordination polymer {[Mn(Hbim)(H₂O)₂]·(H₂O)₂}_n.

1 Experimental

1.1 Materials and measurements

All the materials and reagents were obtained commercially and used without further purification. Elemental (C, H, N) analyses were performed on a Perkin-Elmer 2400 element analyzer. The IR spectra were acquired using Nicolet Avatar 360 FTIR spectrophotometer. Thermogravimetry analyses (TGA) were performed on a simultaneous SDT thermal analyzer (STA449C, Netzsch) under a flow of N₂ at a heating rate of 10 °C · min⁻¹ between ambient temperature and 800 °C. Magnetic property was studied under Quantum Design SQUID magnetometer on the MPMS-7 system.

1.2 Synthese of 1

A mixture of MnCl₂ (0.126 g, 1 mmol), H₂bim (0.105 g, 0.5 mmol), NaOH (0.021 g, 0.25 mmol) and H₂O (10 mL) was stirred for 30 min in air and then sealed in a 23 mL Teflon reactor and kept under autogenous pressure at 150 °C for 72 h. The mixture was cooled to room temperature at a rate of 5 °C · h⁻¹, and block rosiness crystals were obtained in a yield of 48% based on Mn. Elemental analysis calcd. for C₉H₁₂MnN₂O₈(%): C, 32.61; H, 3.62; N, 8.45. Found(%): C, 32.63; H, 3.64; N, 8.41. Main IR frequencies (KBr, cm⁻¹): 3 408, 3 138, 2 921, 1 537, 1 468, 1 418, 1 343, 1 184, 1 127, 784, 689, 634, 590.

1.3 Crystal structure analysis

A single crystal with dimension of 0.32 mm×0.27 mm×0.20 mm was mounted on a glass fiber for data collection on a Rigaku Mercury CCD diffractometer operated at 90 kV and 50 mA using Mo K α radiation (λ =0.071 073 nm) at room temperature. Empirical absorption corrections were performed using the program CrystalClear^[12]. The structures were solved by direct methods and refined on F^2 by full-matrix least squares technique using the SHELX-97 program package^[13]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on water molecules were located from difference Fourier maps and refined with distance restraints of O-H 0.084(2) nm, N-H 0.086 (3) nm and H···H 0.139 (2) nm. Selected bond lengths and bond angles are given in Table 1.

CCDC: 805737.

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

Mn(1)-O(4) ⁱ	0.207 91(15)	Mn(1)-N(1) ⁱⁱ	0.217 04(19)	Mn(1)-O(6)	0.224 10(18)
Mn(1)-O(1)	0.212 62(16)	Mn(1)-O(5)	0.217 79(17)		
O(4) ⁱ -Mn(1)-O(1)	143.28(6)	O(4) ⁱ -Mn(1)-O(5)	88.46(6)	O(1)-Mn(1)-O(6)	89.35(6)
O(4) ⁱ -Mn(1)-N(1) ⁱⁱ	116.97(7)	O(1)-Mn(1)-O(5)	93.16(6)	N(1) ⁱⁱ -Mn(1)-O(6)	92.37(7)
O(1W)-Mn(1)-O(6)	171.14(6)	N(1) ⁱⁱ -Mn(1)-O(5)	95.59(7)		
O(1)-Mn(1)-N(1) ⁱⁱ	99.37(7)	O(4) ⁱ -Mn(1)-O(6)	84.46(6)		

Symmetry codes: ⁱ 1/2+x, 1/2-y, 1-z; ⁱⁱ 2-x, -y, 1-z.

2 Results and discussion

2.1 IR spectra

The IR spectra of compound **1** show broad bands

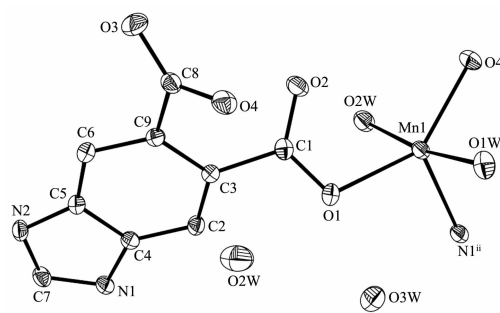
in the region of 2 920 ~3 410 cm⁻¹, which may be assigned to the ν (O-H) stretching vibrations of the water molecules. The bands at 1 538, and 1 468, 1 418, 1 343 cm⁻¹ are associated with the asymmetric (COO) and

symmetric (COO) stretching vibrations.

2.2 Structure description

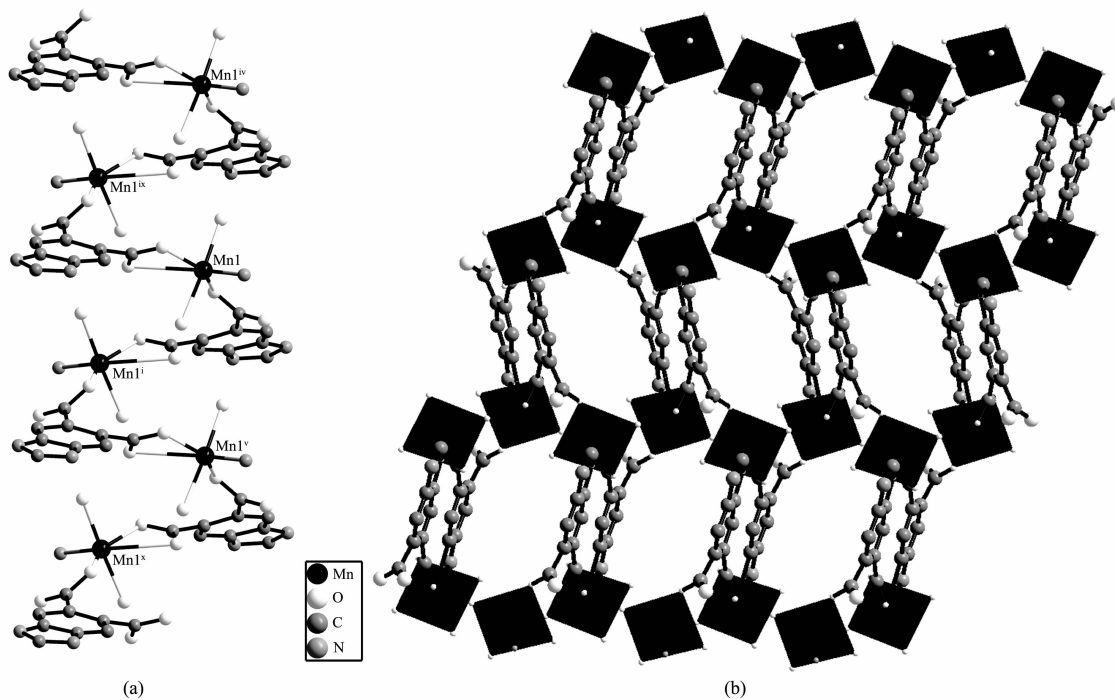
Single-crystal X-ray diffraction analysis reveals that compound **1** displays a 2D coordination polymer constructed by interconnected Mn-carboxylate chains, crystallizing in the space group *Pbca*. An ORTEP plot of **1** is shown in Fig.1. In the asymmetric unit of **1**, there are one Mn(II) ion, one Hbim ligand, two coordinated water molecules and two free water molecules. The Mn(II) centre is five-coordinated by two O-donors of two different Hbim ligands, one N-donor of one Hbim ligand, two O-donors of two water molecules and displays a distorted trigonal bipyramidal coordination sphere. The two carboxylate O atoms and one N atom form a trigonal plane around Mn atom, while two water molecules occupy the axial sites on the trigonal bipyramidal. The Mn-O, Mn-N bond lengths and O-Mn-O, O-Mn-N bond angles ranging from 0.207 92(2) nm to 0.224 14(2) nm and 84.46(5)° to 171.14(6)° (Table 1), respectively, all of which are within the reasonable range of observed values for other five-coordinated Mn(II) complexes based on 1*H*-benzimidazole-5,6-dicarboxylate ligand^[9-10]. The Hbim ligands in **1** exhibit

the same coordination mode with every carboxylate group as monodentate to link two Mn(II) ions, and the N atom in the imidazole ring links one Mn(II) ion. Thus, Mn(II) ions form a 1D Mn-carboxylate alternate chain along the *ac*-plane and Mn...Mn is separated by 0.580 9(2) nm (Fig.2a). Each Hbim ligand also offers a nitrogen in the imidazole ring to connect the adjacent chains. Then, a 2D coordination network including 1D channels of 0.57 nm×0.75 nm (excluding van der Waals radii) within the 2D individual layers along the *c* axis (Fig.2b). The chains within the 2D layers are separated



Symmetry codes: ⁱ 1/2+x, 1/2-y, 1-z; ⁱⁱ 2-x, -y, 1-z; Displacement ellipsoids at the 30% probability level

Fig.1 Coordination environment of Mn(II) atom in complex **1**



Symmetry codes: ^{iv} -1+x, y, z; ^{ix} -1/2+x, -1/2-y, 1-z; ^v 1+x, y, z; ^x 3/2+x, 1/2-y, 1-z

Fig.2 (a) A view of one-dimensional Mn-carboxylate chain structure in **1**; (b) Polyhedral view of layered network in **1** including 1D channel along the *c* axis

by 0.744 0(3) nm as measured by the Mn \cdots Mn distance. The solvent water molecules, which located in cavities of the 2D layered network, allowing them to participate in various O-H \cdots O and N-H \cdots O hydrogen bonds with

the coordinated water molecules, N-H groups of imidazole rings and carboxylate O atoms, which help to stabilize the three-dimensional structure. The H-bond geometrical parameters are reported in Table 2.

Table 2 Hydrogen bonds distances and angles

D-H \cdots A	$d(\text{D-H})$ / nm	$d(\text{H}\cdots\text{A})$ / nm	$d(\text{D}\cdots\text{A})$ / nm	$\angle \text{DHA}$ / ($^\circ$)
O4W-H8W \cdots O3W ⁱⁱⁱ	0.084	0.196	0.277 6(3)	164.6
O4W-H7W \cdots O4	0.084	0.195	0.278 6(2)	170.4
O3W-H6W \cdots O2W ^{iv}	0.084	0.204	0.285 5(2)	164
O3W-H5W \cdots O1	0.084	0.195	0.277 1(2)	164
O2W-H4W \cdots O4W ^v	0.084	0.195	0.276 5(3)	161.9
O2W-H3W \cdots O2 ⁱ	0.084	0.196	0.279 2(2)	168.3
O1W-H2W \cdots O3 ^{vi}	0.084	0.194	0.275 5(2)	164.7
O1W-H1W \cdots O2 ^{vii}	0.084	0.195	0.277 9(2)	170.2
N2-H2A \cdots O3W ^{viii}	0.086	0.195	0.279 0(2)	163.7

Symmetry codes: ⁱⁱⁱ 1-x, -y, 1-z; ^{iv} -1+x, y, z; ^v 1+x, y, z; ^{vi} x, 1/2-y, 1/2+z; ^{vii} -1/2+x, 1/2-y, 1-z; ^{viii} 3/2-x, -y, -1/2+z.

2.3 Thermogravimetric analyses

Thermal gravimetric analyses (TGA) were carried out to examine the thermal stability of **1**. The samples were heated up in flowing N₂ with a heating rate of 10 $^\circ\text{C}\cdot\text{min}^{-1}$. The TGA curve in Fig.3 shows that a gradual weight-loss step of 20.5% (50~200 $^\circ\text{C}$), corresponding to the escape of the two uncoordinated water molecules and two coordinated water molecules (calcd. 21.6%). The weight-loss step that occurs above 400 $^\circ\text{C}$ corresponds to the decomposition of the framework.

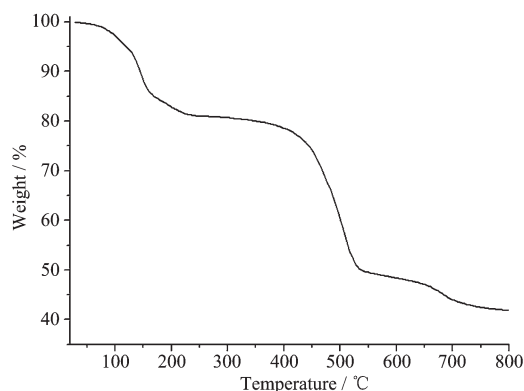


Fig.3 TGA curve of compound **1**

2.4 Magnetic properties

Magnetic susceptibility measurements were performed in the temperature range of 2~300 K with an applied field of 1 000 Oe. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms. The plot of $\chi_{\text{M}}T$ and $1/\chi_{\text{M}}$ versus T is presented in Fig.4. The $\chi_{\text{M}}T$ of Mn(II) at 300 K is 4.69

$\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{K}$, slightly higher than the spin-only value of $4.38 \text{ cm}^3\cdot\text{mol}^{-1}\cdot\text{K}$ for one high-spin Mn(II) ion ($g=2$, $S=5/2$). Upon cooling, the $\chi_{\text{M}}T$ value steadily decreases, and the feature indicates a dominant antiferromagnetic interaction in **1**. The plots of χ_{M}^{-1} versus T from 2~300 K obey the Curie-Weiss law with $4.70 \text{ cm}^3\cdot\text{mol}^{-1}\cdot\text{K}$, $\theta = -12.05(8) \text{ K}$. The observed behaviors indicate that weak antiferromagnetic interactions take place between adjacent manganese centers. The magnetic behavior is similar to those of Mn complexes^[9-10], which the weak antiferromagnetic interactions come from adjacent paramagnetic Mn centers.

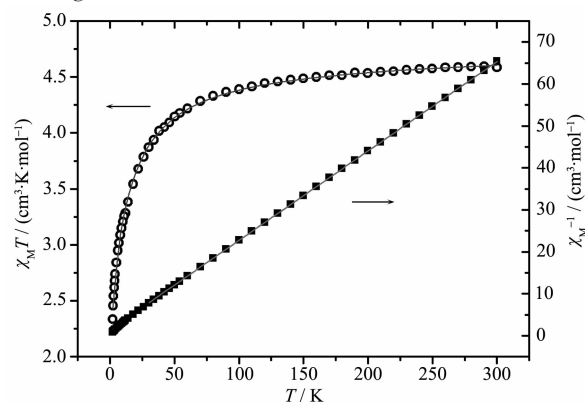


Fig.4 Plots of $\chi_{\text{M}}T$ and χ_{M}^{-1} vs T for **1**

3 Conclusions

In summary, we have synthesized a new 2D manganese coordination polymer $\{[\text{Mn}(\text{Hbim})(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})_2\}_n$, under hydrothermal reaction. Complex **1**

features a 2D layered network with 1D channels of 0.57 nm×0.75 nm within the 2D individual layers along the *c*-axis, which is constructed by the interconnection of adjacent parallel Mn-carboxylate chains. Magnetic studies indicate that the interactions between Mn(II) ions is antiferromagnetic.

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