

# 基于三聚硫氰酸配体的六核镍配合物的合成,晶体结构和荧光性能分析

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**摘要:** 用缓慢挥发法合成了一个六核 Ni(II) 的配位聚合物  $[\text{Ni}_6(\text{H}_2\text{O})_6(\text{HTMT})_6] \cdot 3(\text{C}_2\text{H}_5)_3\text{N} \cdot 7\text{H}_2\text{O}$  (1) ( $\text{H}_3\text{TMT}$ =三聚硫氰酸), 并用红外、元素分析及单晶衍射进行表征。该配合物属于三方晶系,  $R\bar{3}c$  空间群, 晶胞参数为  $a=b=1.869\ 7(3)\ \text{nm}$ ,  $c=3.982\ 5(8)\ \text{nm}$ ,  $\gamma=120^\circ$ 。晶胞体积  $V=12.057(4)\ \text{nm}^3$ ,  $D_c=1.596\ \text{g cm}^{-3}$ ,  $Z=6$ ,  $\mu=1.91\ \text{mm}^{-1}$ ,  $F(000)=6\ 095$ ,  $R=0.047$ ,  $wR=0.151$ 。X 单晶衍射表明, 6 个 Ni(II) 与 6 个 HTMT<sup>2-</sup> 和 6 个水分子形成一个六核的构筑单元, 这个六核构筑单元又通过氢键作用形成三维结构。同时在室温条件下测定了该配合物的荧光性能。

**关键词:** 镍配合物; 三聚硫氰酸; 荧光性能

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## Synthesis, Characterization and Photoluminescent Property of a Hexanuclear Nickel(II) Complex with Trithiocyanuric Acid

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**Abstract:** The title complex,  $[\text{Ni}_6(\text{H}_2\text{O})_6(\text{HTMT})_6] \cdot 3(\text{C}_2\text{H}_5)_3\text{N} \cdot 7\text{H}_2\text{O}$  (1) ( $\text{H}_3\text{TMT}$ =trithiocyanuric acid), was synthesized by slow evaporation, which was characterized by IR, elemental analysis, and single crystal X-ray diffraction. This complex crystallizes in trigonal, space group  $R\bar{3}c$ , with  $a=b=1.8697(3)\ \text{nm}$ ,  $c=3.982\ 5(8)\ \text{nm}$ ,  $\gamma=120^\circ$ ,  $V=12.057(4)\ \text{nm}^3$ ,  $C_{36}\text{H}_{77}\text{N}_{21}\text{Ni}_6\text{O}_{13}\text{S}_{18}$ ,  $M_r=1941.36$ ,  $D_c=1.596\ \text{g cm}^{-3}$ ,  $Z=6$ ,  $\mu=1.91\ \text{mm}^{-1}$ ,  $F(000)=6\ 095$ , the final  $R=0.047$ ,  $wR=0.151$  for  $[\text{Ni}_6(\text{H}_2\text{O})_6(\text{HTMT})_6] \cdot 3(\text{C}_2\text{H}_5)_3\text{N} \cdot 7\text{H}_2\text{O}$  (1) observed reflections ( $I>2\sigma(I)$ ). X-ray diffraction analysis reveals that the six nickel(II) atoms are bridged by six HTMT<sup>2-</sup> and six water molecules into a hexanuclear building unit, the neutral hexanuclear building units are further connected into a three-dimensional framework through the O-H $\cdots$ O and O-H $\cdots$ N hydrogen bonding interactions. The photoluminescent property of complex (1) was also studied at room temperature.

**Key words:** nickel complex; trithiocyanuric acid; photoluminescent property

## 0 Introduction

Much attention has been paid towards characterization of binuclear and polynuclear transition metal complexes in recent years<sup>[1-2]</sup>. In this regard, poly-azine ligands have drawn special

attention<sup>[3-4]</sup>.  $\text{Na}_3\text{TMT} \cdot 9\text{H}_2\text{O}$  also known as 2, 4, 6-trimercapto-triazine or 1, 3, 5-triazine-2, 4, 6-trithiol is an effective analytical reagent and has potential applications in the removal of univalent and divalent heavy metal ions from waste water<sup>[5-7]</sup>.  $\text{H}_3\text{TMT}$  has three N, S donor sets suitable for coordination to

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metal centers, which could display monodentate  $N^-$  or  $S^-$  donor<sup>[8-14]</sup>, bidentate chelating  $[N, S]^-$  donor<sup>[15]</sup> or bridging two metal ions through two of the bis-chelating  $[N, S]^-$  donor sets, and trinucleating coordination mode using all the three available  $[N, S]^-$  donor<sup>[16-22]</sup>. It can form mononuclear, dinuclear and trinuclear complexes. However, hexanuclear nickel complex with  $H_3TMT$  have not been reported up to now. Herein we report the preparation and crystal structure of complex **1**, which exhibits 3D supramolecular network through hydrogen bonding interactions. And its photoluminescent property has been also studied at room temperature.

## 1 Experimental

### 1.1 Material and instruments

All commercially available chemicals and solvents were of reagent grade and used as received without further purification.  $Na_3TMT \cdot 9H_2O$  was recrystallized from  $H_2O/EtOH$ . Crystal structure determination was carried out on a Rigaku Saturn 724 CCD X-ray single crystal diffractometer. C, H, S and N analysis was performed on a FLASH 1112S series Element Analyzer. IR spectra were recorded on a Nicolet 22102 FT-IR spectrometer with KBr pellets in the  $4\,000\sim 400\text{ cm}^{-1}$  region. The fluorescent spectrum was made on a SPVF-1XO fluorescence spectrometer. The TGA measurements were carried out on a STA 449C thermal analyzer from room temperature to  $1\,000\text{ }^\circ\text{C}$  under  $N_2$  atmosphere with a heating rate of  $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ .

### 1.2 Synthesis of complex (1)

To 30 mL  $H_2O$  and 1 mL triethylamine solution of  $NiCl_2 \cdot 6H_2O$  (0.2377 g, 1 mmol) was added another  $H_2O$  solution (60 mL) of  $Na_3TMT \cdot 9H_2O$  (0.4052 g, 1 mmol) under stirring. The mixture was further stirred for 12 h under nitrogen atmosphere at room temperature and then filtered. Upon keeping the filtrate in air for 30 d, black block-shaped crystals of the title complex suitable for X-ray crystal determination were formed at the bottom of the vessel on slowly evaporating the solvent. Anal. Calcd. (%) for  $[Ni_6(H_2O)_6(HTMT)_6] \cdot 3(C_2H_5)_3N \cdot 7H_2O$  (%): C, 22.27;

H, 4.00; N, 15.15; S, 29.72. Found (%): C, 22.30; H, 3.95; N, 15.25; S, 29.68. IR (KBr):  $3\,429\text{ (m)}$ ,  $2\,978\text{ (m)}$ ,  $1\,623\text{ (m)}$ ,  $1\,475\text{ (vs)}$ ,  $1\,228\text{ (s)}$ ,  $1\,151\text{ (s)}$ ,  $1\,005\text{ (s)}$ ,  $869\text{ (s)}$ ,  $774\text{ (w)}$ ,  $738\text{ (w)}$ ,  $488\text{ (w)}\text{ cm}^{-1}$ .

### 1.3 Structure determination and refinement

A single crystal with dimensions of  $0.20\text{ mm} \times 0.20\text{ mm} \times 0.20\text{ mm}$  was put on a RIGAKU SATURN 724 CCD X-ray single crystal diffractometer equipped with a graphite-monochromatic  $Mo\ K\alpha$  radiation ( $\lambda = 0.071\,073\text{ nm}$ ) by using a  $\theta$  scan mode at  $293\text{ (2)}\text{ K}$ . Out of the total 16404 reflections collected in the range of  $3.3680^\circ \leq \theta \leq 29.1313^\circ$ , 2623 were independent with  $R_{int} = 0.029$ , in which 2281 with  $I > 2\sigma(I)$  were observed and used in the succeeding refinements. The crystal structure was solved by direct methods using the SHELXS-97 program<sup>[23]</sup>. All non-hydrogen atoms were refined with anisotropic thermal parameters. The H atoms were placed in calculated positions, and the H atoms of  $HTMT^{2-}$  were found from difference Fourier maps and all their parameters were refined. The disorder of triethylamine with two locations of C7 and C7A led in the refinement to 1:1 ratio in occupancy for each carbon atom. The final refinement including hydrogen atoms converged to  $R = 0.047$ ,  $wR = 0.151$  ( $w = 1/[\sigma^2(F_o^2) + (0.0844P)^2 + 30.1565P]$ , where  $P = (F_o^2 + 2F_c^2)/3$ ),  $S = 1.13$ ,  $\Delta\rho_{max} = 960\text{ e}\cdot\text{nm}^{-3}$ ,  $\Delta\rho_{min} = -67\text{ e}\cdot\text{nm}^{-3}$  and  $(\Delta/\sigma)_{max} = 0.009$ .

The crystallographic data and selected bond lengths and angles are listed in Table 1 and Table 2, respectively.

## 2 Results and discussion

### 2.1 IR spectrum attribution

In the IR spectra, the strong and wide adsorption peak at  $3\,429\text{ cm}^{-1}$  attributes to the O-H stretching vibration of  $H_2O$ , and that at  $2\,978\text{ cm}^{-1}$  belongs to the N-H vibration<sup>[24]</sup>, which is indicative of the trithione form of the TMT ring. The bands at  $1\,475$ ,  $1\,228$ ,  $869\text{ cm}^{-1}$  can be connected with the vibrations of the TMT ring. The vibration shifting comparison with those of free  $Na_3TMT$  ( $1\,439$ ,  $1\,245$  and  $860\text{ cm}^{-1}$ ), suggesting that  $Na_3TMT$  participated in the coordination, which is consistent with the structural

**Table 1** Crystallographic data of complex **1**

Empirical formula	C <sub>36</sub> H <sub>77</sub> N <sub>21</sub> Ni <sub>6</sub> O <sub>13</sub> S <sub>18</sub>	<i>Z</i>	6
Formula weight	1 941.36	<i>D<sub>c</sub></i> / (g·cm <sup>-3</sup> )	1.596
Temperature / K	293(2)	$\mu$ / mm <sup>-1</sup>	1.91
Crystal system	trigonal	Crystal size / mm	0.20×0.20×0.20
Wavelength / nm	0.071073	<i>F</i> (000)	6 095
Space group	$R\bar{3}c$	<i>R</i> <sub>int</sub>	0.029
<i>a</i> / nm	1.869 7(3)	Index ranges	-20< <i>h</i> <17, -16< <i>k</i> <23, -46< <i>l</i> <47
<i>b</i> / nm	1.869 7(3)	Reflections collected	16 404
<i>c</i> / nm	3.982 5(8)	Independent reflections	2623
$\gamma$ / (°)	120	Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
<i>V</i> / nm <sup>3</sup>	12.057(4)	Final <i>R</i> indices ( <i>I</i> > $\sigma$ ( <i>I</i> ))	<i>R</i> =0.047, <i>wR</i> =0.151

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

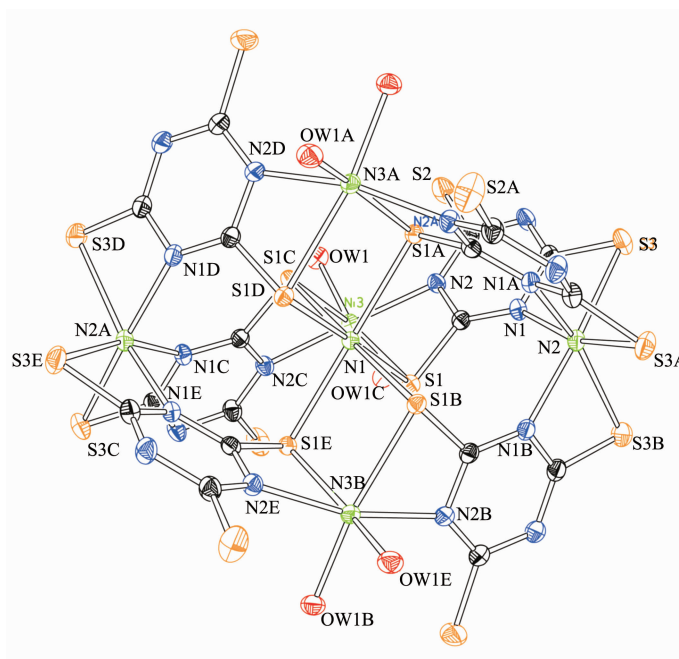
Ni1-S1	0.246 71(10)	Ni2-N1	0.2056 (3)	Ni2-S3	0.251 09(12)
Ni3-OW1	0.206 2(3)	Ni3-N2	0.2067(3)	Ni3-S1	0.2481 4(11)
Ni1-S1-C1	101.44 (12)	N1-Ni2-S3	67.65(9)	N2-Ni3-S1	68.63 (9)
OW1-Ni3-S1	164.98(10)	OW1-Ni3-N2	97.58(13)		

analysis.

## 2.2 Crystal structure description

The title complex **1** crystallizes in trigonal, space group  $R\bar{3}c$ . As shown in Fig.1, X-ray diffraction

reveals that the title compound comprises of hexanuclear building units, neutral triethylamine, as well as lattice water molecules. As for the hexanuclear unit, it is constructed with six Ni(II) atoms, six HTMT<sup>2-</sup>



Hydrogen atoms, triethylamine molecules and crystal H<sub>2</sub>O molecules have been omitted for clarity. Symmetry codes: A:  $-x+y, -x+1, z$ ; B:  $x-y+2/3, -y+4/3, -z-1/6$ ; C:  $y-1/3, x+1/3, -z-1/6$ ; D:  $-y+1, x-y+1, z$ ; E:  $-x+2/3, -x+y+1/3, -z-1/6$

**Fig.1** Molecular structure of the title compound

ligands, six coordination water molecules. In the complex, there are three crystallographically independent Ni(II) atoms with the same coordination mode. The Ni (1) is coordinated by six sulfur atoms from six different HTMT<sup>2-</sup> ligands, and forms a slightly distorted octahedral coordination sphere. As for Ni(2), it is coordinated with three nitrogen and three sulfur atoms from three different ligands into fac-configuration. In the Ni (2)S<sub>3</sub>N<sub>3</sub> distorted octahedral geometry, N1, N1 (A), S3 (B), S3 (A) locate at the equator plane, while N1 (B), S3 occupy the axial positions. The Ni (3) is also six coordinated, however, it is bridged with only two HTMT<sup>2-</sup> ligands with two nitrogen and sulfur atoms, which is quite different from Ni (1) and Ni (2), and two water molecules complete the coordination sphere. The Ni1-S distance is similar to Ni2-S (shown in Table 2), and is longer

than Ni3-S distance, which is much shorter in comparison with those found in [Ni (dpta) (HTMT) (H<sub>2</sub>O)]·H<sub>2</sub>O<sup>[25]</sup> and [Ni(taa)(HTMT)]<sup>[26]</sup>.

In the complex, the coordination water molecules in the hexanuclear building units form strong hydrogen bonding interactions with the lattice water molecules, which connect the hexanuclear into a three-dimensional framework. The uncoordinating nitrogen atom of HTMT<sup>2-</sup> also forms hydrogen bonding interactions (O-H ... N 0.276 4 nm) with the lattice water molecules, which contributes to the crystal packing (Fig.2). Interestingly, the hexanuclear building units connected by the lattice water molecules into a three-dimensional framework with a void about 0.771 6 nm×0.867 8 nm, which accommodates the triethylamine as the guest molecules.

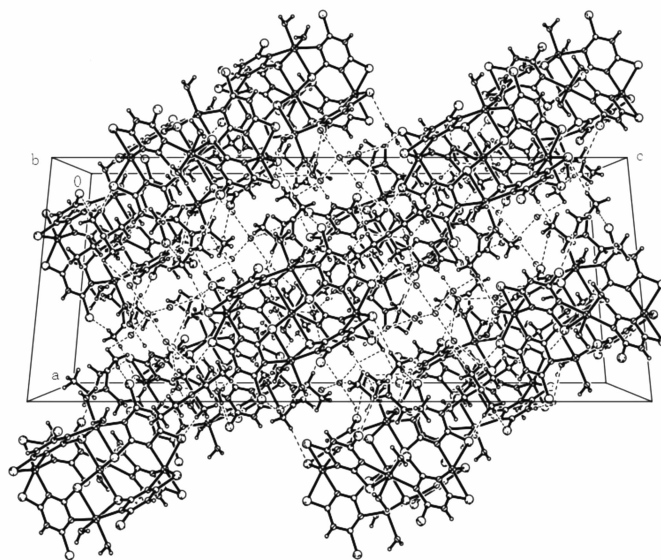


Fig.2 View of the three-dimensional structure

### 2.3 Luminescent property

The luminescent properties of the title complex have been investigated at room temperature. The complex exhibits an intense emission at 538 nm ( $\lambda_{\text{ex}}$ =380 nm) at room temperature (Fig.3), which is a yellow fluorescent. The free ligand Na<sub>3</sub>TMT exhibit weak fluorescent emission at 493nm ( $\lambda_{\text{ex}}$ =426 nm). Compared to the free ligand, the emission maximum of the complex has changed. This may be caused by a

change in the HOMO and LUMO energy levels of HTMT<sup>2-</sup>, or a charge-transfer transition between ligands and metal centers<sup>[27-28]</sup>. These results indicate that complex maybe have potential applications in photochemistry.

### 2.4 Thermogravimetric analysis

The TG analysis for complex **1** has been investigated under N<sub>2</sub>. It exhibits a weight loss of 12.21% at 88~195 °C corresponding to the loss of six

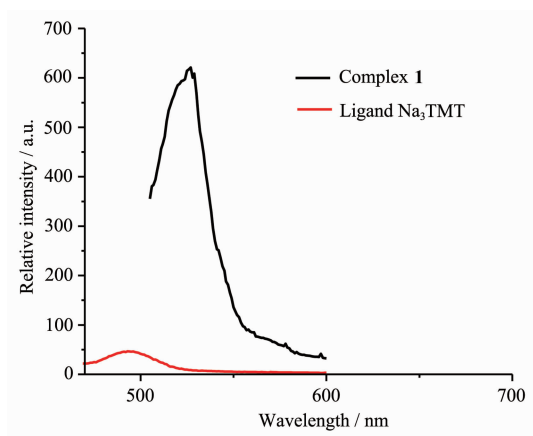


Fig.3 Luminescent behavior of complex **1** and ligand  $\text{Na}_3\text{TMT}$

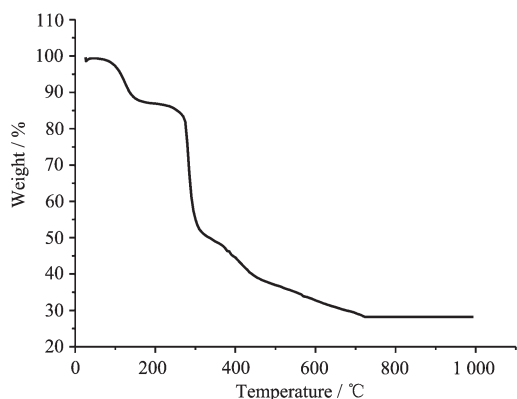


Fig.4 TGA curve of complex **1**

coordinated molecules and seven solvent water molecules (Calcd. 12.11%). Further decomposition occurs in the range of 195~725 °C, which is attributed to the elimination of six  $\text{HTMT}^{2-}$  ligands and three triethylamine molecules (Obsd. 60.51%, Calcd. 59.69%). The remaining product may be NiS (Obsd. 28.19%, Calcd. 28.20%).

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