

# H 键连接的三维超分子化合物 $[M(H_2O)_6](HL)_2$ 的合成、表征与结构 $[H_2L=1-(4\text{-羟基苯})-5\text{-四氮唑硫乙酸}, M=Mn^{II}, Co^{II}, Ni^{II}, Zn^{II}]$

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**摘要:** 利用配体 1-(4-羟基苯)-5-巯基四氮唑( $H_2L$ )和金属盐酸盐在水溶液中反应, 合成了 4 种离子型化合物, 并测定了它们的晶体结构。分析结果显示它们是异质同晶, 都属于  $P\bar{1}$  空间群, 分子通式为  $[M(H_2O)_6](HL)_2 [M=Mn^{II} (1), Co^{II} (2), Ni^{II} (3), Zn^{II} (4)]$ 。在这些化合物中, 中心金属原子都采取六配位模式, 形成一个近乎理想的八面体构型。晶体中通过氢键( $M-OH_2\cdots O-C$ )和偏移面  $\pi-\pi$  堆积作用形成独特的三维超分子网络结构。

**关键词:** 1-(4-羟基苯)-5-巯基四氮唑; 超分子化合物; 氢键;  $\pi-\pi$  堆积作用; 晶体结构

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## Supramolecular Compounds with Three-dimensional Hydrogen-bonded Network $[M(H_2O)_6](HL)_2$ ( $H_2L=1-(4\text{-Hydroxyphenyl})-5\text{-thioacetatetetrazole}$ , $M=Mn^{II}, Co^{II}, Ni^{II}$ and $Zn^{II}$ ): Synthesis, Characterization and Structures

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**Abstract:** The reactions of several divalent transition metals with 1-(4-Hydroxyphenyl)-5-thioacetatetetrazole ( $H_2L$ ) were studied in aqueous solution.  $Mn^{II}$ ,  $Co^{II}$ ,  $Ni^{II}$ , and  $Zn^{II}$  produced ionic products of general formula  $[M(H_2O)_6](HL)_2$ . The four compounds were characterized by crystallographic methods. And the results have shown that their crystals are isostructural and belong to the triclinic  $P\bar{1}$  space group. The metal center in each compound is six-coordinated, forming an ideal octahedral geometry. These neutral formula units make unique three-dimensional supramolecular architectures through hydrogen bonding ( $M-OH_2\cdots O-C$ ) and offset-panel  $\pi-\pi$  stacking interactions and stabilized by electrostatic force. CCDC: 662589, 1; 662590, 2; 662591, 3; 662592, 4.

**Key words:**  $M^{II}$  compounds; supramolecular compounds; hydrogen bonds;  $\pi-\pi$  stacking interactions; crystal structure

## 0 Introduction

Beside the field of molecular chemistry based on the covalent bond, the chemistry of molecular assemblies and of intermolecular bond (supramolecular chemistry) has become a new fascinating area of inter-

est in the last two decades<sup>[1-3]</sup>. Efforts have been done to design and construct such kind of assemblies due to their potential multi-dimensional applications in the field of catalysis, non-linear optics, electrical conductivity, molecular recognition, and crystal engineering<sup>[4]</sup>. Supramolecular inorganic/organic hybrid materials that

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have been so far constructed follow two principal philosophies. Firstly, transition-metal complexes can be assembled into coordination polymers obtained by employing bifunctional ligands such as dicarboxylate as linker between adjacent metal centers. Secondly, weaker intermolecular forces i.e. hydrogen bonding/ $\pi$ - $\pi$  stacking/van der Waals forces etc., connecting the metal complexes, enlarge the dimensionality to give a wide variety of extended supramolecular networks<sup>[5-7]</sup>. Recently, we have concentrated our attention on using H<sub>2</sub>L (synthesized from 1-(4-Hydroxyphenyl)-5-mercaptopotrazole<sup>[8]</sup>) as bridging spacer to obtain polynuclear complexes of transition-metal due to its versatile coordination modes. Meanwhile, we got four title compounds in aqueous solution. Thus, herein we firstly present a systematic structural study of solvent-free HL<sup>-</sup> and the hydrated metal.

## 1 Experimental

### 1.1 Materials and general methods

1-(4-Hydroxyphenyl)-5-mercaptopotrazole was purchased from Aldrich Chemical Co. Inc. All the other reagents for syntheses and analyses were of analytical grade. FTIR spectra (KBr pellets) were taken on a FTIR 170SX (Nicolet) spectrometer and elemental analyses were performed on a EuroEA3000 analyzer. Thermal stability (TG-DTA) studies were carried out on a Shimadzu TA-499C thermal analyzer in 25~800 °C, (10 °C·min<sup>-1</sup>) range under nitrogen atmosphere.

### 1.2 Syntheses of compounds

Compounds **1**~**4** were prepared by mixing 1:2 molar ratio of metal chloridate (M=Mn<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, and Zn<sup>II</sup>) and H<sub>2</sub>L in ethanol/water. The mixture was heated

to 40~50 °C with stirring for 1 h, then filtered and left to stand at the room temperature. Well-shaped crystals suitable for X-ray analyses were obtained by slow evaporation of the filtrate in *ca.* 40%~50% yields within about a week. Elemental analyses results are in good agreement with stoichiometries. Found (%) (**1**) C, 32.59; H, 4.10; N, 16.20; S, 9.70. Calculated for C<sub>18</sub>H<sub>26</sub>MnN<sub>8</sub>O<sub>12</sub>S<sub>2</sub> (%): C, 32.48; H, 3.94; N, 16.84; S, 9.63. (**2**) C, 30.51; H, 3.92; N, 16.20; S, 9.67. Calculated for C<sub>18</sub>H<sub>26</sub>CoN<sub>8</sub>O<sub>12</sub>S<sub>2</sub> (%): C, 32.29; H, 3.91; N, 16.74; S, 9.58. (**3**) C, 32.85; H, 4.00; N, 16.89; S, 9.67. Calculated for C<sub>18</sub>H<sub>26</sub>N<sub>8</sub>NiO<sub>12</sub>S<sub>2</sub> (%): C, 32.30; H, 3.92; N, 16.75; S, 9.58. (**4**) C, 32.10; H, 3.97; N, 16.32; S, 9.59. Calculated for C<sub>18</sub>H<sub>26</sub>N<sub>8</sub>O<sub>12</sub>S<sub>2</sub>Zn (%): C, 31.98; H, 3.88; N, 16.58; S, 9.67.

### 1.3 Crystal structure determination

Take **4** for an example, a single crystal with dimensional 0.266 mm × 0.193 mm × 0.069 mm was used for structural determination at 293(2) K with graphite monochromatic Mo K $\alpha$  radiation ( $\lambda$ =0.071 073 nm) on a Bruker smart CCD. The structure were solved by direct methods and expended using difference Fourier synthesis technique. All non-hydrogen atoms were refined anisotropically by the full matrix least-squares on the  $F^2$ . The hydrogen atoms attached to carbon atoms were located by geometrical calculation, while those attached to oxygen were located from the difference Fourier maps. Calculations were performed with the Siemens SHELXS-97<sup>[9]</sup> and SHELXL-97<sup>[10]</sup> program package. The crystal parameters, data collection and refinement results for complexes **1**~**4** are shown in Table 1. The selected bond distances and angles are listed in Table 2.

CCDC: 662589, **1**; 662590, **2**; 662591, **3**; 662592, **4**.

Table 1 Crystal data and summary of data collection for metal complexes **1**~**4**

Empirical formula	C <sub>18</sub> H <sub>26</sub> MnN <sub>8</sub> O <sub>12</sub> S <sub>2</sub>	C <sub>18</sub> H <sub>26</sub> CoN <sub>8</sub> O <sub>12</sub> S <sub>2</sub>	C <sub>18</sub> H <sub>26</sub> N <sub>8</sub> NiO <sub>12</sub> S <sub>2</sub>	C <sub>18</sub> H <sub>26</sub> N <sub>8</sub> O <sub>12</sub> S <sub>2</sub> Zn
Formula weight	665.53	669.52	669.3	675.96
Temperature / K	296	296	296	296
Crystalline system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
$a$ / nm	0.669 7(2)	0.668 5(1)	0.668 3(1)	0.668 1(7)
$b$ / nm	0.709 4(2)	0.702 3(1)	0.704 6(1)	0.705 2(8)
$c$ / nm	1.497 8(4)	1.488 6(2)	1.483 2(2)	1.486 6(2)
$\alpha$ / (°)	96.786(2)	96.355(1)	96.623(1)	96.625(2)

Continued Table 1

$\beta / (^{\circ})$	97.784(2)	97.877(1)	97.879(1)	97.850(2)
$\gamma / (^{\circ})$	105.667(1)	105.910(1)	106.121(1)	105.83(1)
$V / \text{nm}^3$	0.669 79(3)	0.657 58(2)	0.655 90(2)	0.658 88(1)
$Z$	1	1	1	1
$F(000)$	343	345	346	348
$D_{\text{calc}} / (\text{g} \cdot \text{cm}^{-3})$	1.64	1.691	1.694	1.704
$\mu(\text{Mo } K\alpha) / \text{mm}^{-1}$	0.725	0.889	0.976	1.168
Crystal size / mm	$0.23 \times 0.11 \times 0.09$	$0.30 \times 0.18 \times 0.15$	$0.31 \times 0.17 \times 0.09$	$0.27 \times 0.19 \times 0.07$
Range of $h, k, l$	$-8 \sim 8, -9 \sim 9, -18 \sim 19$	$-8 \sim 8, -9 \sim 9, -19 \sim 19$	$-8 \sim 8, -8 \sim 9, -19 \sim 19$	$-8 \sim 8, -9 \sim 9, -19 \sim 18$
Reflections collected	10 804	10 467	9 821	5 901
Independent reflections	3 065	2 984	2 957	2 889
Observed reflections	2 591	2 793	2 545	2 592
$\theta$ range / $(^{\circ})$	$1.39 \sim 27.62$	$1.40 \sim 27.56$	$1.40 \sim 27.61$	$2.80 \sim 27.48$
$R, wR (I > 2\sigma(I))$	0.030 1, 0.082 4	0.025 5, 0.072 1	0.031 8, 0.082 9	0.031 9, 0.086 3
$R, wR$ (all data)	0.038 4, 0.094 2	0.027 3, 0.073 5	0.039 6, 0.087 6	0.035 9, 0.088 5
Parameters	215	215	215	215
Goodness of fit on $F^2$	1.013	1.02	1.003	1.011
Residual electron densities / $(\text{e} \cdot \text{nm}^{-3})$	$565 \sim -305$	$257 \sim -265$	$308 \sim -285$	$873 \sim -219$

Table 2 Selected bond lengths (nm) and angles ( $^{\circ}$ ) for complexes 1~4

	1	2	3	4
M(1)-O(1W)	0.215 8(1)	0.207 6(1)	0.204 3(2)	0.206 6(2)
M(1)-O(2W)	0.217 3(1)	0.209 0(1)	0.205 3(2)	0.208 7(2)
M(1)-O(3W)	0.219 0(1)	0.210 7(1)	0.208 0(2)	0.211 9(2)
S(1)-C(7)	0.173 6(2)	0.173 3(1)	0.173 3(2)	0.173 5(2)
N(1)-C(7)	0.135 4(2)	0.135 5(2)	0.135 1(2)	0.135 0(3)
N(1)-N(2)	0.135 8(2)	0.135 6(2)	0.136 0(2)	0.135 8(2)
N(2)-N(3)	0.128 5(2)	0.128 7(2)	0.128 4(2)	0.128 7(3)
N(3)-N(4)	0.135 2(2)	0.135 4(2)	0.135 3(2)	0.135 4(3)
N(4)-C(7)	0.132 6(2)	0.132 5(2)	0.132 7(2)	0.132 4(3)
O(1W)-M(1)-O(2W)	90.06(6)	90.23(5)	91.07(6)	90.91(7)
O(1W)-M(1)-O(3W)	91.89(7)	92.94(5)	92.49(7)	92.47(7)
O(2W)-M(1)-O(3W)	92.27(6)	92.25(5)	92.36(6)	92.38(7)

## 2 Results and discussion

The title complexes have similar IR spectra due to their isostructure. Take **4** for an example, the IR spectrum reveals the presence of a large number of different hydrogen bonding between 3 200 and 3 500  $\text{cm}^{-1}$  with the strongest peaks at 3 378  $\text{cm}^{-1}$  which can be ascribed to O-H stretching vibration. The strong bond at 1 740 and 1 600  $\text{cm}^{-1}$  are due to the asymmetry and symmetry COO<sup>-</sup> stretching vibration of HL<sup>-</sup>. The three moderately strong stretching vibration peaks between 1 289 and

1 598  $\text{cm}^{-1}$  can be ascribed to the tetrazole/benzene ring stretching vibration.

These complexes are air stable at room temperature, however, alike decompositions occurred at elevated temperature. The coordination water content has been verified by TGA in 25~800  $^{\circ}\text{C}$  range under a nitrogen atmosphere. Still take **4** for an example, the first weight loss of 16.13%, from 105 to 130  $^{\circ}\text{C}$ , corresponds to six water molecules (calculated 16.14%) coordinatively bonded to the metal ion. Upon further heating, a second weight loss from 155 to 280  $^{\circ}\text{C}$  is observed,

which maybe due to the loss of part of  $\text{HL}^-$ . The final process is accompanied by the decomposition of the  $\text{HL}^-$  at above  $300\text{ }^\circ\text{C}$ , ultimately giving the final solid product to be  $\text{Zn}_2\text{O}_3$ <sup>[11,12]</sup>.

The X-ray crystal structures of the title complexes show that they are isomorphous and isostructural (see Table 1). The neutral compounds consist of one  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$  cation and two  $\text{HL}^-$  anions, as shown in Fig. 1, a labeled diagram of the Zn complex **4** is as an example, in which the complex has a crystallographic center with the Zn atom situated at the center of (0, 0.5, 0). In the cation, the metal atom is surrounded by six aqua ligands, exhibiting an ideal octahedral geometry.

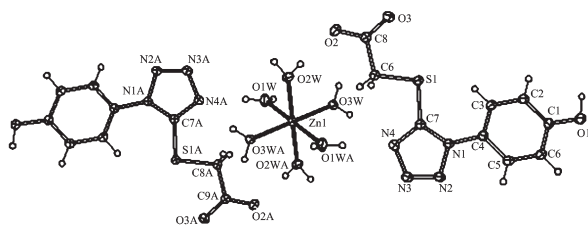


Table 4 Hydrogen bond lengths(nm) and bond angles( $^{\circ}$ ) in 4

D-H $\cdots$ A	Distance of D $\cdots$ A / nm	Angle of D-H-A / ( $^{\circ}$ )
O(1W)-H(1WA) $\cdots$ N(4)#1	0.286 8(2)	166.3
O(1W)-H(1WB) $\cdots$ O(2)#2	0.274 4(2)	167.8
O(2W)-H(2WB) $\cdots$ O(2)#3	0.272 7(2)	162.8
O(3)-H(3B) $\cdots$ O(1)#4	0.257 6(2)	173.7
O(3W)-H(3WB) $\cdots$ N(3)#5	0.284 7(2)	172.6
O(3W)-H(3WA) $\cdots$ O(3)#6	0.278 0(2)	169.6
O(2W)-H(2WA) $\cdots$ O(2)	0.288 1(2)	176.7

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

#4:  $-x+1, -y+1, -z+1$ ; #5:  $x-1, y, z$ ; #6:  $-x+2, -y+2, -z+1$ .

terations.

In conclusion, the supramolecular structure depends mostly on three kinds of interactions: the electrostatic force, hydrogen bonding and offset-panel  $\pi$ - $\pi$  stacking. The electronic charge of ions decides the ratio of the two units of the cation and anion in the compound system. The bonding force mainly comes from the electrostatic interaction between the two building blocks, meanwhile the hydrogen bonding and  $\pi$ - $\pi$  stacking leading to the orientation and selectivity in the building of the two units. The corporate effects of the three kinds of interactions make the crystal structures more stable.

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