

吡啶-2,3,5,6-四甲酸双核锰(II)配合物的合成及结构

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摘要: 合成了一个双核锰配合物 $[\text{Mn}_2(\text{H}_2\text{pdtc})_2(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$ (H_2pdtc =吡啶-2,3,5,6-四甲酸), 并利用红外光谱、元素分析、X-射线单晶衍射分析及磁性分析等手段对其进行了表征及研究。该配合物为三斜晶系, $P\bar{1}$ 空间群, 晶胞参数 $a=0.841\ 66(13)\ \text{nm}$, $b=0.933\ 75(14)\ \text{nm}$, $c=1.024\ 29(16)\ \text{nm}$, $\alpha=111.248(2)^\circ$, $\beta=90.733(2)^\circ$, $\gamma=115.161(2)^\circ$, $V=0.665\ 66(18)\ \text{nm}^3$, $Z=1$ 。结构分析表明, 该配合物有一个双核单元, 且该双核单元通过分子间氢键及 $\pi\cdots\pi$ 堆积作用形成三维超分子网状结构。

关键词: 锰配合物; 吡啶-2,3,5,6-四甲酸; 氢键; 晶体结构

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Synthesis, Crystal Structure of a Binuclear Mn(II) Complex with Pyridine-2,3,5,6-tetracarboxylic Acid

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Abstract: A complex $[\text{Mn}_2(\text{H}_2\text{pdtc})_2(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$ (H_2pdtc =Pyridine-2,3,5,6-tetracarboxylic acid) has been synthesized and characterized by elemental analysis, FTIR, X-ray single crystal diffraction analysis, studied by magnetic susceptibility. It belongs to triclinic system, $P\bar{1}$ space group with $a=0.841\ 66(13)\ \text{nm}$, $b=0.933\ 75(14)\ \text{nm}$, $c=1.024\ 29(16)\ \text{nm}$, $\alpha=111.248(2)^\circ$, $\beta=90.733(2)^\circ$, $\gamma=115.161(2)^\circ$, $V=0.665\ 66(18)\ \text{nm}^3$, $Z=1$. The complex has a binuclear unit, and the dimeric units are alternatively assembled into a 3D supramolecular network structure by intermolecular hydrogen bonds and $\pi\cdots\pi$ interactions. CCDC: 632116.

Key words: manganese(II) complex; pyridine-2,3,5,6-tetracarboxylic acid; hydrogen-bond; crystal structure

Pyridine carboxylic acids can form stable complexes with the transition metal ions and rare earth metal ions. Taking Pyridine carboxylic acids as the ligands, the structures of coordination polymers can be varied by the selections of metal centers as well as synthetic methods. Another important significance of pyridine carboxylic acids is that they are biological substance with biological activity in vivo. The complexes of pyridine carboxylic acids have been widely studied and applied in many fields such as

stereochemistry, magnetism, reaction mechanism, biochemical simulation systems, and analytical chemistry fields^[1]. Up to now, there are a large number of complexes derived from pyridine carboxylic acids with transition metal and/or rare earth metal ions^[2]. Whereas, the reports on the complexes of pyridine-2,3,5,6-tetracarboxylic acid (H_2pdtc) are few^[3]. Pyridine-2,3,5,6-tetracarboxylic acid is able to form different structures with transition and rare earth or even the main group metal ions owing to its possessing a good

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number of coordination sites. Polynuclear complexes come into being more easily because of its N- and O-donors^[4-5]. As a result, the better character is expected to appear. Herein, we report a new coordination polymer $[\text{Mn}_2(\text{H}_2\text{pta})_2(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$, which is a binuclear complex. The complex owns a three-dimensional supramolecular network structure due to the intermolecular hydrogen bonds and $\pi \cdots \pi$ interactions.

1 Experimental

1.1 Reagent and apparatus

Pyridine-2,3,5,6-tetracarboxylic acid was synthesized according to the reported method^[2a]. And the other reagents were commercially available and used without further purification. Elemental analysis (C, H, and N) was carried out with a Perkin-Elmer 240 CHN elemental analyzer. Infrared spectra of the complex was obtained with a BIO-RAD FTS 3000 instrument in the range 4 000~400 cm^{-1} using a KBr pellet. Thermal analysis curve (TG) was obtained from a NETZSCH TG 209 thermal analyzer in a static air atmosphere using a sample size of 5~10 mg with a heating rate of 10 $^{\circ}\text{C} \cdot \text{min}^{-1}$.

1.2 Synthesis of complex $[\text{Mn}_2(\text{H}_2\text{pdtc})_2(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$ (**1**)

A mixture of H_2pdtc (0.076 8 g, 0.3 mmol), $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$ (0.070 2 g, 0.3 mmol) and H_2O (25 mL) was stirred for 2 h. The colorless crystals of **1** were obtained after the filtrate was standed at room temperature for two weeks. Yield: 0.051 3 g, 45% (based on Mn(II) salts). Elemental analysis calcd. for $\text{C}_{18}\text{H}_{22}\text{Mn}_2\text{N}_2\text{O}_{24}$ (%): C 28.44, H 2.92, N 3.68; found(%): C 28.61, H 2.88, N 3.75.

1.3 X-ray crystallography

The single crystal X-ray diffraction data collection for complex **1** was performed with a BRUKER SMART-1000 CCD diffractometer, equipped with graphite-monochromatized Mo $K\alpha$ radiation with a radiation wavelength of 0.071 073 nm, using φ - ω scan. The crystal structure was solved by direct methods and non-hydrogen atoms were obtained with Fourier synthesis. All the calculation was accomplished by using program of SHELXS-97 and SHELXL-97^[6-7]. Crystal data collection and refinement details are summarized in Table 1, selected bond lengths and angles are listed in Table 2.

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Table 1 Crystal data and structure refinement

Empirical formula	$\text{C}_{18}\text{H}_{22}\text{Mn}_2\text{N}_2\text{O}_{24}$	$D_c / (\text{Mg} \cdot \text{m}^{-3})$	1.897
Formula weight	760.26	Absorption coefficient / mm^{-1}	1.064
Temperature / K	293(2)	Max. and Min. transmission	1.000 000 and 0.598 389
Crystal system	Triclinic	$F(000)$	386
Space group	$P\bar{1}$	Crystal size / mm	0.26×0.22×0.16
a / nm	0.841 66(13)	θ range for data collection / ($^{\circ}$)	2.18~25.00
b / nm	0.933 75(14)	Reflections collected	3 386
c / nm	1.024 29(16)	R_{int}	0.013 4
α / ($^{\circ}$)	111.248(2)	Number of parameters	210
β / ($^{\circ}$)	90.733(2)	Goodness-of-fit on F^2	1.073
γ / ($^{\circ}$)	115.161(2)	Final R indices ($I > 2\sigma(I)$)	$R_1=0.032$ 3, $wR_2=0.081$ 5
Volume / nm^3	0.665 66(18)	R indices (all data)	$R_1=0.036$ 4, $wR_2=0.085$ 7
Z	1	Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	609 and -427

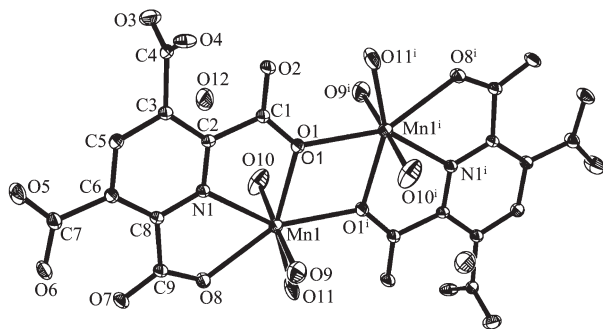
2 Results and discussion

2.1 Crystal structure descriptions

Single crystal X-ray diffraction analysis reveals that complex **1** belongs to triclinic system, $P\bar{1}$ space group. The molecular structure and coordination

environments of metal centers are shown in Fig.1. It shows that the symmetric unit consists of two Mn(II) ions, two $\text{H}_2\text{pdtc}^{2-}$, six coordinated water molecules and two uncoordinated water molecules. The Mn(II) ion is seven-coordinated and exhibits a distorted pentagonal bipyramid geometrical coordination environment. The

equatorial sites are occupied by ONO (O1, N1, O8) donor from the carboxyl groups at 2,6-position of pyridine ring of H_2pdtc , one water molecule (O11) and one bridging O atom (O1ⁱ) from another adjacent $pdtc$ ligand, while the axial sites are occupied by two water molecules (O9, O10). The two seven-coordinated Mn(II) ions are bridged by two O atoms (O1, O1ⁱ). **1** is a binuclear complex, the distance between the two Mn(II) ions in the molecular is 0.378 45(7) nm. The Mn-O distances range from 0.213 9(2) to 0.236 82(16) nm and the average bond length is 0.225 6 nm, which are a little longer than normal ranges found in other manganese complexes^[8]. The atoms of O1, Mn1, O1ⁱ, Mn1ⁱ are coplanar. The plane is a parallelogram and the two angles O1-Mn1-O1ⁱ of 71.22(6)° and Mn1-O1-Mn1ⁱ of 108.78(6)° are complementary. Bond angles related are presented in Table 2. For the $pdtc$ ligand, the carboxyl groups are partly deprotonated, and each

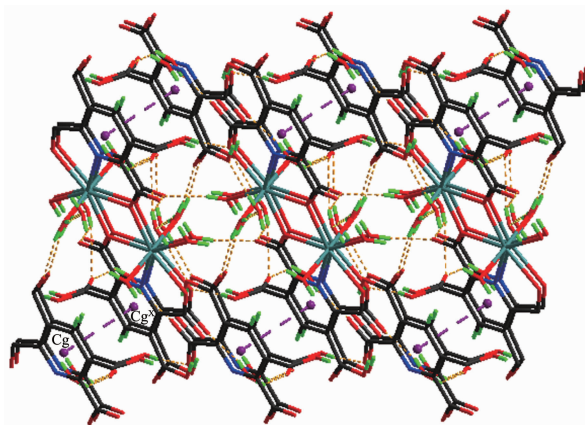


Symmetry code: ⁱ -x+1, -y+1, -z+1; H atoms have been omitted for clarity

Fig.1 Molecular structure of complex **1** with 30% probability ellipsoid

H_2pdtc^{2-} anion is coordinated with two Mn(II) cations. Each Mn(II) cation is connected with two H_2pdtc^{2-} anions.

In the complex, carboxylate group chelates with metal in the mono/di-dentate mode. complex **1** has an extensive capacity to hydrogen bonds through H_2pdtc^{2-} , coordinated water and uncoordinated water. Details of hydrogen bonds within **1** are contained in Table 3. In the crystal building of **1**, the complex is held together by $\pi \cdots \pi$ interactions between the $pdtc$ ligand. The centroid-to-centroid distance is 0.389 1 nm ($Cg \cdots Cg^x$, symmetry code: ^x -1-x, 3-y, 2-z) in **1**. The intermolecular hydrogen bonds also make the complex own a three-dimensional supramolecular network structure (Fig.2).



Symmetry code: ^x -1-x, 3-y, 2-z; $\pi \cdots \pi$ stacking interactions between the chains are indicated as "----" and hydrogen bonding interactions are indicated as "....."

Fig.2 3D supramolecular structure built up by hydrogen bonding interactions and $\pi \cdots \pi$ interactions in **1**

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

Mn(1)-O(10)	0.213 9(2)	Mn(1)-N(1)	0.235 09(18)	Mn(1)-O(11)	0.219 12(19)
Mn(1)-O(8)	0.235 61(16)	Mn(1)-O(9)	0.219 3(2)	Mn(1)-O(1) ⁱ	0.236 82(16)
Mn(1)-O(1)	0.228 65(16)				
O(11)-Mn(1)-O(9)	93.20(10)	O(10)-Mn(1)-O(1)	83.97(9)	O(10)-Mn(1)-O(11)	88.33(10)
O(11)-Mn(1)-O(1)	150.83(7)	O(10)-Mn(1)-O(8)	98.69(9)	O(9)-Mn(1)-O(1)	94.01(8)
O(11)-Mn(1)-O(8)	72.85(6)	O(10)-Mn(1)-N(1)	91.32(7)	O(9)-Mn(1)-O(8)	83.14(7)
O(11)-Mn(1)-N(1)	138.20(7)	O(11)-Mn(1)-O(1) ⁱ	80.45(6)	O(9)-Mn(1)-N(1)	88.50(7)
O(9)-Mn(1)-O(1) ⁱ	90.82(7)	O(1)-Mn(1)-N(1)	70.26(6)	O(1)-Mn(1)-O(1) ⁱ	71.22(6)
O(1)-Mn(1)-O(8)	136.12(6)	N(1)-Mn(1)-O(1) ⁱ	141.32(6)	N(1)-Mn(1)-O(8)	65.91(6)
O(8)-Mn(1)-O(1) ⁱ	152.18(6)	O(10)-Mn(1)-O(1) ⁱ	88.02(8)	O(10)-Mn(1)-O(9)	177.91(9)

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

Table 3 Hydrogen bond lengths and angles for complex 1

D-H...A	d(D-H) / nm	d(H...A) / nm	d(D...A) / nm	∠(DHA) / (°)
O4-H4...O8 ⁱⁱ	0.082	0.180	0.261 2(2)	169.60
O9-H9A...O3 ⁱⁱⁱ	0.085	0.225	0.286 1(3)	129.41
O9-H9B...O7 ^{iv}	0.085	0.209	0.293 2(3)	167.29
O10-H10A...O5 ^v	0.085	0.197	0.280 4(3)	166.02
O10-H10B...O12	0.085	0.184	0.268 5(3)	170.41
O11-H11B...O2 ^{vi}	0.085	0.241	0.316 3(3)	147.55
O12-H12A...O6 ^{vii}	0.086	0.195	0.280 2(3)	172.09
O12-H12B...O2 ^{viii}	0.085	0.223	0.292 3(3)	138.66
O12-H12B...O3 ^{ix}	0.085	0.239	0.300 0(3)	128.87

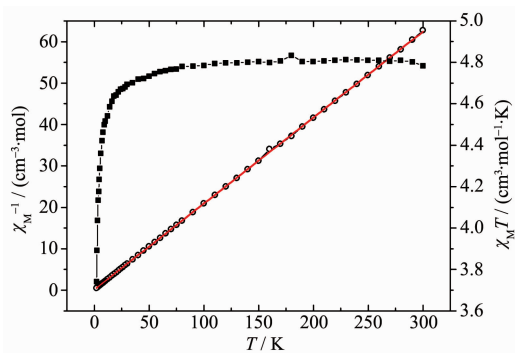
Symmetry code: ⁱ $x-1, y-1, z$; ⁱⁱⁱ $x, y+1, z$; ^{iv} $-x+2, -y+2, -z+2$; ^v $x, y, z-1$; ^{vi} $x+1, y+1, z$; ^{vii} $-x+2, -y+1, -z+2$; ^{viii} $-x+1, -y, -z+1$.

2.2 IR result

The IR spectrum of **1** has been employed to distinguish the coordination modes of the carboxylate groups. In the IR spectrum, water absorption bands appear at 3468 cm^{-1} and may be attributed to asymmetric and symmetric O-H stretching modes. The carboxyl group absorption band appears at 1724 cm^{-1} , which indicates the partial deprotonation of the pyridine-2,3,5,6-tetracarboxylic acid (H_4pdtc) ligand. The absorption bands of the carboxylate groups are observed at 1575 and 1359 cm^{-1} .

2.3 Magnetic properties

The magnetic susceptibilities, $1/\chi_M$, $\chi_M T$, of the complex **1** were measured in the range $0\sim 300\text{ K}$ at a magnetic field of 1000 G , and the plots of $1/\chi_M$ and $\chi_M T$ versus T are shown in Fig.5. For the binuclear complex **1**, the observed $\chi_M T$ value at 295 K is $4.79\text{ cm}^3\cdot\text{K}\cdot\text{mol}^{-1}$ (corresponding to an effective moment $\mu_{\text{eff}}=6.18\text{ B.M.}$), which is larger than the theoretical value expected for two non-interacting high-spin Mn^{II} ions^[9]



Red straightline shows the Curie-Weiss fitting curve

Fig.5 Temperature dependence of $\chi_M T$ (■) and $1/\chi_M$ (○) values versus T for complex **1**

with $S=5/2$ each ($4.38\text{ cm}^3\cdot\text{K}\cdot\text{mol}^{-1}$ or $\mu_{\text{eff}}=5.92\text{ B.M.}$). And $\chi_M T$ values gradually decrease upon lowering the temperature. With the assumption of non-interacting spins, the data may be fit to a Curie-Weiss law: $\chi_M = \frac{C}{T-\theta}$. A Curie-Weiss fit of the data yields a small negative Weiss constant θ of -0.70268 K , which indicates almost ideal Curie behavior. This magnetic behavior indicated a very weak antiferromagnetic interaction between the two $\text{Mn}(\text{II})$ ions in complex **1**. Related oxygen bridged $\text{Mn}(\text{II})$ complexes often show ferromagnetic interactions^[8,10].

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