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# 基于偶氮苯-4,4′-二甲酸配体的锰(Ⅱ)配合物的合成、晶体结构及性质研究

付 峰* 郭海康 唐 龙 吴亚盘 侯向阳 任宜霞
(延安大学化学与化工学院,陕西省化学反应工程重点实验室,延安 716000)

**摘要**: 利用水热反应合成了一种新的锰配合物[Mn(ADB)(phen)($H_2O$)$_2$]$_n$ (**1**)($H_2$ADB=偶氮苯-4,4′-二甲酸,phen=邻菲啰啉),运用元素分析、红外光谱、热重分析、电化学等方法对它进行了研究,并通过 X 射线单晶衍射测定了配合物的单晶结构。晶体结构表明,配合物属三斜晶系,空间群为 $P\bar{1}$,晶胞参数 $a$=0.762 00(13) nm,$b$=0.915 30(15) nm,$c$=1.826 2(2) nm,$\alpha$=88.467(3)°,$\beta$=84.145(2)°,$\gamma$=77.542(2)°。配合物 **1** 的中心锰离子是六配位,具有扭曲的八面体结构,偶氮苯-4,4′-二甲酸连接相邻的锰离子形成了一维“之”字链,进而链与链之间通过 $\pi$-$\pi$ 堆积和氢键相互作用拓展成三维超分子结构。磁学性质研究表明该配合物为反铁磁性。

**关键词**: 锰(Ⅱ)配合物; 偶氮苯-4,4′-二甲酸; 晶体结构; 磁性质
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# Synthesis, Crystal Structure and Properties of Manganese(Ⅱ) Compound with Azobenzen-4,4′-dicarboxylic Acid Ligand

FU Feng* GUO Hai-Kang TANG Long WU Ya-Pan HOU Xiang-Yang REN Yi-Xia
(*Department of Chemistry and Chemical Engineering, Shaanxi Key Laboratory of Chemical Reaction Engineering, Yan'an University, Yan'an, Shaanxi* 716000, *China*)

**Abstract:** A coordination complex [Mn(ADB)(phen)($H_2O$)$_2$] (**1**) (ADB=azobenzen-4,4′-dicarboxylic acid ion, phen=1,10-phenanthroline) have been synthesized by hydrothermal reaction and characterized by elemental analysis, IR spectra, thermal analysis and electrochemical property, and the crystal structures were determined by single crystal X ray diffraction. Single-crystal X ray diffraction analyses indicate that complex belongs to triclinic system and the space group is $P\bar{1}$, the parameters of the crystal cell for the complex are $a$=0.762 00(13) nm, $b$=0.915 30(15) nm, $c$=1.826 2(2) nm, $\alpha$=88.467(3)°, $\beta$=84.145(2)°, $\gamma$=77.542(2)°. The manganese centre is six-coordinated, with a distorted octahedral geometry. The Mn(Ⅱ) center is connected to form a 1D zigzag chain structure bridged by azobenzen-4,4′ -dicarboxylic acid ligand, further extended into a 3D supramolecular structure through $\pi$-$\pi$ stacking and hydrogen bonding interactions. Magnetic property of **1** is investigated and exhibited antiferromagnetic interactions. CCDC: 847696.

**Key words:** manganese complex; azobenzen-4,4′-dicarboxylic acid; crystal structure; magnetic property

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*通讯联系人。E-mail:yadxfufeng@126.com

The syntheses and design of metal-organic frameworks (MOFs) have attracted considerable attention in supramolecular and materials chemistry, due to their intriguing architectures[1-3] and wide potential applications[4-6] such as gas adsorption and separation, luminescent sensors, molecule magnets, and catalyst. Effective strategy to construct these coordination polymers is to select suitable multidentate ligands to integrate metal ions to a desired framework. Carboxylate-based ligands are especially interesting because of their various coordination modes[7-10]. Polycarboxylate aromatic ligands, such as 1,2-benzenedicarboxylate and 1,3,5-benzenetricarboxylate have been extensively employed to synthesize such metal-organic complexes in possession of multidimensional networks and interesting properties[11-13]. Azobenzen-4,4′-dicarboxylic acid ($H_2ADB$) ligand [14-16], as a member of multidentate O-donor, has been also used. In this context, we select azobenzen-4,4′-dicarboxylic acid and 1,10-phenanthroline as mixed ligands, on the basis of the following considerations: (i) azobenzen-4,4′-dicarboxylic acid have two carboxylate groups, and they may act as linkers to connect metal ions into higher dimensional structures via varied coordination fashions; (ii) phenanthroline (phen) is a good ligand for transition metal ions and can construct supramolecular structure via hydrogen bonds and $\pi$-$\pi$ aromatic interactions. Herein we report the azobenzen-4,4′-dicarboxylate complex with 1,10-phenanthroline, [Mn(ADB)(phen)($H_2O$)$_2$] (**1**), which shows a zigzag chain 1D coordination framework. Moreover, the properties of complex were also investigated.

## 1 Experimental

### 1.1 Materials and physical measurements

All reagents and solvents were commercially available and analytical grade. Elemental analyses were performed on a Perkin-Elmer 2400 element analyzer. IR spectra were recorded on a SHIMADZU FTIR-8400 spectrometer using KBr pellet. Using a NETZSCH STA 449C thermogravimetric analyzer perform thermogravimetric analyses. The magnetic susceptibilities were obtained on crystalline samples using a Quantum Design MPMS SQUID magnetometer.

### 1.2 Synthesis of [$Mn_3$(ADB)(phen)($H_2O$)]$_n$

A mixture of $H_2ADB$ (0.081 g, 0.3 mmol), phen (0.099 g, 0.05 mmol), $Mn(Ac)_2\cdot 4H_2O$ (0.123 g, 0.5 mmol), $CH_3CH_2OH$ (2 mL), and $H_2O$ (6 mL) was stirred evenly and heated in a 20 mL Teflon-lined autoclave at 120 ℃ for 4 d, followed by slow cooling (5 ℃·h$^{-1}$) to room temperature. The resulting mixture was washed with $H_2O$, and yellow stick crystals were collected and dried in air. Yield: 56% (based on Mn). Elemental analysis Calcd. for $C_{26}H_{20}MnN_4O_6$(%): C 57.89, H 3.74, N 10.39, Found (%): C 57.47, H 3.94, N 10.56. IR (KBr, cm$^{-1}$): 3 390(s), 3 066(s), 2 366(vs), 1 667(s), 1 532(w), 1 395(vs), 792(s), 719(w), 630(vs), 500(vs).

### 1.3 Crystal structure determination

Single crystal structure determination by X-ray diffraction was performed on a Bruker Smart Apex Ⅱ CCD diffractometer equipped with a graphite monochromatized Mo $K\alpha$ radiation ($\lambda$=0.071 073 nm) at 296(2) K. 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 the use of (SHELX-97) crystallographic software package[17-18]. Crystal data and details on refinements are summarized in Table 1. Selected bond distances and angles are listed in Table 2.

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## 2 Results and discussion

### 2.1 Structure description

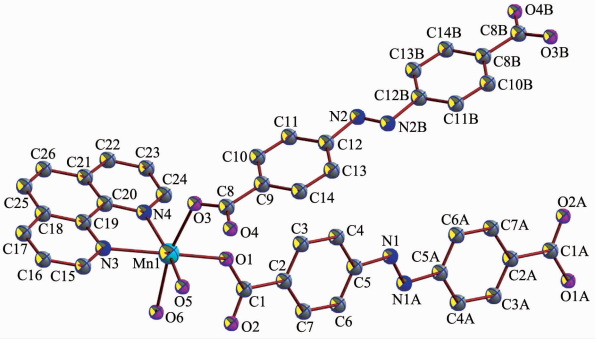
As shown in Fig.1, the asymmetric unit consists of one crystallographically Mn(Ⅱ) ion, one azobenzen-4,4′-dicarboxylic acid ion, one phen molecule and two coordinated water molecules. Each Mn(Ⅱ) centre is six-coordinated by four oxygen atoms from two asymmetrical monodentate carboxylate groups and two water molecules and two nitrogen atoms from a chelating phen ligand, forming a distorted octahedral geometry. The Mn-O and Mn-N bond lengths are in the range of 0.213 2(4)~0.216 6(4) nm and 0.213 2(4)~0.226 9(4) nm, respectively, which are similar to

**Table 1 Crystal data and structure refinement for complex**

| | | | |
|---|---|---|---|
| Empirical formula | $C_{26}H_{20}MnN_4O_6$ | $D_c$ / (g·cm$^{-3}$) | 1.448 |
| Formula weight | 539.40 | Absorption coefficient / mm | 0.583 |
| Crystal system | Triclinic | $\theta$ range for data collection / (°) | 2.24 to 25.00 |
| Space group | $P\bar{1}$ | Indices range ($h$, $k$, $l$) | $-9 \leqslant h \leqslant 8$, $-10 \leqslant k \leqslant 6$, $-21 \leqslant l \leqslant 21$ |
| $a$ / nm | 0.762 0(13) | Reflections collected | 6 425 |
| $b$ / nm | 0.915 3(15) | Independent reflections | 4 270 ($R_{int}$=0.032 3) |
| $c$ / nm | 1.826 2(2) | Data / restraints / parameters | 4 270 / 1 / 334 |
| $\alpha$ / (°) | 88.467(3) | $F$(000) | 554 |
| $\beta$ / (°) | 84.145(2) | Goodness-of-fit on $F^2$ | 1.018 |
| $\gamma$ / (°) | 77.542(2) | Final $R$ | $R_1$=0.053 7, $wR_2$=0.112 9 |
| $V$ / nm$^3$ | 1.237 2(3) | $R$ indices (all data) | $R_1$=0.098 3, $wR_2$=0.138 6 |
| $Z$ | 2 | Largest diff. peak and hole / (e·nm$^{-3}$) | 693, −334 |

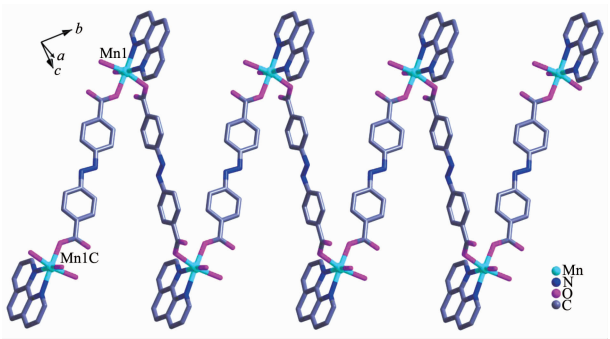
**Table 2 Selected bond lengths (nm) and angles (°)**

| | | | | | |
|---|---|---|---|---|---|
| Mn(1)-O(1) | 0.213 2(3) | Mn(1)-O(5) | 0.216 6(3) | Mn(1)-N(3) | 0.226 9(3) |
| Mn(1)-O(3) | 0.215 3(3) | Mn(1)-O(6) | 0.224 7(2) | Mn(1)-N(4) | 0.225 0(3) |
| O(1)-Mn(1)-O(3) | 84.16(10) | O(3)-Mn(1)-O(6) | 166.76(9) | O(5)-Mn(1)-N(4) | 166.05(12) |
| O(1)-Mn(1)-O(5) | 96.93(11) | O(5)-Mn(1)-O(6) | 87.74(10) | O(6)-Mn(1)-N(4) | 99.30(11) |
| O(3)-Mn(1)-O(5) | 85.77(10) | O(1)-Mn(1)-N(4) | 95.66(12) | O(1)-Mn(1)-N(3) | 166.14(12) |
| O(1)-Mn(1)-O(6) | 85.19(10) | O(3)-Mn(1)-N(4) | 89.57(11) | O(3)-Mn(1)-N(3) | 103.84(11) |



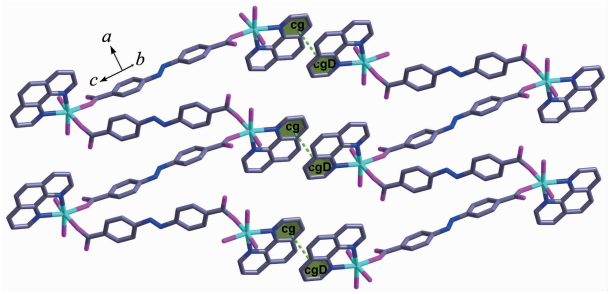

Hydrogen atoms areomitted for clarity; Symmetry codes: A: $x$, $1+y$, $-1+z$; B: $-1+x$, $y$, $-1+z$

Fig.1 Coordination environment of the Mn atoms




Symmetry codes: C: $1-x$, $-y$, $2-z$

Fig.2 Part of the zigzag polymeric chain




Centroid-to-centroid distance 0.368 5 nm; Symmetry codes: D: $-x$, $-y+2$, $-z+1$

Fig.3 Zigzag polymeric chains which stack through $\pi$-$\pi$ stacking interactions to form a 2D sheet

reported Mn coordination polymers[19].

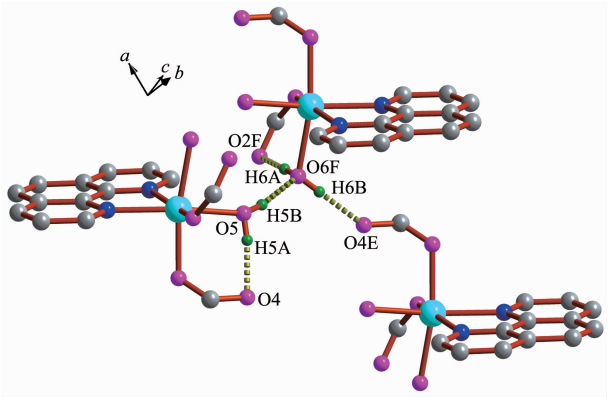
In complex **1**, each ADB dianion acts as a $\mu_2$-bridge linking two Mn atoms into a zigzag chain, which the ADB ligands adopts bis-(monodentate) coordination mode (Fig.2). The chain become more stable by the intramolecular hydrogen bonds (O5−H(5A)⋯O(4), O6−H(6A)⋯O(2)). Additionally, these chains interact via $\pi$-$\pi$ stacking interactions (centroid-to-centroid distance=0.368 5 nm) between two pyridyl rings from two different phen molecules, generating a 2D sheet (Fig.3). Neighboring 2D layers are further

**Table 3　Hydrogen bond lengths and bond angles**

| D–H···A | *d*(D-H) / nm | *d*(H···A) / nm | *d*(D···A) / nm | ∠DHA / (°) |
|---|---|---|---|---|
| O5–H(5A)···O(4) | 0.085 | 0.184 4 | 0.268 6 | 170.10 |
| O5–H(5B)···O(6) | 0.085 | 0.187 3 | 0.271 4 | 170.02 |
| O6–H(6A)···O(2) | 0.085 | 0.172 9 | 0.257 8 | 176.39 |
| O6–H(6B)···O(4) | 0.085 | 0.183 1 | 0.268 0 | 176.64 |

Hydrogen atoms areomitted for clarity; Symmetry codes: A: *x*, 1+*y*, −1+*z*; B: −1+*x*, *y*, −1+*z*.

connected to each other by intermolecular hydrogen bonds (O5–H(5B)···O(6), O6–H(6B)···O(4)) to form the final 3D supramolecular architecture (Fig.4). The detailed data of hydrogen bonds are shown in Table 3.




Symmetry codes: E: 2–*x*, 1–*y*, 1–*z*; F: 1–*x*, 1–*y*, 1–*z*

Fig.4　Hydrogen bonding interactions

## 2.2　IR spectroscopy

In the IR spectrum, there are a strong $\nu$(OH) band at 3 035~3 400 cm$^{-1}$ and a wide band of water molecule at 400~600 cm$^{-1}$, which shows the existence of coordinated water molecule in the complex. Meanwhile, the spectrum of complexe exhibit a $\nu_{as}(COO^-)$ and a $\nu_s(COO^-)$ peak at 1 167, 1 392 cm$^{-1}$, respectively. The value of $\Delta\nu=[\nu_{as}(COO^-)-\nu_s(COO^-)]$ is 225 cm$^{-1}$, indicating that the protonated carboxylate group of two $H_2ADB$ ligands adopted bis-(monodentate) coordination mode[20].

## 2.3　Thermal analysis

Thermogravimetric analyses were performed under a air atmosphere with a heating rate of 10 ℃·min$^{-1}$ using a NETZSCH STA 449C thermogravimetric analyzer. The TG curve (Fig.5) indicates that the weight loss of the complex can be divided into three steps. The first weight loss is 7.02% from 120 to 170 ℃, corresponding to the loss of three water molecules in the complex (Calcd. 6.67%).The second weight loss of 33.17% in the temperature range 250 to 380 ℃ corresponds to the release of phen ligands (Calcd. 33.40% ).The third weight-loss of 50.67% occurs between 420 to 520 ℃, giving manganese oxides as the final decomposition product which constitute 12.89% (Calcd. 13.14%).

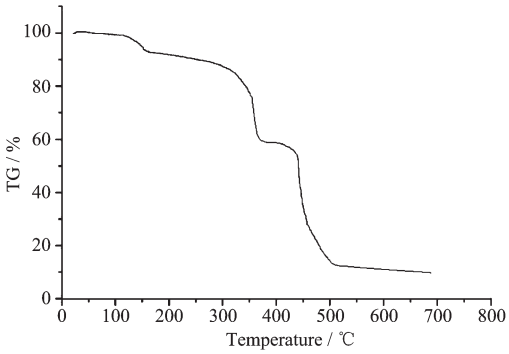



Fig.5　TG curves of complex **1**

## 2.4　Cyclic voltammetry

Using cyclic voltammetric measurement to complex, tri-electrode system chose glass/C as working electrode, Pt as auxiliary electrode and Ag/AgCl as reference electrode.The solvent is the mixture of methanol and water with complex concentration of $1\times10^{-4}$ mol·L$^{-1}$. The KCl (0.1 mol·L$^{-1}$) solution was used as the supporting electrolyte and the scanning rate is 100 mV·s$^{-1}$ in this experiment. The voltammetry curves (Fig.6) exhibits a pair of redox

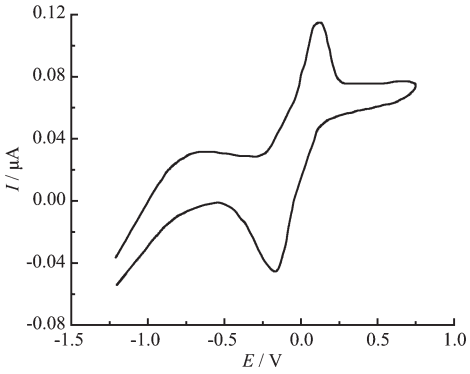
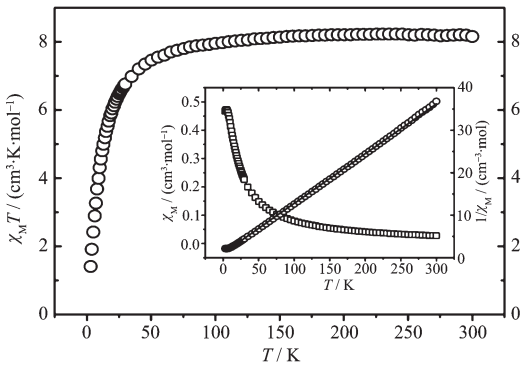



Fig.6　Cyclic voltammogram of the complex **1**

peaks which is observed with oxidation potential of + 0.125 V and reduction potential of −0.125 V. The specific value of a pair of oxidation and reduction potential is near one which show that the Mn(Ⅱ) complex is more stable than the Mn(Ⅲ) one in this system.

### 2.4 Magnetic properties

The magnetic properties of complex **1** were investigated over the temperature range 3~300 K in a field of 10 kOe. The magnetic susceptibilities $\chi_M$ and $\chi_M T$ versus $T$ plots are shown in Fig.7. For complex **1**, the experimental $\chi_M T$ value at 300 K is 8.160 $cm^3 \cdot K \cdot mol^{-1}$, slightly smaller than the spin-only value (8.750 $cm^3 \cdot K \cdot mol^{-1}$) expected for the spin-only Mn(Ⅱ) ion ($S$= 5/2). The $\chi_M T$ value of **1** remains almost constant from 300 to 100 K, and then decreases on further cooling, reaching a value of 1.397 $cm^3 \cdot K \cdot mol^{-1}$ at 3 K. This behavior indicates a dominant antiferromagnetic interaction between the Mn(Ⅱ) ions in the structure. The temperature dependence of the reciprocal susceptibilities ($1/\chi_M$) obeys the Curie-Weiss law above 3 K with $\theta$=−9.08 K, $C$=8.54 and $R$=1.418×10$^{-4}$. The values of $\theta$ for **1** indicate weak antiferromagnetic interactions between the adjacent Mn(Ⅱ) ions.




Insert: Plot of thermal variation of $\chi_M$ and $\chi_M^{-1}$ for complex **1**

Fig.7 Thermal variation of $\chi_M T$ for complex **1**

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