

## 配位聚合物 $\{[\text{Zn}(\text{TSC})(\text{MAL})]\cdot\text{H}_2\text{O}\}_n$ 的制备及结构表征

李胜利<sup>1</sup> 吴杰颖<sup>\*,1</sup> 田玉鹏<sup>1,2</sup> Fun Hoong Kun<sup>3</sup>

(<sup>1</sup> 安徽大学化学化工学院, 合肥 230039)

(<sup>2</sup> 南京大学配位化学国家重点实验室, 南京 210093)

(<sup>3</sup>X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia)

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## Preparation and Structure Characterization of Coordination Polymer: $\{[\text{Zn}(\text{TSC})(\text{MAL})]\cdot\text{H}_2\text{O}\}_n$

LI Sheng-Li<sup>1</sup> WU Jie-Ying<sup>\*,1</sup> TIAN Yu-Peng<sup>1,2</sup> FUN Hoong-Kun<sup>3</sup>

(<sup>1</sup>Department of Chemistry, Anhui University, Hefei 230039)

(<sup>2</sup>State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093)

(<sup>3</sup>X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia)

**Abstract:** The novel  $\text{Zn}^{\text{II}}$  complex,  $\{[\text{Zn}(\text{TSC})(\text{MAL})]\cdot\text{H}_2\text{O}\}_n$  (**1**), where TSC is thiosemicarbazide and MAL is malonate radicle), was synthesized by self-assembling from the reaction of stoichiometric zinc chloride, thiosemicarbazide and malonic acid in solution at pH 4.5~5.0. The structural and physicochemical properties were characterized by X-ray diffraction, infrared spectroscopy, electronic spectra and thermal analysis. The crystal data for the title coordination polymer: Monoclinic,  $P2_1/c$ ,  $\beta=107.808(1)^\circ$ ,  $a=0.93759(1)$  nm,  $b=1.11083(1)$  nm,  $c=0.92100(2)$  nm,  $Z=2$ ,  $\mu=2.919\text{ mm}^{-1}$ ,  $R_1=0.0390$ ,  $wR_2=0.0994$ . The structure feature is that the bridging dicarboxylates effectively link the zinc centers to form polymeric chain in a zig-zag way, which is stabilized by N-H $\cdots$ O, N-H $\cdots$ S and O-H $\cdots$ O hydrogen bonds. CCDC: 231861.

**Key words:** self-assembly; coordination polymer; supramolecular; crystal structure

## 0 Introduction

In the past years, the assembly of coordination polymers on the basis of simply adding building units and connecting them become achievable due to the development of crystallography and synthetic chemistry<sup>[1,2]</sup>. Some complexes are of interest not only for

their unusual structures and the simple synthetic methods used to prepare them, but also because they allow the preparation of high-nuclearity complexes in which several potentially interesting metal centres are linked in a well defined spatial array. As the most efficient means for construction of highly organized structure and rational design of functional materials,

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\*通讯联系人. E-mail: jywu1957@163.com

第一作者: 李胜利, 男, 37 岁, 博士, 副教授; 研究方向: 配位化学。

transition metal directed self-assembly has emerged as a new and major motif in supramolecular architecture and received considerable attention from researchers in areas ranging from chemistry to solid state physics and biology<sup>[3,4]</sup>.

Meantime, crystal engineering based on the use of either coordinative bonds or weaker intermolecular hydrogen bonds has attracted much interest. The latter interaction can influence the metal co-ordination geometry and the incorporation of metal ions into hydrogen-bonded extended arrays primarily due to its relative strength and directionality. The flexibility and dynamic character of the hydrogen bond are often regarded as the key factors in the structural adjustment of supramolecules and as part of the design strategy for the development of new functional materials<sup>[5,6]</sup>.

Among the different NS donors, thiosemicarbazide and its derivative metal complexes have been studied extensively because of the large number of potentially useful biological properties, especially the antitumor activity<sup>[7]</sup>. Thiosemicarbazides and dicarboxylates serve as two examples of important ligands with bidentate coordination mode. As part of our studies on investigating the effective synthesis and the property of supramolecules containing thiosemicarbazides and dicarboxylates, we report herein the synthesis and crystal structure of a novel coordination polymer,  $\{[\text{Zn}(\text{TSC})(\text{MAL})]\cdot\text{H}_2\text{O}\}_n$  **1**.

## 1 Experimental

### 1.1 Materials and methods

All the starting chemicals were analytical reagent grade and used as purchased (Purity  $\geq 98.0\%$ ). Elemental analyses were performed with a Perkin-Elmer 240 instrument. IR spectra were recorded with a Nicolet FTIR 170SX instrument (KBr discs) in the 4 000~400  $\text{cm}^{-1}$  region. The far-IR spectra (500~100  $\text{cm}^{-1}$ ) were recorded in Nujol mulls between polyethylene sheets. UV-Vis spectra were recorded with an UV-265 spectrophotometer. TGA analyses were recorded with a Perkin-Elmer Pris-1 DMDA-V1 analyzer in an atmosphere of nitrogen at a heating rate of 5  $^{\circ}\text{C}\cdot\text{min}^{-1}$ .

### 1.2 Synthesis of the $\{[\text{Zn}(\text{TSC})(\text{MAL})]\cdot\text{H}_2\text{O}\}_n$

The title compound was prepared by the synthetic method of self-assembly. Aqueous solutions of zinc chloride (0.300 g, 2.20 mmol), thiosemicarbazide (0.200 g, 2.20 mmol), and malonic acid (0.229 g, 2.20 mmol) were mixed together at room temperature with stirring and the solution was controlled at pH 4.5~5.0. After 15 minutes, the mixture was filtered. The resulting filtrate was kept standing and evaporated slowly in atmosphere. Several days later, the colorless and transparent square shaped single crystals suitable for X-ray analysis were obtained. Yield 0.46 g (75%). Anal. Calc. for  $\{[\text{Zn}(\text{TSC})(\text{MAL})]\cdot\text{H}_2\text{O}\}_n$  (%): C, 17.36; H, 3.25; N, 15.18; Found(%): C, 17.31; H, 3.27; N, 15.39. IR ( $\text{cm}^{-1}$ ): 3 513.7m, 3 288m, 3 007.8m, 1 637.9 ms, 1 613.0m, 1 560.3s, 1 450.9m, 1 381.9m, 1 347.0ms, 1 273.1w, 1 222.6w, 1 169.3w, 1 075.9m, 968.5w, 937.2 w, 730.2m, 699.2m, 455.75m and 338.05m.

### 1.3 Electronic spectra

Linear absorption spectrum of **1** in DMF (dimethyl formamide) was determined with 1 cm path and a concentration of  $1 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$ . The electronic spectrum of the complex shows distinctly a strong and symmetrical absorption band at about 275.2 nm, which may be attributed to an intraligand  $\pi \rightarrow \pi^*$  transition located on the bidentate dicarboxylate and thiosemicarbazide ligands.

### 1.4 Crystal structure determination

High optical quality crystal suitable for X-ray diffraction analysis was grown from the reaction mother solution (RMS) by solvent-evaporation method and then separated and dried. A single crystal of **1** with dimensions of 0.46 mm  $\times$  0.34 mm  $\times$  0.24 mm was selected for the experiment. Data collection ( $2.28^{\circ} < \theta < 25.00^{\circ}$ ) was performed using a Siemens SMART CCD area detector diffractometer with Mo  $K\alpha$  radiation ( $\lambda = 0.071\ 073 \text{ nm}$ ) with an  $\omega$ -scan mode. The structure was solved with direct method and refined using full-matrix least-squares method, giving for **1** a final  $R_1$  value of 0.039 0 and  $wR_2$  of 0.099 4 for 129 parameters and 1 512 unique reflections with  $I \geq 2\sigma(I)$ . The program SHELXTL<sup>[8]</sup> (Sheldrick, 1997) was used in the procedure.

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## 2 Results and discussion

### 2.1 Synthesis

In our experiments, compound **1** was prepared by mixing three starting materials (zinc chloride, thiosemicarbazide, and malonic acid) in aqueous solution at room temperature in the target ratio. Large square shaped crystals were obtained in good yield and were quite stable in air. This building-block approach of self-assembly has been adopted for the construction of a co-ordination polymer illustrating both the importance of metal-ion geometry and the effect that ligand backbone can have on network structure. For the pH value plays an important role in the ionization and coordinating action of the dicarboxylic acid, the system must be controlled at pH 4.5~5.0 in order to avoid the by-products of other complexes<sup>[9]</sup>. It is the ionization of malonic acid in the sourish solution, as well as the coordination mode of dicarboxylate ion and thiosemicarbazide, which actually determine the geometry of the crystal structure.

### 2.2 IR spectroscopy

The IR spectrum of compound **1** exhibits medium strong bands at 3 513.7, 3 288 and 3 007.8  $\text{cm}^{-1}$ , which can be assigned to  $\nu(\text{OH})$  of the free water and  $\nu(\text{NH})$  of the thiosemicarbazide coordinated. The bands at 1 637.9, 1 613.0, 1 560.3, 1 450.9, 1 381.9 and 1 347.0  $\text{cm}^{-1}$  may be attributed to the vibrations of  $\delta(\text{NH})$  and  $\nu(\text{CO}_2)$ . Several weak bands at 1 273.1, 1 222.6, 1 169.3, 1 075.9, 968.5 and 937.2  $\text{cm}^{-1}$  in the spectrum are assigned to  $\nu(\text{C-N})$  and  $\nu(\text{C=S})$ . The medium bands at about 730.2 and 699.2  $\text{cm}^{-1}$  may be assigned to the outward vibrations of  $\delta(\text{NH}_2)$ , where the assignments shown are based on assignments made for related compounds<sup>[9,10]</sup>. The far-IR spectra (500~100  $\text{cm}^{-1}$ ) of **1** displays a medium band at 338.05  $\text{cm}^{-1}$  which may be assigned to metal-sulphur stretching; a band at higher frequency of 455.75  $\text{cm}^{-1}$ , can be assigned to metal-nitrogen stretching<sup>[11,12]</sup>.

### 2.3 Thermal analyses and solubility

In order to study the thermal stability of the title compound, thermogravimetric analysis (TGA) was per-

formed under a flow of nitrogen gas on a 5.49 mg sample of **1**. The TGA curve showed one striking weight loss of 0.35 mg (6.38%) at 119.4  $^{\circ}\text{C}$ , corresponding to the removal of uncoordinated water (calcd. 6.51%) from the compound. The curve showed a sharp weight loss of 2.29 mg (41.70%) at 240.1  $^{\circ}\text{C}$ , indicating the formation of  $\text{ZnSO}_4$  (calcd. 41.63%). No weight loss was recorded before this decomposition temperature suggesting the high stability of the main structure.

In addition to the favorable thermal stability, the solubility of **1** was also examined and found it is soluble in common solvents such as water, methanol, ethanol, acetonitrile and DMF, slightly soluble in acetone, nearly insoluble in methylene chloride, chloroform and acetic ether.

### 2.4 Description of the structure

Crystallographic data and structure refinement are given in Table 1, selected bond lengths (nm) and angles ( $^{\circ}$ ) for the complex are shown in Table 2. The ORTEP drawing of complex **1** with the atom numbering scheme is shown in Fig.1; structure of the one-dimensional chain and the molecular packing diagram are shown in Fig.2.

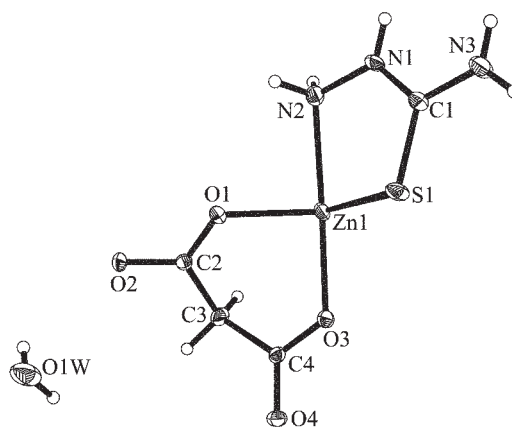


Fig.1 Structure of complex **1** (displacement ellipsoids at the 50% probability level)

X-ray analysis reveals that complex **1** is a coordination polymer in which thiosemicarbazide acts as N,S-chelate and malonate as O,O-chelate in a *trans* conformation. Molecules of water are incorporated but not coordinated in the crystal. The asymmetric unit of **1** consists of a zinc center to which one thiosemicar-

Table 1 Crystal data and structure refinement for complex 1

Empirical formula	C <sub>8</sub> H <sub>18</sub> N <sub>6</sub> O <sub>10</sub> S <sub>2</sub> Zn <sub>2</sub>	<i>F</i> (000)	560
Formula weight	553.14	Crystal size / mm	0.46 × 0.34 × 0.24
Temperature / K	293(2)	$\theta$ range for data collection / (°)	2.28 to 25.00
Wavelength / nm	0.071 073	Limiting indices	-10 ≤ <i>h</i> ≤ 11, -11 ≤ <i>k</i> ≤ 12, -10 ≤ <i>l</i> ≤ 10
Crystal system	Monoclinic	Reflections collected / unique	3 424 / 1 512 [ <i>R</i> (int)=0.051 2]
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	Completeness to $\theta=25.00^\circ$	94.3%
<i>a</i> / nm	0.937 59(1)	Max. and min. transmission	0.540 9 and 0.347 0
<i>b</i> / nm	1.110 83(1)	Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
<i>c</i> / nm	0.921 00(2)	Data / restraints / parameters	1 512 / 0 / 129
$\beta$ / (°)	107.808(1)	Goodness-of-fit on <i>F</i> <sup>2</sup>	1.066
Volume / nm <sup>3</sup>	0.913 26(2)	Final <i>R</i> indices [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> =0.039 0, <i>wR</i> <sub>2</sub> =0.099 4
<i>Z</i>	2	<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> =0.040 6, <i>wR</i> <sub>2</sub> =0.100 4
Calculated density / (Mg·m <sup>-3</sup> )	2.012	Extinction coefficient	0.008 2(19)
Absorption coefficient / mm <sup>-1</sup>	2.919	Largest diff. peak and hole / (e·nm <sup>-3</sup> )	678 and -607

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

Zn(1)-O(1)	0.200 6(2)	Zn(1)-N(2)	0.222 5(3)	O(2)-C(2)	0.125 8(4)
Zn(1)-O(2A)#1	0.203 8(2)	Zn(1)-S(1)	0.232 97(8)	O(2)-Zn(1)#2	0.203 8(2)
Zn(1)-O(3)	0.206 5(2)	O(1)-C(2)	0.125 8(4)	O(3)-C(4)	0.128 4(3)
O(1)-Zn(1)-O(2)#1	102.24(9)	O(1)-Zn(1)-S(1)	120.16(7)	C(2)-O(2)-Zn(1)#2	113.78(19)
O(1)-Zn(1)-O(3)	90.13(8)	O(2)#1-Zn(1)-S(1)	136.41(6)	C(4)-O(3)-Zn(1)	122.88(19)
O(2)#1-Zn(1)-O(3)	92.62(8)	O(3)-Zn(1)-S(1)	96.66(6)	N(1)-N(2)-Zn(1)	111.04(19)
O(1)-Zn(1)-N(2)	88.04(9)	N(2)-Zn(1)-S(1)	81.15(7)	O(1)-C(2)-O(2)	120.9(3)
O(2)#1-Zn(1)-N(2)	91.32(9)	C(1)-S(1)-Zn(1)	97.44(11)		
O(3)-Zn(1)-N(2)	175.94(9)	C(2)-O(1)-Zn(1)	122.5(2)		

Symmetry transformations used to generate equivalent atoms: #1: *x*, -*y*+3/2, *z*-1/2; #2: *x*, -*y*+3/2, *z*+1/2.

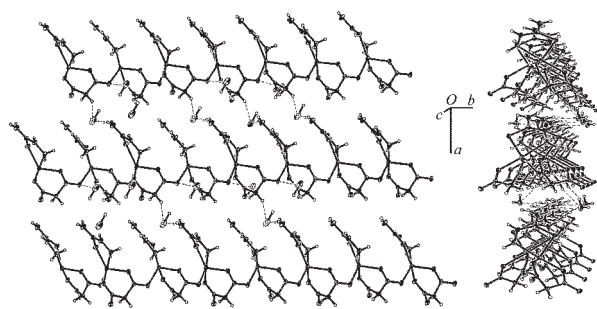


Fig.2 Projection of polymeric chains of complex 1 (on the *ab* plan)

Hydrogen bonds are indicated by dashed lines.

bazide and one malonate anion ligand are coordinated. The striking feature is that, the malonate anion ligands serve to link the asymmetric units into one-dimensional infinite spiral chain effectively by employing terminate O(1) and O(2) atoms to bridge the neighbouring metal centres in a *cis* conformation.

In the structure of **1**, the center zinc atom is NS3O-penta-coordinated. Coordination bond lengths of Zn(1)-S(1), Zn(1)-N(2), Zn(1)-O(1), Zn(1)-O(3) and Zn(1)-O(2A) are normal. The bond lengths for C(1)-N(1) and C(1)-S(1) are 0.133 3(4) nm and 0.171 3(3) nm, respectively, agreeing well with our previously synthesized compounds<sup>[13,14]</sup>. Moreover in Table 2, bond angles of O(1)-Zn(1)-O(3), C(2)-O(1)-Zn(1), C(2)-O(2)-Zn(1)#2 and O(1)-C(2)-O(2) indicating the spatial orientations of related bonds which construct the coordination geometry and build up the backbone of the infinite chain in a zig-zag way. As illustrated in Fig.1 and 2, there are two types of chelate ring in the structure unit. One is a five-member ring of Zn1, S1, C1, N1 and N2; the other is a six-member ring of Zn1, O1, C2, C3, C4 and O3. The thiosemicarbazide ligand in the former ring is almost planar (Mean devi-

ation 0.001 45 nm), with the N3 atom displaced by 0.005 20 nm and the coordinated Zn1 atom displaced by 0.076 95 nm. Such neighbouring planes are nearly parallel to each other (Dihedral between them  $8.3^\circ$ ).

As illustrated in Fig.2, the infinite chains and the solvent water molecules are linked together in the structure via weak hydrogen bonding interactions. Selected hydrogen bonds for instance, N(1)–H(1A)···O(3), N(2)–H(2A)···S(1) and N(3)–H(3A)···O(4) [symmetry code:  $1-x, -1/2+y, 1/2-z$ ], N(3)–H(3B)···O(1W) [symmetry code:  $1-x, 2-y, 1-z$ ] and C(3)–H(3D)···O(1W) [symmetry code:  $2-x, 2-y, 2-z$ ], are observed in the packing structure. Where permitted by the relative orientations of the carboxylates, a combination of hydrogen bonds [N(1)···O(3) 0.279 2(4), H(1A)···O(3) 0.200 08 nm, N(1)–H(1A)···O(3)  $152.61^\circ$ ; N(3)···O(4) 0.287 7(4), H(3A)···O(4) 0.202 29 nm, N(3)–H(3A)···O(4)  $172.30^\circ$ ; N(3)···O(1W) 0.293 9(5), H(3B)···O(1W) 0.210 48 nm, N(3)–H(3B)···O(1W)  $163.23^\circ$ ; O(1W)···O(2) 0.292 4(4), H(21W)···O(2) 0.251 88 nm, O(1W)–H(21W)···O(2)  $126.46^\circ$ ] in addition to the weak interactions [C(3)···O(1W) 0.327 7(4), H(3D)···O(1W) 0.242 61 nm, C(3)–H(3D)···O(1W)  $146.22^\circ$ ; N(2)···S(1) 0.339 3(3), H(2A)···S(1) 0.252 51 nm, N(2)–H(2A)···S(1)  $162.05^\circ$ ], help to stabilize the crystal system. The components of the polymer, thiosemicarbazide and water, provide the donors (N and O atoms) which serve to link the acceptors (O atoms) of adjacent dicarboxylate and water molecules through hydrogen bonds mentioned above, contributing to the formation of the polymer.

### 3 Conclusions

The title new coordination polymer has been successfully synthesized by self-assembling from aqueous solution and characterized by conventional methods. The present study shows a novel complex with such an interesting structure can be designed in various ways using suitable ligands and metal ions. As a result of distinct ionization and coordination of the dicarboxylic acid in solution, the pH value must be controlled in the synthetic route so as to avoid the presence of byproducts. As illustrated by X-ray diffraction analysis, the structure feature is the bridging dicar-

boxylates which effectively link the zinc centers into polymeric chains in a zig-zag way. Hydrogen bonding interactions stabilize the crystal system and link the infinite chains together into a supramolecular structure. This research suggests that hydrogen bonds represent an effective class of intermolecular force and play an important role in molecular recognition and self-organization, probably leading to a densely packed arrangement favoring the formation of a highly crystalline, ordered material. Further studies on related properties are currently under investigation.

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