



## 一维链状锰(II)三氮唑配合物的合成,结构与磁性质

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### Synthesis, Structure and Magnetic Property of a One-Dimensional Chain Manganese Compound with 1,2,4-Triazole

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**Abstract:** A novel one-dimensional chain manganese(II) compound  $[\text{Mn}(\text{trz})_2\text{Cl}][\text{phthH}]$ , ( $\text{trz}$ =1,2,4-triazole,  $\text{phthH}$ =hydrogen phthalate), **1**, was synthesized and structurally characterized. It crystallizes in monoclinic system, space group  $P2_1/c$  with  $a=1.381\ 1(11)$  nm,  $b=0.815\ 5(7)$  nm,  $c=0.735\ 4(6)$  nm,  $\beta=94.667(15)^\circ$ ,  $V=0.825\ 5(12)$  nm<sup>3</sup>. It consists of one dimensional cationic manganese(II) chain and uncoordinated hydrogen phthalate anions. The manganese(II) ions are bridged with two 1,2,4-triazoles and one chloride anion along the cationic chain, in which the weak antiferromagnetic exchange occurs between manganese(II) atoms. CCDC: 267461.

**Key words:** manganese complex; triazole; one-dimensional; magnetic property

## 0 Introduction

Recently polynuclear transition metal complexes containing of 1,2,4-triazole or its derivatives with substituents on 3,5-positions have attracted growing interest due to their interesting magnetic properties with the aim to design novel molecular magnetic materials<sup>[1]</sup>. To date, many binuclear, linear trinuclear and polymeric metal compounds with 1,2,4-triazole or its derivatives have been reported since these ligands can easily link metal ions together via the 1,2-bridging mode<sup>[1]</sup>. Some iron(II) complexes are found to be spin-cross molecular system, which has potential applications in molecular switch and molecular devices<sup>[2]</sup>. Some

one-dimensional chain iron(II) or copper(II) compounds with three bridging 1,2,4-triazoles have attracted particular interest<sup>[2-4]</sup>. Another type of one-dimensional chain compounds bridged with one triazole and two chloride atoms was reported for  $\text{CuCl}_2(\text{Htrz})$ <sup>[4]</sup>. There is no example of one-dimensional chain bridged with two triazole or one halide ligands. However this bridging moiety has been observed in a linear trinuclear cobalt(II) complex<sup>[5]</sup>. On the other hand, considerable number of manganese(II) compounds of 1,2,4-triazole or its derivatives including mononuclear<sup>[6]</sup>, binuclear<sup>[7]</sup>, trinuclear<sup>[8]</sup> and 2D-polymer<sup>[9]</sup> are known. No one-dimensional chain manganese(II) compound with 1,2,4-triazole or its derivatives is available in literature. Here

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we report the synthesis, crystal structure and magnetic property of one-dimensional chain  $[\text{Mn}(\text{trz})_2\text{Cl}][\text{phthH}]$ , ( $\text{trz}$ =1,2,4-triazole,  $\text{phthH}$ =hydrogen phthalate), **1**.

## 1 Experimental

### 1.1 Materials and instruments

All reagents are received commercially and used without further purification. Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240C analytical instrument. IR spectrum was run on a VECTOR 22 Bruker spectrophotometer with KBr pellets in the 4000~400  $\text{cm}^{-1}$  region. DC magnetic susceptibilities on powder sample of **1** were carried out with a Quantum Design MPMS-XL SQUID magnetometer in the range of 1.8~300 K. The applied magnetic field was 2 kG and the data were corrected for diamagnetism using Pascal's constants.

### 1.2 Synthesis of the title compound

To a solution of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (1.18 g, 6.0 mmol) and 1,2,4-triazole (0.42 g, 6.0 mmol) in 10 mL MeOH was added potassium hydrogen phthalate (0.61 g, 3.0 mmol) and the mixture was stirred for 2 hours to give a white precipitate. After filtration the collected solid was dried in air and then dissolved in 10 mL water.

The resulting solution was stood in the air for several days to yield the crystals of **1**. Yield 40%. Analysis found (%): C, 36.58; H, 2.64; N, 21.42. Calculated for  $\text{C}_{12}\text{H}_{11}\text{ClMnN}_6\text{O}_4$  (%): C, 36.61; H, 2.82; N, 21.35. IR: 3447m, 3128s, 2978w, 1594w, 1556vs, 1420s, 1299s, 1185w, 1043s, 792m, 731s, 696m, 638s.

### 1.3 Determination of crystal structure

Diffraction data of **1** were collected on a Bruker Apex CCD diffractometer equipped with graphite monochromatized Mo  $K\alpha$  radiation ( $\lambda=0.071\ 03\ \text{nm}$ ) at 293 K using a  $\omega/2\theta$  scan mode. A total 4278 reflections were collected in  $2\theta$  range  $5.0^\circ$  to  $52.0^\circ$ , of which 1602 were independent reflections and 1184 reflections with  $I>2\sigma(I)$  were considered as observed. An empirical absorption correction was applied to the data. The structure was solved by direct methods and refined by full-matrix least-squares calculation on  $F^2$  using SHELXTL program package<sup>[10]</sup>. All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were generated geometrically. The crystal data and the refinement parameters are listed in Table 1 and the selected bond lengths and bond angles are shown in Table 2.

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Table 1 Crystal data and structure refinement for the title complex

Empirical formula	$\text{C}_{12}\text{H}_{11}\text{ClMnN}_6\text{O}_4$	Calculated density / ( $\text{Mg} \cdot \text{m}^{-3}$ )	1.58
Formula weight	393.66	Absorption coefficient / $\text{mm}^{-1}$	0.991
Crystal system	Monoclinic	$F(000)$	396
Space group	$P2_1/c$	Limiting indices	$-16 \leq h \leq 15, -9 \leq k \leq 10, -8 \leq l \leq 8$
$a / \text{nm}$	1.381 1(11)	Reflections collected / unique	4278 / 1602 [ $R_{\text{int}}=0.044\ 6$ ]
$b / \text{nm}$	0.815 5(7)	Data / restraints / parameters	1184 / 0 / 111
$c / \text{nm}$	0.735 4(6)	Goodness-of-fit on $F^2$	1.001
$\beta / (^\circ)$	94.667(15)	Final $R$ indices [ $I>2\sigma(I)$ ]	$R_1=0.047\ 3, wR_2=0.095\ 9$
Volume / $\text{nm}^3$	0.825 5(12)	$R$ indices (all data)	$R_1=0.075\ 1, wR_2=0.101\ 4$
$Z$	2	Largest diff. peak and hole / ( $\text{e} \cdot \text{nm}^{-3}$ )	386 and -864

Table 2 Selected bond lengths (nm) and angles ( $^\circ$ )

Mn(1)-Cl(1)	0.253 5(2)	Mn(1)-Cl(1C)	0.253 5(2)	Mn(1)-N(2)	0.222 3(4)
Mn(1)-N(2C)	0.222 3(4)	Mn(1)-N(1B)	0.223 1(4)	Mn(1)-N(1D)	0.223 1(4)
Cl(1)-Mn(1)-N(2)	91.12(8)	Cl(1C)-Mn(1)-N(2C)	91.12(8)	Cl(1)-Mn(1)-N(1B)	90.64(9)
Cl(1C)-Mn(1)-N(1D)	90.64(9)	N(1D)-Mn(1)-N(2)	93.63(11)	N(1B)-Mn(1)-N(2C)	93.63(11)
Cl(1)-Mn(1)-N(2C)	88.88(8)	Cl(1C)-Mn(1)-N(2)	88.88(8)	N(1D)-Mn(1)-Cl(1C)	89.36(9)
Cl(1C)-Mn(1)-N(1B)	89.36(9)	N(1B)-Mn(1)-N(2)	86.37(11)	N(1D)-Mn(1)-N(2C)	86.37(11)
N(2)-Mn(1)-N(2C)	180.00	N(1B)-Mn(1)-N(1D)	180.00	Cl(1)-Mn(1)-Cl(1C)	180.00

Symmetry codes: B:  $-x, y, 3/2-z$ ; C:  $-x, -y, 1-z$ ; D:  $x, -y, -1/2+z$ .

## 2 Results and discussion

### 2.1 Crystal structure of **1**

**1** consists of the one-dimensional cationic chain  $[\text{Mn}(\text{trz})_2\text{Cl}]^+$  and uncoordinated hydrogen phthalate anion. The structure of the fragment of the one-dimensional cationic manganese(II) chain is illustrated in Fig.1, where two 1,2,4-triazole in 1,2-bridging mode and one chloride anion join the manganese(II) ions along the polymeric chain. There is a symmetry center located on the manganese atom. The distorted octahedral coordination around the manganese(II) ion is realized by four nitrogen atoms from the 1,2,4-triazole and two bridging chloride anions. The corresponding Mn-N bonds (0.222 3(4) nm, 0.223 1(4) nm) are in good agreement with the reported Mn-N(1,2,4-triazole) bond distances<sup>[7-9]</sup>. Mn-Cl bond distances of 0.253 5(2) nm are comparable to those Mn(II)-Cl (bridging) bonds found for polynuclear manganese(II)-chloride complexes, for example,  $[\text{Mn}_4(\mu\text{-Cl})_6(\text{THF})_{12}]^{2+}$  (0.247 5(2) ~ 0.257 9(3) nm)<sup>[11]</sup>. In order to verify the assignment of the oxidation state of manganese ion, bond valence sum (BVS) calculations<sup>[12]</sup> were performed for manganese ion. A BVS value of 2.108 was thus obtained, which suggested that the oxidation state of manganese ion is essentially +2. Therefore the anion of **1** is hydrogen phthalate.

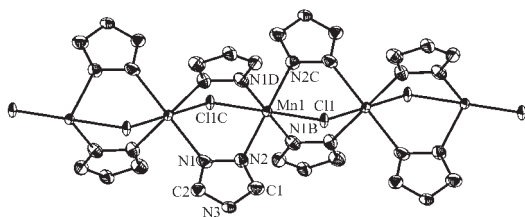


Fig.1 Structure of the one-dimensional manganese chain of **1**

The crystal packing of **1** is shown in Fig.2. There are hydrogen bonding between the N3 of 1,2,4-triazole

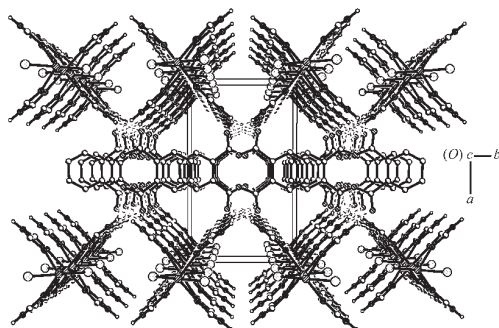


Fig.2 Perspective view of the crystal structure of **1** along the *c*-axis

and O1A atom of the  $\text{phthH}^-$  anion with N3-O1A (A:  $x, 1-y, -1/2+z$ ) distance of 0.275 5(5) nm, which links the  $[\text{Mn}(\text{trz})_2\text{Cl}]^+$  chains into the three-dimensional network.

### 2.2 Magnetic property

The magnetic susceptibility data for polycrystalline samples of **1** is displayed in Fig.3 as plots of  $\chi_m$  and  $\chi_m T$  versus temperature (*T*). The room temperature value of  $\chi_m T$  is  $3.93 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$  for **1**, which decreases upon lowering the temperature to reach a value of  $0.077 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$  at 1.8 K. A weak antiferromagnetic interaction between manganese(II) ions is apparent in **1**. The data were corrected for diamagnetism using Pascal's constant  $1.75 \times 10^{-4} \text{ cm}^3 \cdot \text{mol}^{-1}$  and then analyzed via the following equation<sup>[13]</sup> assuming isotropic Heisenberg pairwise interactions between manganese(II) ions in a linear chain.

$$\chi_m T = N\beta^2 g^2 S(S+1) / 3kT[(1+u)/(1-u)]$$

$$u = \coth[2JS(S+1)/kT] - kT[2JS(S+1)]^{-1}$$

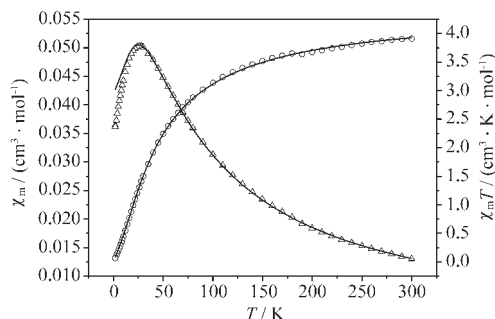


Fig.3 Plots of  $\chi_m$  ( $\Delta$ ) and  $\chi_m T$  ( $\circ$ ) vs temperature for the title complex, where the solid line represents the theoretical curve with the best parameters

The least-square fits gave  $g=2.01$ ,  $J=-2.09 \text{ cm}^{-1}$ ,  $R=4.2 \times 10^{-5}$  ( $R=\sum |(\chi_m T)_{\text{exp}} - (\chi_m T)_{\text{calc}}|^2 / \sum (\chi_m T)_{\text{exp}}^2$ ), which shows that only weak antiferromagnetic interaction occurs between manganese(II) ions along the one-dimensional chain. This  $J$  value is comparable with that observed in triply-bridged trinuclear manganese(II) compound  $[\text{Mn}_3(\text{Ettrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$  ( $J=-0.6 \text{ cm}^{-1}$ )<sup>[8b]</sup> and other one-dimensional manganese(II) chain compounds ( $-0.25 \sim -10.0 \text{ cm}^{-1}$ )<sup>[14]</sup>.

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