研究简报

配位聚合物[Mn(4,4′-bpy)$_{1.5}$(H$_2$O)$_3$](ClO$_4$)·(4,4′-bpy)(L)·H$_2$O 的水热合成和晶体结构

黄妙龄
(泉州师范学院化学系,泉州 362000)

关键词: 锰(Ⅱ); 4,4′-联吡啶; 配位聚合物; 晶体结构
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Hydrothermal Synthesis and Crystal Structure of Coordination Polymer [Mn(4,4′-bpy)$_{1.5}$(H$_2$O)$_3$](ClO$_4$)·(4,4′-bpy)(L)·H$_2$O

HUANG Miao-Ling
(*Department of Chemistry Quanzhou Normal University, Quanzhou, Fujian* 362000)

Abstract: The title compound, [Mn(4,4′-bpy)$_{1.5}$(H$_2$O)$_3$](ClO$_4$)·(4,4′-bpy)(L)·H$_2$O(1), where L=2,4,6-trimethylbenzoic acid, was synthesized and its crystal structure was determined by X-ray diffraction analysis. The crystal is of triclinic, space group $P\bar{1}$ with a=2.929 9(6) nm, b=1.036 4(2) nm, c=8.222 0(1) nm, α=105.300(2)°, β=97.495(2)°, γ=91.118(2)°, V=1.884 0(4) nm^3, Z=2, M_r=780.10, D_c=1.375 g·cm^{-3}, μ=0.483 mm^{-1}, F(000)=812, R=0.055 4, wR=0.135 2. The Mn atoms are octahedrally coordinated by three N atoms of three 4,4′-bipyridine ligands and three O atoms of water. The complex shows a one-dimensional chain structure bridged by water and 4,4′-bipyridine molecules. CCDC: 615707.

Key words: Mn(Ⅱ); 4,4′-bipyridine; coordination polymer; crystal structure

0 Introduction

The rational design and synthesis of metal-organic frameworks (MOFs) with specific topologies have been the most important subjects of intensive current researches in coordination chemistry, supramolecular chemistry and materials science[1-6].

The coordination polymers can be specially designed by careful selection of the metal ions with definite coordination geometry, the structure of the connecting ligands, the nature of counteranions, and the reaction conditions. Further- more, 4,4′ -bpy is an excellent bridging ligand, and so far a number of one-, two- and three-dimensional infinite metal-4,4′ -bpy frameworks have already been generated[7,8].

In this paper, we describe the synthesis and structure of a novel polymeric complex with 4,4′-bipy and 2,4,6-trimethylbenzoic acid as the building blocks, [Mn(4,4′-bpy)$_{1.5}$(H$_2$O)$_3$](ClO$_4$)·(4,4′-bpy)(L)·H$_2$O (1). The complex has a one-dimensional chain structure bridged by water and 4,4′-bipyridine molecules.

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E-mail:hml301@163.com
作者:黄妙龄,女,31 岁,讲师;研究方向:配位化学。

1 Experimental

1.1 Materials and instruments

All the regents and solvents were used as commercial sources without further purification. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. The IR spectra were recorded on Shimadzu FTIR-8700 spectrophotometer using KBr discs. TG curves was recorded on a Perkin-Elmer Pyris Diamond thermoanalyser in flow of N_2, in the temperature range from 20 ℃ to 800 ℃, with a heating rate of 10 ℃·min^{-1}.

1.2 Synthesis of the title compound

The compound was hydrothermal synthesized under autogenous pressure. A mixture of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.181 g, 0.5 mmol), 2,4,6-trimethylbenzoic acid (0.165 g, 1 mmol), 4,4′-bipyridine (0.156 g, 1 mmol), NaOH (0.041 g, 1 mmol), and H_2O (10 mL, 0.55 mmol) was heated in a 25 mL capacity Teflon-lined reaction vessel at 160 ℃ for 5 days, the reaction mixture was cooled to room temperature over a period of 24 h. The product was collected by filtration, washed with H_2O and air-dried, Yields based on Mn: 46%. Molecular formula is $C_{35}H_{39}ClMnN_5O_{10}$. Elemental analysis calc. (%) C 53.83, H 4.99, N 8.97; found (%): C 53.27, H 5.08, N 9.06. Main IR bands (cm^{-1}) 3 413(vw, br), 1 683 (s),1 633(s), 1 608(s), 1 558(m), 1 411(m), 1 398(vs, br), 1 222(w), 1 116(vs), 1 089(s), 1 064(vw), 856(w), 808 (vw), 627(w), 490(w).

1.3 Crystal structure determination

A pale yellow crystal with dimensions of 0.18 mm × 0.12 mm × 0.10 mm was selected for the measurement. The diffraction data were collected at 294 K on a Bruker Smart 1000 CCD diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ radiation (λ = 0.071 073 nm). A total of 10 693 reflections were collected in the range of $1.32° \leqslant \theta \leqslant 26.40°$ by using an ω-scan mode, of which 7 561 were unique and used in the succeeding structure calculations. The structure was solved by direct methods and difference Fourier syntheses. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced geometrically. All calculations were performed with SHELXTL-97 package. Crystal data and structure refinement parameters are listed in Table 1.

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Table 1 Crystal data and structure parameters for the title complex

Empirical formula	$C_{35}H_{39}ClMnN_5O_{10}$	Z	2
Formula weight	780.10	Absorption coefficient / mm^{-1}	0.483
Temperature / K	294(2)	F(000)	812
Crystal system	Triclinic	Crystal size / mm	0.18 × 0.12 × 0.10
Space group	$P\bar{1}$	θ / (°)	1.32 to 26.40
a / nm	0.797 6(11)	Limiting indices	$-9 \leqslant h \leqslant 9, -19 \leqslant k \leqslant 18, -20 \leqslant l \leqslant 11$
b / nm	1.527 1(2)	Reflections collected / unique	7 561 (R_{int}=0.025 0)
c / nm	1.619 9(2)	Refinement method	Full-matrix least-squares on F^2
α / (°)	105.300(2)	Data / restraints / parameters	7 561 / 86 / 509
β / (°)	97.495(2)	Goodness of fit on F^2	1.046
γ / (°)	91.118(2)	Final R indices [$I>2\sigma(I)$]	R_1=0.05 54, wR_2=0.135 2
V / nm^3	1.884 0(4)	Largest diff. peak and hole / (e·nm^{-3})	522 and −451
D_c / (g·cm^{-3})	1.375		

2 Results and discussion

2.1 Crystal structure of the title complex

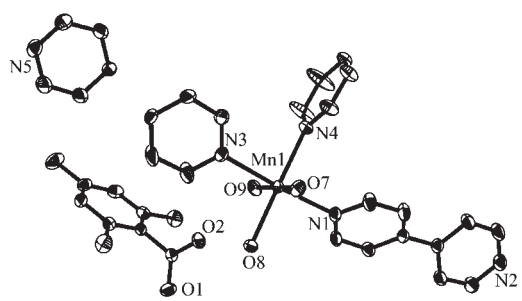
The molecular structure of the title complex is shown in Fig.1, and the 1D chain structure in Fig.2. The selected bond lengths and bond angles are given in Table 2.

The single-crystal structure reveals that, in 1, the Mn(Ⅱ) ions are bridged by μ_2-OH_2 molecules and 4,4′-bipyridine forming one-dimensional zigzag chain. The asymmetric unit contains one Mn^{2+}, perchlorate anion, one noncoordinated L ligand, four H_2O molecules and

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

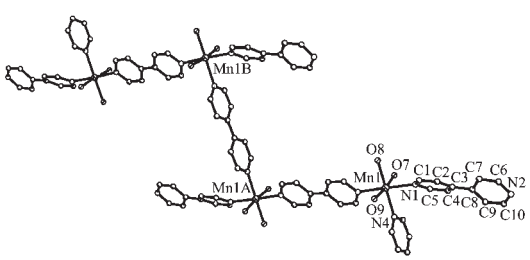
Mn(1)-O(8)	0.218 1(2)	Mn(1)-O(9)	0.220 0(3)	Mn(1)-N(1)	0.228 3(3)
Mn(1)-O(7)	0.218 2(2)	Mn(1)-N(4)	0.226 7(3)	Mn(1)-N(3)	0.229 1(3)
O(8)-Mn(1)-O(7)	91.65(10)	O(9)-Mn(1)-N(4)	90.88(11)	O(8)-Mn(1)-N(3)	92.58(10)
O(8)-Mn(1)-O(9)	83.76(10)	O(8)-Mn(1)-N(1)	90.96(10)	O(7)-Mn(1)-N(3)	87.65(10)
O(7)-Mn(1)-O(9)	174.19(9)	O(7)-Mn(1)-N(1)	89.12(10)	O(9)-Mn(1)-N(3)	88.99(10)
O(8)-Mn(1)-N(4)	173.97(11)	O(9)-Mn(1)-N(1)	94.50(11)	N(4)-Mn(1)-N(3)	90.08(11)
O(7)-Mn(1)-N(4)	93.86(11)	N(4)-Mn(1)-N(1)	86.70(11)	N(1)-Mn(1)-N(3)	175.28(12)

two and half 4,4′-bipyridine molecules. As depicted in Fig.1, the Mn atoms are each octahedrally coordinated by three N atoms of different bipy ligands and three O atoms of three H_2O molecules. The Mn-O bond distances fall in the region 0.218 1~0.220 0 nm and Mn-N bond distances averaged to 0.228 0 nm are practically identical within the experimental limitation (Table 2), which are close to those in [Mn(4,4′-bpy)$_2$(H_2O)$_4$](ClO_4)$_2$(4,4′-bpy)$_4$[9].



Free water molecules and perchlorate anion are omitted for clarity

Fig.1　Molecular structure of the title complex showing the displacement ellipsoids of 30% probability



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

Fig.2　1D chain structure for the complex

An interesting structural feature is that the adjacent linear polymeric chains are interconnected by hydrogen bonds consisting of the coordinated aqua molecules, perchlorate anion, and carboxylate oxygen atoms of L into a three-dimensional structure. As shown in Fig.3, L acts as a link of the adjacent linear polymeric chains by hydrogen bonding interactions. Each aqua molecule donates protons to form hydrogen bonds with two oxygen atoms from different L. (See Table 3) Thus, the complex is consolidated by hydrogen bonds in the range of 0.266 6(5)~0.272 5(7) nm and extended into a three-dimensional supramolecular structure. The channels of the cationic coordination network are occupied by lattice water molecules and the large anionic ClO_4^- and L molecules which are present for charge neutrality of the overall structure. On the other hand, the ligands 4,4′-bpy display different coordination modes. One acts as a μ-bridge and links [Mn(H_2O)$_3$(4,4′-bpy)$_{0.5}$]$^{2+}$ into a linear polymeric cation chain with the adjacent Mn⋯Mn separation of 1.165 5 nm, the other 4,4′-bipy coordinates to the Mn atom in a monodentate mode (See Fig.2).

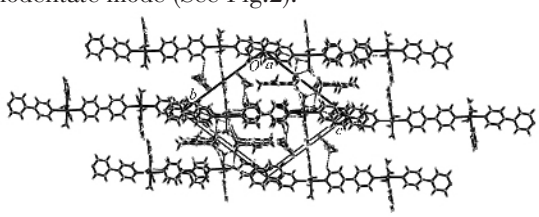


Fig.3　Packing of the complex in a cell along a axis

2.2　Spectra characteristics

The infrared spectra of the title complex has been recorded and some important assignments are shown above. In the IR spectra, the band at 3 413 cm^{-1}, due to the ν (O-H) absorptions of water molecules. The IR spectrum of the complex shows characteristic bands of the carboxyl ate groups in the usual region at 1 683, due to the absorptions of free 2,4,6-trimethylbenzoic acid molecules. The strong absorption at 1 633 cm^{-1} and 1 608 cm^{-1} is attributable to the ν(C=N) vibration of the ligand, and the very strong absorptions at 1 116 and 1 089 cm^{-1} indicate the presence of the perchlorate ion.

Table 3 Parameters of hydrogen bonds for the complex

D–H···A	*d*(D-H) / nm	*d*(H-O) / nm	*d*(D-O) / nm	∠D-H-A / (°)
O(7)–H(7A)···N(5)#1	0.085 6	0.194 2	0.279 6	175.21
O(7)–H(7B)···O(10)#1	0.085 2	0.192 8	0.276 4	166.38
O(8)–H(8A)···O(2)	0.085 6	0.190 6	0.269 4	152.23
O(8)–H(8B)···O(1)#4	0.085 2	0.181 9	0.266 6	171.97
O(9)–H(9A)···O(2)	0.085 4	0.189 6	0.272 6	166.59
O(9)–H(9B)···O(10)#3	0.085 4	0.188 8	0.272 9	173.48
O(10)–H(10A)···N(2)#5	0.085 5	0.191 1	0.276 2	172.52
O(10)–H(10B)···O(1)#6	0.085 4	0.184 3	0.269 3	172.70

#1: $-x$, $-y+1$, $-z+1$; #2: $-x+1$, $-y+1$, $-z+2$; #3: $-x+1$, $-y+1$, $-z+1$; #4: $-x$, $-y$, $-z+1$; #5: x, $y+1$, $z-1$; #6: x, $y+1$, z.

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