



## 一个新的噻二唑衍生物 $\text{H}_2\text{ADTZ}$ 与锰的二维聚合物的合成与晶体结构

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### Synthesis, Crystal Structure and Properties of a New Thiadiazolen Two-dimensional Polymer of $\text{H}_2\text{ADTZ}$ with $\text{Mn(II)}$

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**Abstract:** A new 1,3,4 thiadiazole-derivative ligand 2,5-(s-acetic acid) dimercapto-1,3,4 thiadiazole ( $\text{H}_2\text{ADTZ}$ ) and its one-dimensional manganese polymer  $\text{Mn}(\text{ADTZ}) \cdot 4\text{H}_2\text{O}$  had been synthesized and structurally characterized by X-ray single crystal diffraction in this paper. The  $\text{Mn(II)}$  ion is coordinated with a distorted octahedron by two oxygen atoms from neighboring two deprotonated ligands  $\text{ADTZ}^{2-}$  and other four oxygen atoms from four coordinated water molecules. The structural feature of the title compound is the formation of one-dimensional manganese chains polymer through the bridging of dioxygen O-O units. In the solid state structure of the complex, one-dimensional manganese chains are joined together by the weak intermolecular hydrogen bonds and vander Waals interactions forming a two-dimensional supramolecular compound. Furthermore, the UV spectra and electro-chemical properties of the title compound were also investigated. CCDC: 260532.

**Key words:**  $\text{Mn(II)}$ ; polymer; thiadiazole-derivative; hydrogen bonds; cyclic voltammetry

## 0 Introduction

Up to now, people's research interest focuses on the self-assembly of supramolecular architectures prepared from multifunctional ligands and transition metals<sup>[1-3]</sup>. Recently, thiadiazole compounds have attracted increasing attention due to their potential applications in the fields of poly material<sup>[2]</sup>, preventing bacterial infection<sup>[3]</sup>, poly material<sup>[4]</sup>, selective catalysts<sup>[5]</sup> and so

on. The compound 1,3,4-thiadiazole is itself a potentially versatile ligand, particularly its derivatives are very interesting bridging ligands<sup>[6]</sup>. the considerable attention of research activity in the field has been focused on those thiadiazole derivatives containing-nitrogen<sup>[7]</sup> because of an excellent coordination capability of the nitrogen atom, but the complexes of the ligand 1,3,4 thiadiazole-based with some metal ions are lacking due to the diversity of the binding modes of

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carboxyl group<sup>[8]</sup> and the variety of the dihedral between the plane of carboxyl group and ring plane<sup>[9]</sup>.

In this paper, we synthesized a new ligand 2,5-(*s*-acetic acid) dimercapto-1,3,4 thiadiazole(H<sub>2</sub>ADTZ) and its corresponding complex Mn(ADTZ)·4H<sub>2</sub>O. The crystal structures of the complex was characterized by X-ray diffraction. The results indicated that the Mn(II) ion was in a distorted octahedron coordination environment with two oxygen atoms from neighboring two deprotonated ligands ADTZ<sup>2-</sup> and four water molecules. Besides, some properties of the complex such as <sup>1</sup>H NMR, IR, electro-spectra and cyclic voltammetry had also been determined and characterized.

## 1 Experimental

### 1.1 Materials and physical techniques

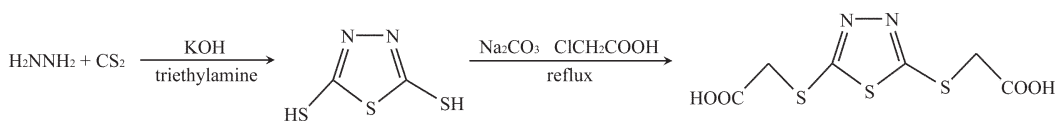
All reactions and manipulations were conducted under normal circumstance. All reagents were of the highest grade commercially available and used without further purification.

IR spectra were recorded on a Nicolet NEXUS 470-FITR spectrophotometer. <sup>13</sup>C NMR spectra were recorded at room temperature on Bruker DXP 400 spectrometers, Carbon, hydrogen and nitrogen analyses

were carried out on a Carlo-Erba 1106 elemental analyzer.

### 1.2 Synthesis of 2,5-(*s*-acetic acid) dimercapto-1,3,4 thiadiazole (H<sub>2</sub>ADTZ)

The starting material 2,5-dimercapto-1,3,4-thiadiazole was obtained according to the literature<sup>[10]</sup>. The target ligand H<sub>2</sub>ADTZ was synthesized by following method (See Scheme 1): adding 2,5-dimercapto-1,3,4 thiadiazole (1.5 g, 10 mmol) to a stirred aqueous solution of chloroacetic acid (1.89 g, 20 mmol) and sodium carbonate (1.06 g, 10 mmol). After the reaction mixture was stirred and refluxed for 3 h, then cooled and filtered. Ethanol was then added, yielding a white solid. The product was then washed with ethanol and air-dried, yield, 2.2 g(82.71%). m.p. 164~165 °C, IR (cm<sup>-1</sup>): 3 479(OH), 1 724(C=O), 1 577(C=N), 680(C-S). <sup>13</sup>C NMR(400 MHZ, D<sub>2</sub>O): 173.556(C=O), 167.708 (C of the thiadiazole ring), 37.910 (CH<sub>2</sub>). Anal. Calcd (%) for C<sub>6</sub>H<sub>6</sub>N<sub>2</sub>S<sub>3</sub>O<sub>4</sub>: C: 27.07; H: 2.26; N: 10.53; Found (%): C: 27.62; H: 2.18; N:10.89. The ligand H<sub>2</sub>ADTZ is insoluble in common organic solvents, such as methanol, ethanol, acetone, DMF and DMSO, only it is soluble in water.



Scheme 1

### 1.3 Preparation of Mn(ADTZ) 4H<sub>2</sub>O

A solution of the ligand H<sub>2</sub>ADTZ (0.026 6 g, 0.1 mmol) in water (4 mL) was added dropwise to a solution of Mn(NO<sub>3</sub>)·6H<sub>2</sub>O (0.028 7 g, 0.1 mmol) in water (2 mL). The resulting solution was filtered. The colorless filtrate was allowed to stand at room temperature. Colorless crystals suitable for X-ray single crystals analysis were obtained over 12 h. IR spectra (cm<sup>-1</sup>): 3 086(-OH), 1 564 (C=O), 1 426(C=N), 656(C-S). Anal. Calcd (%) for MnC<sub>6</sub>H<sub>12</sub>N<sub>2</sub>S<sub>3</sub>O<sub>8</sub>: C: 18.41, H: 3.07, N: 7.16, Mn:14.07. Found(%): C:18.79; H:2.95; N:7.61; Mn:13.53.

### 1.4 Crystallography

Crystal data and experimental details for the title compound are given in Table 1. All measurements were made on a Bruker CCD-AREA imaging plate area dectector with graphite monochromized Mo K $\alpha$

radiation ( $\lambda$ =0.007 107 3 nm). The sample selected for investigation has dimension of 0.20 mm × 0.18 mm × 0.18 mm. All data were collected at a temperature of 291(2) K using the  $\omega$ -2 $\theta$  scan technique and corrected for Lorenz-polarization effects. A correction for secondary extinction was applied.

The structure were solved by direct methods and expended using the difference Fourier technique. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 4 467 observed reflections and 275 variable parameters. All calculations were performed using SHELX-97 crystallographic software package<sup>[11]</sup>. Selected bond lengths and bond angled are listed in Table 2.

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Table 1 Crystal data and structure refinement for the complex

Empirical formula	C <sub>6</sub> H <sub>12</sub> MnN <sub>2</sub> O <sub>8</sub> S <sub>3</sub>	Absorption coefficient / mm	1.4
Formula weight	391.3	<i>F</i> (000)	398
Temperature/ K	291(2)	Crystal size/mm	0.20 × 0.18 × 0.18
Wavelength/nm	7.107 3	$\theta$ range for data collection / (°)	2.02 to 27.50
Crystal system	Monoclinic	Index ranges	0 ≤ <i>h</i> ≤ 6, -12 ≤ <i>k</i> ≤ 13, -17 ≤ <i>l</i> ≤ 17
Space group	<i>P</i> 2/ <i>c</i>	Reflections collected/unique	2 685 / 1 546 [ <i>R</i> (int) = 0.022 5]
<i>a</i> / nm	0.5330 6(11)	Completeness to 2 $\theta$ =27.50	94.40%
<i>b</i> / nm	1.009 8(2)	Max. and min. transmission	0.786 7 and 0.767 1
<i>c</i> / nm	1.330 6(3)	Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
$\alpha$ / (°)	90	Data/restraints / parameters	1 546 / 0 / 109
$\beta$ / (°)	95.48(3)	Goodness-of-fit on <i>F</i> <sup>2</sup>	1.149
$\gamma$ / (°)	90	Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> =0.038 6, <i>wR</i> <sub>2</sub> =0.103 8
Volume / nm <sup>3</sup>	0.7130(3)	<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> =0.046 3, <i>wR</i> <sub>2</sub> =0.107 1
<i>Z</i>	2	Extinction coefficient	0.035(4)
Calculated density / (Mg·m <sup>-3</sup> )	1.823	Largest diff. peak and hole / (e·nm <sup>-3</sup> )	0.470×10 <sup>-3</sup> and -538

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

Atoms	Lengths / nm	Atoms	Angles / (°)	Atoms	Angles / (°)
Mn(1)-O(1)#1	0.216 5(2)	O(1)#1-Mn(1)-O(1)	92.01(13)		
Mn(1)-O(1)	0.216 5(2)	O(1)#1-Mn(1)-O(4)	86.59(9)	O(4)#1-Mn(1)-O(3)#1	87.23(10)
Mn(1)-O(4)	0.217 8(2)	O(1)-Mn(1)-O(4)	97.68(9)	O(3)-Mn(1)-O(3)#1	95.03(15)
Mn(1)-O(4)#1	0.217 8(2)	O(1)#1-Mn(1)-O(4)#1	97.68(9)	C(1)-O(1)-Mn(1)	103.55(15)
Mn(1)-O(3)	0.219 9(2)	O(1)-Mn(1)-O(4)#1	86.59(9)	Mn(1)-O(3)-H(3F)	85.99(19)
Mn(1)-O(3)#1	0.219 9(2)	O(4)-Mn(1)-O(4)#1	173.88(15)	Mn(1)-O(3)-H(3E)	132.08(18)
		O(1)#1-Mn(1)-O(3)	173.50(9)	Mn(1)-O(4)-H(4F)	127(3)
O(1)-C(1)	0.125 7(3)	O(1)-Mn(1)-O(3)	86.83(10)	Mn(1)-O(4)-H(4E)	114(4)
O(1)-C(1)	0.125 0(3)	O(4)-Mn(1)-O(3)	87.23(10)	Mn(1)-O(4)-H(4F)	109(3)
O(3)-H(3F)	0.085(5)	O(4)#1-Mn(1)-O(3)	88.64(10)	Mn(1)-O(4)-H(4E)	131(4)
O(3)-H(3E)	0.080(6)	O(1)#1-Mn(1)-O(3)#1	86.83(10)	H(3F)-O(3)-H(3E)	104(5)
O(4)-H(4F)	0.100(5)	O(1)-Mn(1)-O(3)#1	173.50(9)	H(4F)-O(4)-H(4E)	109(5)

Symmetry transformations used to generate equivalent atoms: #1: -*x*, *y*, -*z*+1/2; #2: -*x*+1, *y*, -*z*+1/2.

## 2 Results and discussion

### 2.1 Synthesis

The utilization of 2,5-dimercapto-1,3,4 thiadiazole as ‘parent’ material is an effective route for preparation of a novel multidentate ligand containing 1,3,4 thiadiazole. Our experimental process revealed that target ligand H<sub>2</sub>ADTZ was obtained in good yield under relatively mild conditions.

It's noted that under the varied molar ratio of ligand H<sub>2</sub>ADTZ and Mn<sup>2+</sup> ion from 1:1 to 1:4, or add some KSCN to the solution, the same compound Mn(ADTZ)·4H<sub>2</sub>O was only obtained. That's to say, one H<sub>2</sub>ADTZ only can coordinate to one Mn<sup>2+</sup> ion forming

a mononuclear complex. It's similar to the ligand H<sub>2</sub>ADTZ, the complex is insoluble in common organic reagents, and but it is soluble in water.

### 2.2 Crystal Structure of Mn(ADTZ)·4H<sub>2</sub>O

The molecular structure of the complex was determined by single crystal X-ray diffraction analysis. The molecule crystallize in the space group *P*2/*c*. One-dimensional chain polymer structure of Mn(ADTZ)·4H<sub>2</sub>O is shown in Fig.1.

The Mn(II) ion is in a six-coordinated geometry in which two oxygen atoms O1 and O1A come from neighboring two deprotonated ligands ADTZ<sup>2-</sup> and four oxygen atoms from four coordinated water molecules, O3 and O3A as well as O4 and O4A occupy the e-

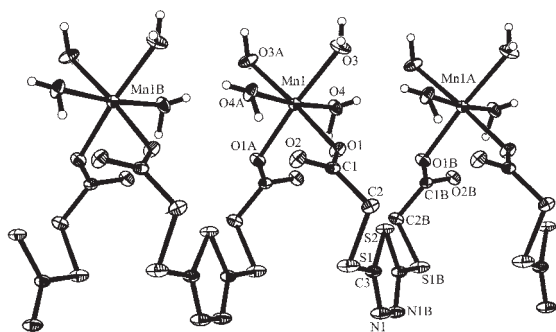


Fig.1 One-dimensional chain polymer structure of  $\text{Mn}(\text{ADTZ}) \cdot 4\text{H}_2\text{O}$

quatorial plane and the axial plane, respectively. Mn-O distances range from 0.219 9(2) to 0.216 5(2) nm. The geometry about the six-coordinate manganese atom can best be described as slightly distorted octahedron, with equatorial angles in the range  $95.03(15)^\circ \sim 86.83(10)^\circ$ , and an axial angle in the range  $97.68(9)^\circ \sim 86.59(9)^\circ$ . The Mn-O distances can be comparable to those of other Mn(II) coordination polymers, for example, Mn-O distances range in  $\text{Mn}_2(\text{TPA})_2(\text{CA})(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$  from 0.215 5(2)~0.221 4(2) nm, (TPA=tris(2-pyridylmethyl) amine, CA=dianion of chloranilic acid)<sup>[12]</sup>, and it's also similar to the Mn-O lengths of oxalate-bridged Mn(II) complex<sup>[13]</sup>. The dihedral angle between the thiadiazole rings and the planes O1-O1A-O3-O3A is  $74.9^\circ$ .

In the crystal structure of  $\text{Mn}(\text{ADTZ}) \cdot 4\text{H}_2\text{O}$ , both carboxyl groups of the ligand  $\text{H}_2\text{ADTZ}$  are completely deprotonated, thus each deprotonated  $\text{ADTZ}^{2-}$  carries two negative charges and needs to balance the two positive charges of Mn(II) ion. The unique structural feature of the title compound is the formation of one-dimensional manganese chains polymer through the bridging of dioxygen O-O units rather than halide ions, as shown in Fig.1. Only similar bridging mode was previously reported by Song J.L. and co-workers<sup>[14]</sup>. Interestingly, in the solid state structure of the complex one-dimensional manganese chains are joined together by the weak intermolecular hydrogen bonds and van der Waals interactions forming a two-dimensional supramolecule (Fig.2). As can be seen from Fig.2, there are three kinds of intramolecular hydrogen bonds and one kind of intermolecular bond. One is O4 unit of one coordination water molecule from the  $\text{Mn}(\text{ADTZ}) \cdot 4\text{H}_2\text{O}$  unit and O2 from a carboxyl of the

$\text{Mn}(\text{ADTZ}) \cdot 4\text{H}_2\text{O}$  unit [ $\text{O4} \cdots \text{O2} = 0.263$  8,  $\text{H4F} \cdots \text{O2} = 0.171$  1 nm,  $\text{O4-H4F} \cdots \text{O2} = 152.19^\circ$ ]. The other arises from the interaction of O3 unit of another coordination water molecule from the  $\text{Mn}(\text{ADTZ}) \cdot 4\text{H}_2\text{O}$  unit and O2 from a carboxyl of the  $\text{Mn}(\text{ADTZ}) \cdot 4\text{H}_2\text{O}$  unit [ $\text{O3} \cdots \text{O2} = 0.268$  7,  $\text{H3E} \cdots \text{O2} = 0.190$  4,  $\text{O3-H3E} \cdots \text{O2} = 164.38^\circ$ ]. The third originates from O4 and O3 unit between the two coordination water molecules from the  $\text{Mn}(\text{ADTZ}) \cdot 2\text{H}_2\text{O}$  unit [ $\text{O4} \cdots \text{O3} = 0.293$  7,  $\text{H4E} \cdots \text{O3} = 0.225$  6,  $\text{O4-H4E} \cdots \text{O3} = 160.18^\circ$ ]. The last one is an intermolecular hydrogen bonds between O3 unit of the coordination water molecule from the  $\text{Mn}(\text{ADTZ}) \cdot 4\text{H}_2\text{O}$  unit and N1 of neighboring  $\text{Mn}(\text{ADTZ}) \cdot 4\text{H}_2\text{O}$  unit [ $\text{O3} \cdots \text{N1} = 0.280$  3,  $\text{N1} \cdots \text{H3F} = 0.199$  7 nm,  $\text{O3-H3F} \cdots \text{N1} = 166.27^\circ$ ]. The crystal packing viewing of the complex along the *a*-axis can be seen in Fig.2.

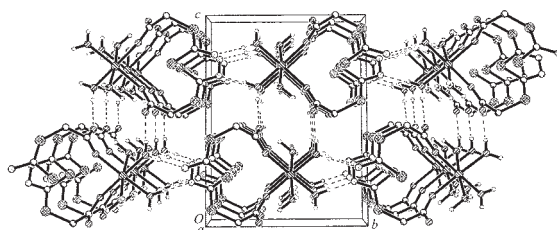


Fig.2 Crystal packing viewing of  $\text{Mn}(\text{ADTZ}) \cdot 4\text{H}_2\text{O}$  along the *a*-axis

## 2.3 Absorption spectra and electro-chemical properties

UV spectra of the complex  $\text{Mn}(\text{ADTZ}) \cdot 4\text{H}_2\text{O}$  was determined in a water solution. The complex displays one strong absorption peak in 290 nm, which may be attributed to the intraligand  $\pi-\pi^*$  transition of the free ligand, as the free ligand ADTZ also exhibits an absorption band at a similar wavelength.

The electrochemical properties of  $\text{Mn}(\text{ADTZ}) \cdot 4\text{H}_2\text{O}$  was investigated by cyclic voltammetry (CV) in water. The cyclic voltammogram of the title compound is shown in Fig.3. We examined the redox potential of the complex in water. It exhibits a quasi-reversible redox process assignable to the Mn(III)/Mn(II) redox couple and its redox potential is 0.333 V (versus Ag/AgCl reference electrode). The separation between the cathodic and anodic peak potentials,  $\Delta E_p = |E_{pa} - E_{pc}|$ , is 250 mV. The free ligand  $\text{H}_2\text{ADTZ}$  is proved not be electroactive over the range -1.2 to +1.8 V. In an effective mimic of superoxide dismutase, while a reduction potential value of a transition metal ion is below

Table 3 Hydrogen-bonds for P2/c (nm and °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠(DHA)
O(3)-H(3F)...O(2)#3	0.081(3)	0.187(4)	0.268 0(3)	174(3)
O(4)-H(4F)...O(2)#1	0.102(4)	0.170(4)	0.263 8(3)	152(3)
O(4)-H(4E)...O(3)#2	0.070(4)	0.226(4)	0.293 9(3)	163(5)
O(3)-H(3E)...N(1)#4	0.087(4)	0.200(4)	0.282 5(3)	159(4)

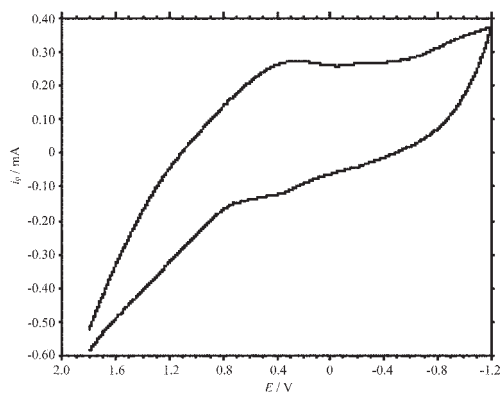


Fig.3 Cyclic voltammogram (scan rate  $0.2 \text{ V} \cdot \text{s}^{-1}$ ) of  $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$  aqueous solution of the complex at a glass carbon electrode (298 K) with Ag/AgCl as reference electrode

$0.65 \text{ V}$  ( $E^\circ(\text{O}_2/\text{O}_2^-)$ ) and above  $-0.33 \text{ V}$  ( $E^\circ(\text{O}_2/\text{O}_2^-)$ ), the catalysis can take place but toxic singlet oxygen cannot be formed<sup>[14]</sup>, for example, the hexaquo-manganous ion hasn't catalysis owing to the high standard reduction potential of the couple  $\text{Mn}^{3+}/\text{Mn}^{2+}$  ( $1.51 \text{ V}$ ). since  $E^\circ(\text{O}_2^-/\text{H}_2\text{O}_2)$  is  $0.94 \text{ V}$  at  $\text{pH}=7$ , the equilibrium of the reaction  $\text{Mn}^{2+} + \text{O}_2^- \rightleftharpoons \text{Mn}^{3+} + \text{H}_2\text{O}_2$  lies to the left. Therefore, we suppose that  $\text{Mn}(\text{ADTZ}) \cdot 4\text{H}_2\text{O}$  might exhibit a favorable catalysis. The catalysis research of the title compound is carrying forward.

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## References:

- [1] DU Chen-Xia(杜晨霞), XUE Dong-Xu(薛东旭), CHENG Xiao-Ning(程晓宁), et al. (*Chinese J. Inorg. Chem.*), **2004**, **20**(8):955~958
- [2] Fan Y T, Xue D X, Li G, et al. *J. Mol. Struct.*, **2004**, **693**:1~8
- [3] LU Hui-Jie(卢会杰), GAO Jie(高洁), DU Chen-Xia(杜晨霞), et al. (*Chinese J. Inorg. Chem.*), **2003**, **19**(2):174~178
- [4] Muaikeel Al, Nayef S, Emary Ei, et al. *European Polymer Journal*, **2003**, **39**(2):211~218
- [5] Hirotoishi S, Kazuhiko T, et al. *Catalysis Communications*, **2001**, **2**:145~150
- [6] Song J L, Dong Z C, Zeng H Y, et al. *Inorg. Chem.*, **2003**, **42**:2136~2140
- [7] (a) Masahiko M, Megumu M, et al. *Inorg. Chim. Acta*, **1999**, **290**:153~158  
(b) Alzuet G, Ferrer-Llusar S, Borrás J, et al. *Polyhedron*, **2000**, **19**:725~730
- [8] (a) Zhang H X, Kang B S, Xu A W, et al. *J. Chem. Soc. Dalton Trans.*, **2001**, **17**:2559~2566  
(b) Hou H W, Li G, Li L K, et al. *Inorg. Chem.*, **2003**, **42**:428~435
- [9] Eddaoudi M, Kim J, Wachter J B, et al. *J. Am. Chem. Soc.*, **2001**, **123**:4368~4369
- [10] NIE Guo-Cao(聂国朝). *Jingxi Huagong Zhongjianti(精细化工中间体)*, **2003**, **33**(5):32~34
- [11] Sheldrick G M. *SHELX-97 Program for the Solution and Refinement of Crystal Structure*. University of Göttingen, Germany, **1997**.
- [12] Dao D X, Chun Y D, Xiang S Y, et al. *Polyhedron*, **1998**, **17**:2647~2653
- [13] Deguenon D, Bernardinelli G, Tuchagues J P. et al. *Inorg. Chem.*, **1990**, **29**:3031~3037
- [14] Song Jun-Ling, Dong Zhen-Chao, Zeng Hui-Yi, et al. *Inorg. Chem.*, **2003**, **42**:2136~2140