

## 含三唑基希夫碱的锰配合物的合成及结构

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**摘要:** 合成了 4-(4-氯苯基亚甲基)亚胺-1,2,4-三唑希夫碱配体(L), 以及希夫碱的配合物 $[\text{Mn}(\text{SO}_4)(\text{H}_2\text{O})_2\text{L}]_n$ , 并对配合物进行了结构表征。该配合物是 1 个用硫酸根桥连而成的一维链状配位聚合物, 相邻的链通过水分子和硫酸根的氢键相互作用形成了二维超分子结构。利用 DSC 技术测试了配合物和固体推进剂主要组分(HMX, NC, RDX)的二元混合体系的热分解行为。本文也对配合物做了元素, 红外光谱分析。

**关键词:** 希夫碱; 结构分析; 锰配合物; 超分子结构

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## Syntheses and Structure Analyses of One Triazole Schiff Base Manganic Complex

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**Abstract:** A Schiff base ligand 4-(4-*H*-1,2,4-triazol-4-yl)-4-*Cl*-phenylmethanimine (L) was prepared. And complex  $[\text{Mn}(\text{SO}_4)(\text{H}_2\text{O})_2\text{L}]_n$  with Schiff base (L) has been synthesized and structurally characterized. The complex exhibits a one-dimensional polymeric structure with sulfate bridges, and two-dimensional supramolecular network is formed through hydrogen bonding interactions between water molecules and sulfate anions. The complex and binary mixture of complex and propellant (HMX, NC, RDX) were characterized by DSC technology. In addition, elemental analysis, IR analysis are presented. CCDC: 733542.

**Key words:** Schiff base; structural analysis; manganic complex; supramolecular structure

## 0 Introduction

1,2,4-Triazoles are widely used ligands in coordination chemistry. They can be coordinated to a metal ion in different modes, bidentate-bridging or monodentate, depending on the position and the nature of the substituent at the triazole ring<sup>[1]</sup>. Both have been observed and, moreover, sometimes in the same coordination compound. If the N4 positions of the triazole ring are substituted they can bridge transition metal ions through an N1,N2-coordination mode, this

mode leads to polynuclear complexes that often demonstrate magnetic exchange interactions<sup>[2-4]</sup>. Especially, some complexes containing 4-substituted-1,2,4-triazole have spin-crossover properties, which could be used in molecular-based memory devices, displays and optical switches<sup>[3-9]</sup>. Depending on different synthesis conditions, triazole substituents, and anion used, a variety of compounds including triply triazole-bridged, doubly triazole-bridged and a single 1,2,4-triazole bridge have been reported, and the metal ions are usually bridged additionally by small anions such as

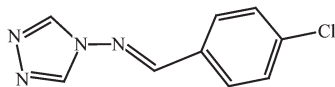
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$\text{Cl}^-$  [10],  $\text{F}^-$  [11],  $\text{N}_3^-$  [12-13],  $\text{SO}_4^{2-}$  [14],  $\text{OH}^-$  [15-19], or  $\text{NCS}^-$  [20]. Because ligands of negatively charged are needed to ease the effect of the repulsion of the two metal ions [21-22]. To date, only limited number of complexes with 4-substituted-1,2,4-triazole have been described, and only a few crystal structures are known.

We have prepared the compound of 4-salicylideneamino-1,2,4-triazole ( $\text{L}=\text{satz}$ ), and reported the synthesis, crystal structure and thermal stability of its two complexes:  $[\text{Zn}(\text{L})_2(\text{SCN})_2]$  and  $[\text{Co}_2(\text{L})_5(\text{SCN})_4] \cdot \text{H}_2\text{O}$  [23]. Herein, we prepared the compound of 4-(4-*H*-1,2,4-triazol-4-yl)-4-*Cl*-phenylmethanimine ( $\text{L}=\text{Clphtr}$ , Scheme 1), and reported the synthesis and crystal structure of its one coordination polymer:  $[\text{Mn}(\text{SO}_4)(\text{H}_2\text{O})_2\text{L}]_n$ .



Scheme 1 4-(4-*H*-1,2,4-triazol-4-yl)-4-*Cl*-phenylmethanimine ( $\text{L}$ )

## 1 Experimental

### 1.1 Materials and instruments

All reagents and solvents were commercially available and were used without further purification. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Infrared (IR) spectra were recorded on a Bruker FTIR instrument as KBr pellets (4 000~400  $\text{cm}^{-1}$ ). The DSC analysis were conducted on a P. E. 2100 Company thermal analyzer.

### 1.2 Preparation of title compound

#### 1.2.1 Synthesis of Clphtr ( $\text{L}$ )

4-Chlorobenzaldehyde (0.444 6 g, 3 mmol) was added into a methanol solution (50 mL) of 4-amino-4-*H*-1,2,4-triazole (0.254 7 g, 3 mmol), and a small quantity of acetic acid also were added as catalyzer, the mixture was refluxed for 6 h. Upon standing overnight

at the room temperature, the solution deposited white crystals that were isolated by filtration, washed with a small amount of ethanol and ether, and dried under vacuum and white acerosc crystals were obtained from cooling solution, yield 58% based on 4-amino-4-*H*-1,2,4-triazole, m.p. 196  $^{\circ}\text{C}$ . IR data (KBr,  $\text{cm}^{-1}$ ): ( $\nu_{\text{C}=\text{N}}$ ) 1 625(s), 1 606(m), ( $\nu_{\text{C}-\text{C}}$ ) 1 087(s), ( $\delta_{\text{C}-\text{H}}$ ) 880(s), 801(m). Anal. Calcd. for  $\text{C}_9\text{H}_7\text{N}_4\text{Cl}$  (%): C, 52.31; H, 3.41; N, 27.11. Found(%): C, 52.40; H, 3.48; N, 27.05.

#### 1.2.2 Synthesis of $[\text{Mn}(\text{SO}_4)(\text{H}_2\text{O})_2\text{L}]_n$

An aqueous solution (4 mL) of  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (0.034 4 g, 0.2 mmol) was added into a mixed solution (14 mL, ethanol and DMF volume ratio is 5/2) of Clphtr (0.055 9 g, 0.25 mmol) with stirring, and the mixture solution was stirred at room temperature for 1 h and filtered. Colorless crystal was obtained from the filtrate at room temperature for six weeks, in a yield 29% based on Mn. IR data (KBr,  $\text{cm}^{-1}$ ): 3 408 ( $\nu_{\text{O}-\text{H}}$ , m), 3 252 ( $\nu_{\text{O}-\text{H}}$ , m), 1 646 ( $\nu_{\text{C}=\text{N}}$ , w), 1 597 ( $\nu_{\text{C}=\text{N}}$ , m), 1 203 ( $\nu_{\text{s}-\text{O}}$ , w), 1 122 ( $\nu_{\text{s}-\text{C}}$ , s). Anal. calcd for  $\text{C}_9\text{H}_{11}\text{ClN}_4\text{O}_6\text{SMn}$ (%): C 27.46, H 2.82, N 14.23; Found(%): C 27.40, H 2.84, N 14.27.

### 1.3 X-ray structure determination

One colorless block-like crystal were selected. All single crystal X-ray experiments were performed on a Bruker Smart Apex CCD diffractometer equipped with graphite monochromatized Mo  $K\alpha$  radiation ( $\lambda=0.071\,073\,\text{nm}$ ) using  $\varphi$ - $\omega$  scan mode. The single-crystal structures of complexes were both solved by direct methods and refined with full-matrix least-squares refinements based on  $F^2$  using SHELXS 97 and SHELXL 97 [24-25]. All non-hydrogen atoms were located using subsequent Fourier-difference methods. In all cases hydrogen atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms. Crystallographic data are summarized in Table 1, Table 2 and Table 3.

CCDC: 733542.

Table 1 Crystallographic data for the title complex

Formula	$\text{C}_9\text{H}_{11}\text{ClN}_4\text{O}_6\text{SMn}$	$V / \text{nm}^3$	1.413 4(6)
Formula weight	393.66	$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.85
$T / \text{K}$	273(2)	$Z$	4
Crystal system	Monoclinic	Crystal size / mm	0.31×0.22×0.13
Space group	$P2_1/c$	Measured data	6 756

Continued Table 1

$a / \text{nm}$	1.953 3(5)	Unique data	2 518
$b / \text{nm}$	0.655 75(16)	$R_{\text{int}}$	0.052 1
$c / \text{nm}$	1.152 1(3)	$\theta / (^{\circ})$	2.18 to 25.09
$\alpha / (^{\circ})$	90	$F(000)$	796
$\beta / (^{\circ})$	106.707	Absorption coefficient / $\text{mm}^{-1}$	1.306
$\gamma / (^{\circ})$	90	Final $R$ indices ( $I > 2\sigma(I)$ )	$R_1=0.143\ 9, wR_2=0.317\ 5$

Table 2 Selected bond lengths (nm) and bond angles ( $^{\circ}$ ) for the title complex

Mn(1)-O(1)	0.218 2(5)	Mn(1)-O(2W)	0.225 7(6)	N(3)-C(1)	0.136 3(11)
Mn(1)-O(2)	0.215 1(5)	Mn(1)-N(1)	0.224 3(7)	N(3)-C(2)	0.134 7(11)
Mn(1)-O(3)	0.218 4(5)	N(1)-C(1)	0.129 8(12)	N(4)-C(3)	0.126 9(11)
Mn(1)-O(1W)	0.222 2(6)	N(2)-C(2)	0.130 5(11)		
O(1W)-Mn(1)-N(1)	103.5(2)	O(1)-Mn(1)-O(2)	170.6(2)	O(2)-Mn(1)-N(1)	92.7(2)
O(1W)-Mn(1)-O(1)	86.2(2)	O(1)-Mn(1)-O(3)	87.3(2)	O(2)-Mn(1)-O(2W)	86.4(2)
O(1W)-Mn(1)-O(2)	87.6(2)	O(1)-Mn(1)-N(1)	81.8(2)	N(1)-Mn(1)-O(2W)	83.3(2)
O(1W)-Mn(1)-O(3)	87.2(2)	O(1)-Mn(1)-O(2W)	100.5(2)	C(3)-N(4)-N(3)	116.5(7)
O(1W)-Mn(1)-O(2W)	171.1(2)	O(2)-Mn(1)-O(3)	99.6(2)	N(4)-C(3)-C(4)	120.6(7)

Table 3 Hydrogen bonding interactions for the title complex

D-H $\cdots$ A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{D-H}\cdots\text{A} / (^{\circ})$
O(1W)-H(1WA) $\cdots$ O(4)a	0.085	0.190	0.274 6(8)	179.8
O(1W)-H(1WB) $\cdots$ O(2W)b	0.085	0.206	0.290 8(8)	179.6
O(2W)-H(2WB) $\cdots$ O(4)	0.085	0.197	0.273 2(7)	149.0
O(2W)-H(2WA) $\cdots$ O(4)c	0.085	0.185	0.270 0(8)	179.9

Symmetry codes: a:  $-x+1, y-1/2, -z+3/2$ ; b:  $x, -y+3/2, z+1/2$ ; c:  $-x+1, -y+1, -z+1$ .

#### 1.4 Conditions of the DSC analysis

The DSC analysis were conducted in static air atmosphere, the heating rate of DSC was  $10.0\ ^{\circ}\text{C} \cdot \text{min}^{-1}$ . Sample preparation was by mechanical mixing of the complex and three main components of high-energy propellant (HMX, RDX and NC), and mass ratio of

complex with three main components of high-energy propellant were respectively 1/3. Weight of the sample was about 1~2 mg. The  $\alpha\text{-Al}_2\text{O}_3$  was used as reference material in the DSC measurements. Thermodynamic data are summarized in Table 4.

Table 4 Data of determined by DSC

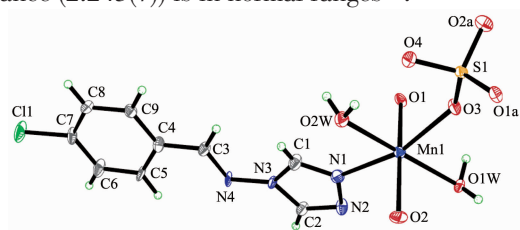
System	$T_{\text{onset}} / ^{\circ}\text{C}$	$T_{\text{p}} / ^{\circ}\text{C}$	$\Delta T_{\text{p}} / ^{\circ}\text{C}$	$\Delta H / (\text{J} \cdot \text{g}^{-1})$	$\Delta H' / (\text{J} \cdot \text{g}^{-1})$
Complex	316.79	468.04	—	352.1	—
HMX	282.96	287.46	—	-1 247	—
HMX-complex	274.12	284.40	-3.06	-977.3	269.7
NC	188.34	212.45	—	-1 517	—
NC-complex	172.77	212.45	0.00	-1 314	203
RDX	210.35	241.08	—	-364.9	—
RDX-complex	217.36	236.75	-4.33	-259.4	105.5

$T_{\text{onset}}$ : Temperature corresponding to the intersection of the baseline and the tangent of the maximum decomposition rate;  $T_{\text{p}}$ : Maximum peak temperature of the exothermic first-stage decomposition reaction;  $\Delta H$ : Incremental enthalpy of thermal decomposition, the exothermic is negative;  $\Delta T_{\text{p}}=T_{\text{p}}(\text{mix})-T_{\text{p}}(\text{propellant})$ ;  $\Delta H'=\Delta H(\text{mix})-\Delta H(\text{propellant})$ .

## 2 Results and discussion

### 2.1 Crystal structure of $[\text{Mn}(\text{SO}_4)(\text{H}_2\text{O})_2\text{L}]_n$

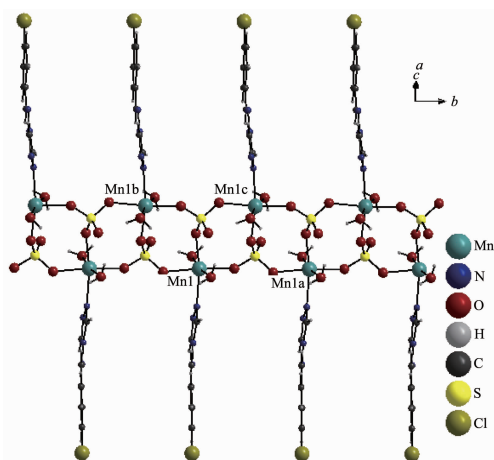
The complex  $[\text{Mn}(\text{SO}_4)(\text{H}_2\text{O})_2\text{L}]_n$  is one-dimensional polymeric structure. As shown in Fig.1, the  $[\text{Mn}(\text{SO}_4)(\text{H}_2\text{O})_2\text{L}]_n$  complex exhibits one manganese coordination geometry. The coordination geometry of the manganese ion is six-coordinate distorted octahedron, defined by three oxygen atoms from three different sulfate anions, one nitrogen atom from one Schiff base ligand and by two oxygen atoms from water molecules, which occupy the axial positions of a distorted octahedral coordination geometry. The bond angles around the metal atoms are not very close to  $90^\circ$  ( $81.8(2)^\circ$  to  $100.5(2)^\circ$ ). So the manganese site exhibits a distorted octahedron coordination. 4-(4-*H*-1,2,4-triazol-4-yl)-4-*Cl*-phenylmethanimine (L = Clphtr) act as monodentate triazole-N donor ligand, the Mn-N distance ( $2.243(7)$ ) is in normal ranges<sup>[26]</sup>.



Symmetry code: a:  $1-x, 1/2+y, 3/2-z$

Fig.1 Coordination environment of Mn(II) in the title complex

As shown in Fig.2,  $[\text{Mn}(\text{SO}_4)(\text{H}_2\text{O})_2\text{L}]$  complex form a chain structure linked through bridging sulfate

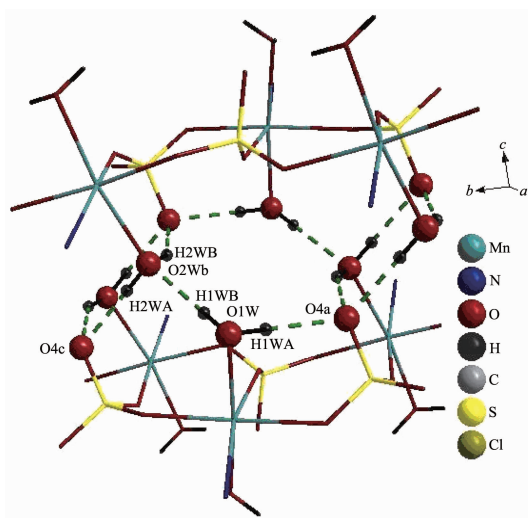


Symmetry codes: a:  $x, 1+y, z$ ; b:  $1-x, -0.5+y, 1.5-z$ ; c:  $1-x, 0.5+y, 1.5-z$

Fig.2 A one-dimensional chain of  $[\text{Mn}(\text{SO}_4)(\text{H}_2\text{O})_2\text{L}]_n$  chain

groups, running parallel to the *b* axis. Each sulfate group adopts a  $\mu_3$  coordination mode, using three oxygen donors and leaving a single {S-O} group on each sulfate site.

There are significant hydrogen bonds, shown in Fig.3. The one-dimensional chains are linked as two-dimensional layer via hydrogen bonding interactions of coordinated water molecules and sulfate anions. The water molecules (O1W) act as donor for  $\text{SO}_4^{2-}$  ions and water molecules (O2W), and forms annular  $R_6^4$  (12) type<sup>[27-29]</sup>. The water molecules (O2W) act as donor for  $\text{SO}_4^{2-}$  ions and forms annular  $R_4^2$  (8) type. The annular  $R_6^4$  (12) type are linked as one-dimensional chain via annular  $R_4^2$  (8) type, thus leading to the formation of  $[(\text{H}_2\text{O})_4(\text{SO}_4^{2-})_2]$  core.



Symmetry codes: a:  $-x+1, y-1/2, -z+3/2$ ; b:  $x, -y+3/2, z+1/2$ ; c:  $-x+1, -y+1, -z+1$

Fig.3 Perspective view of the self-assembled two-dimensional supramolecular structure of the complex

### 2.2 Infrared spectrum analysis

In the IR spectra, the peaks were observed between  $3\,408$  and  $3\,252\text{ cm}^{-1}$ , which are related to the stretching vibrations str (O-H) of the  $\text{H}_2\text{O}$ . The strong band appearing between  $1\,646\text{ cm}^{-1}$  is assignable to str (C=N) of the triazole ring. Compared with the str (C=N) peak of the triazole ring, the C=N stretching frequencies in complex are generally shifted to higher frequencies, which is evidenced as the coordination of the metal with triazole N. The IR spectra of metal

complexes show typical bands of Schiff base with strong peaks assigned to the str (C=N) in the 1 600~1 610  $\text{cm}^{-1}$  region<sup>[30]</sup>, which are not shifted in the complexes compared with the corresponding free ligand. It is evidenced that the nitrogen atom in the group C=N dose not coordinate to the metal ion, which is consistent with the structural analysis.

### 2.3 DSC analysis

Under the experimental conditions the heat flow rate of sample equal Enthalpy variable rate of sample. In Fig.4, 5, 6, the left vertical axes respectively express

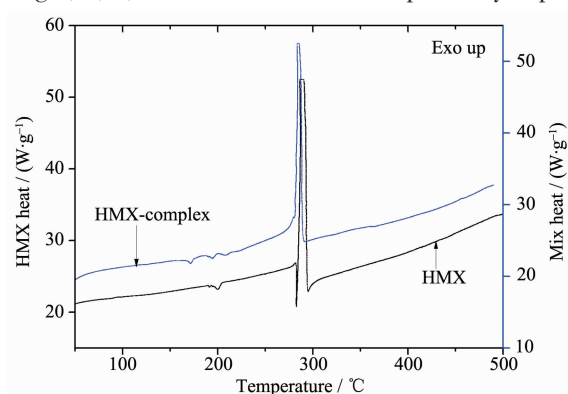


Fig.4 DSC curve of HMX and binary mixture

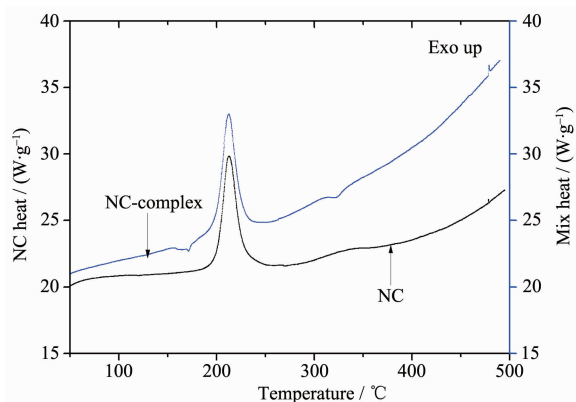


Fig.5 DSC curve of NC and binary mixture

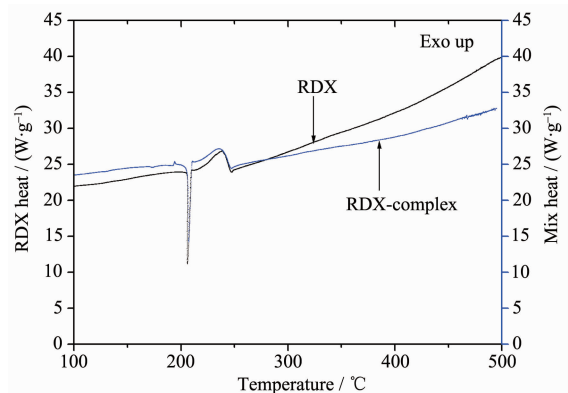


Fig.6 DSC curve of RDX and binary mixture

the heat flow rate of HMX, NC and RDX, the right vertical axes respectively express the heat flow rate of binary mixture, and unit is  $\text{W} \cdot \text{g}^{-1}$ . From Fig. 4, 5, 6 and Table 4, we can get the following information:

(1) The thermal decomposition temperature of HMX and RDX was reduced through adding complex, but decrease of temperature was a minor extent. The thermal decomposition temperature of binary mixture and NC almost the same.

(2) The generated energy of binary mixtures thermal decomposition were lower than generated energy of HMX, NC and RDX alone thermal decomposition. First, this was mainly due to strong hydrogen bonds interaction; second, the ligand was a triazole Schiff base, and its nitrogen content was also significantly reduced relative to the triazole, therefore contribute little in terms of energy.

### 3 Conclusions

In summary, we successfully synthesized one novel complex of Schiff base  $[\text{Mn}(\text{SO}_4)(\text{H}_2\text{O})_2\text{L}]_n$ . The compound is a neutral one-dimensional polymeric structure, which contain monodentate L ligand and  $\mu_3$  coordination mode  $\text{SO}_4^{2-}$ . The hydrogen-bonding interactions among water molecules and sulfate anions play a key role for the formation and stability of complex. A one-dimensional chain of alternating annular  $R_6^4$  (12) and  $R_4^2$  (8) type is assembled by the water molecules and sulfate anions. Compared characteristic parameters of thermal decomposition of mixed system and those of the propellant components alone, and found the thermal decomposition temperatures of mixed system were decreased, but the enthalpy variable indicated that the complex may be not used as energetic catalyst because of low nitrogen content.

### References:

- [1] Haasnoot J G. *Coord. Chem. Rev.*, **2000**,**200**:131-185
- [2] Asaji T, Sakai H, Nakamura D. *Inorg. Chem.*, **1983**,**22**:202-207
- [3] Ferrer S, Haasnoot J G, Reedijk J, et al. *Inorg. Chem.*, **2000**, **39**:1859-1867
- [4] Shakirova O G, Virovets A V, Naumov D Y, et al. *Inorg.*

- Chem. Commun.*, **2002**, *5*:690-693
- [5] Koningsbruggen P J, Garcia Y, Codjovi E, et al. *J. Mater. Chem.*, **1997**, *7*:2069-2075
- [6] Garcia Y, van Koningsbruggen P J, Lapouyade R, et al. *Chem. Mater.*, **1998**, *10*:2426-2433
- [7] Garcia Y, van Koningsbruggen P J, Codjovi E, et al. *J. Mater. Chem.*, **1997**, *7*:857-858
- [8] Kahn O, Martinez C J. *Science*, **1998**, *279*:44-48
- [9] Asaji T, Sakai H, Nakamura D. *Inorg. Chem.*, **1983**, *22*(2):202-206
- [10] Elena A, Sacramento F, Joaquín B, et al. *Eur. J. Inorg. Chem.*, **2006**, *2006*(24):5115-5125
- [11] Liu B, Guo G C, Huang J S. *J. Solid State Chem.*, **2006**, *179*(10): 3136-3144
- [12] Liu J C, Fu D G, Zhuang J Z, et al. *J. Chem. Soc., Dalton Trans.*, **1999**(14):2337-2342
- [13] Lysenko A B, Govor E V, Domasevitch K V. *Inorg. Chim. Acta*, **2007**, *360*:55-60
- [14] van Koningsbruggen P J, Gatteschi D, de Graaff R A G, et al. *Inorg. Chem.*, **1995**, *34*:5175-5182
- [15] Virovets A V, Podberezskaya N V, Lavrenova L G. *Zh. Strukt. Khim.*, **1997**, *38*:532-538
- [16] Ferrer S, Aznar E, Lloret F, et al. *Inorg. Chem.*, **2007**, *46*:372-374
- [17] Lysenko A B, Govor E V, Krautscheid H, et al. *Dalton Trans.*, **2006**:3772-3776
- [18] Zhou J H, Cheng R M, Song Y, et al. *Inorg. Chem.*, **2005**, *44*:8011-8022
- [19] Drabent K, Ciunik Z, Ozarowski A. *Inorg. Chem.*, **2008**, *47*:3358-3365
- [20] van Albada G A, de Graaff R A G, Haasnoot J G, et al. *Inorg. Chem.*, **1984**, *23*:1404-1408
- [21] Vos G, de Graaff R A G, Haasnoot J G, et al. *Inorg. Chem.*, **1984**, *23*:2905-2910
- [22] Antolini L, Fabretti A C, Gatteschi D, et al. *Inorg. Chem.*, **1991**, *30*:4858-4860
- [23] ZHANG Yin-Li (张引莉), CHEN San-Ping (陈三平), FAN Gang (范广), et al. *Chin. J. Chem. (Zhongguo Huaxue)*, **2009**, *27*:1697-1702
- [24] Sheldrick G M. *SHELXS-97, Program for X-ray Crystal Structure Determination*, Göttingen University, Germany, **1997**.
- [25] Sheldrick G M. *SHELXL-97, Program for X-ray Crystal Structure Refinement*, Göttingen University, Germany, **1997**.
- [26] Liu B, Xu L, Guo G C, et al. *J. Mol. Struct.*, **2006**, *825*:79-86
- [27] Etter M C. *Acc. Chem. Res.*, **1990**, *23*:120-126
- [28] Rittner M C. *J. Phys. Chem.*, **1991**, *95*:4601-4610
- [29] Bernstein J, Davis R E, Shimoni L, et al. *Angew. Chem. Int. Ed. Eng.*, **1995**, *34*:1555-1573
- [30] CHE Tu-Lin (车兔林), GAO Quan-Chang (高全昌), ZHAO Jian-She (赵建社), et al. *Chin. J. Chem. (Zhongguo Huaxue)*, **2008**, *26*(6):1079-1084