

原位水热合成一个新颖的银四唑配位聚合物

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摘要: 在水热条件下, 硝酸(3-氰基吡啶)银以及叠氮化钠反应, 成功地组装了一个二维层状银四唑配位聚合物[mono(5-(3-pyridyl) tetrazolato)Ag] (**1**), 并对其进行了表征。晶体结构分析表明, 化合物 **1** 结晶在三斜晶系, 其空间群分别为 $P\bar{1}$ ($a=0.626\,08(10)$ nm, $b=0.784\,98(13)$ nm, $c=0.805\,84(12)$ nm, $\alpha=75.171(4)^\circ$, $\beta=76.653(3)^\circ$, $\gamma=68.332(3)^\circ$, $V=0.351\,67(10)$ nm³, $Z=2$), 银的配位环境为四配位并形成略为变形的四面体构型。室温下, 化合物 **1** 显示强的蓝色荧光(495 nm 和 521 nm)。

关键词: 银; 原位; 四唑配位聚合物; 水热合成; 荧光

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Indirectly *In-Situ* Hydrothermal Preparation of a Novel Ag Tetrazole Coordination Polymer

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Abstract: The reaction of Ag(3-cyanopyridine)NO₃ with NaN₃ in presence of water and ethanol affords an unprecedented 2D layered tetrazole coordination polymer, [mono(5-(3-pyridyl) tetrazolato)Ag], [(3-PTZ)Ag] (**1**), which is characterized by single crystal X-ray determination, IR and fluorescent spectrum. The local coordination geometry around the Ag ion can be best described as a slightly distorted tetrahedron. The fluorescent emission spectrum of **1** at the solid-state at room temperature shows that maximal emission peak occurs in 495 and 521 nm, respectively. Crystal data for **1**, C₆H₄AgN₅, triclinic, $P\bar{1}$, $a=0.626\,08(10)$ nm, $b=0.784\,98(13)$ nm, $c=0.805\,84(12)$ nm, $\alpha=75.171(4)^\circ$, $\beta=76.653(3)^\circ$, $\gamma=68.332(3)^\circ$, $V=0.351\,67(10)$ nm³, $Z=2$. CCDC: 267340.

Key words: Ag; *in situ*; tetrazole coordination polymer; hydrothermal synthesis; fluorescence

0 Introduction

Sharpless and Demko have reported a safe, convenient, and environmentally friendly synthetic approach for generating 5-substituted 1H-tetrazoles in water^[1]. Generally, 1H-tetrazole derivatives are prepared by addition of azide to nitriles in the presence of Lewis acid (Zn²⁺) as a catalyst (actually the preparation reaction is a *in-situ* assembly metal coordination formation process, or catalyst is also a reactive agent) through the decomposition of Lewis acid (Zn²⁺) coordination polymer or (complex), as shown in Scheme 1.

Inspired by Sharpless's pioneering work^[1], we have repeated the reactions reported by Demko and Sharpless under such conditions and are very interested in the metal coordination polymers because they have displayed many novel structure modes and functionalities such as second harmonic generation, strong fluorescent (or phosphorescent) emission and chirality. On the other hand, these metal complexes are easily produced crystals in such reaction system that may allow structural elucidation of the solid intermediates^[2]. To this end, all of metal Lewis acids are non-oxidative metal ions such as Zn²⁺ and Cd²⁺^[3]. As a continuation

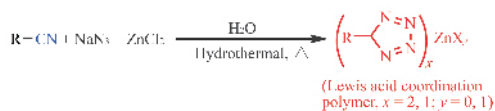
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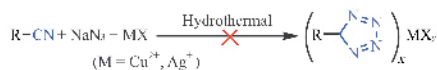
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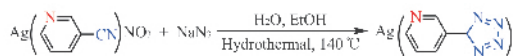
of the exploration of functional metal tetrazole coordination polymers, we followed the above-mentioned method to directly try to get the same kind of complex with copper(II) and silver(I). Unfortunately, we failed to get the expected product or it did not work because both of copper(II) and silver(I) are easily reduced in the *in-situ* [2+3] tetrazole reaction system, as shown in Scheme 2. Evidently, how to get such tetrazole coordination polymer containing Ag^+ ion under hydrothermal (or solvothermal) treatment conditions remains a great challenge. However, it is well known that the coordination polymer containing Ag^+ can be applied to decrease its concentration to reach the low oxidation-reducing potential to protect Ag^+ reduction. Consequently, we use an Ag^+ coordination polymer to replace AgNO_3 as a Lewis acid to conduct the above-mentioned [2+3] cycloaddition reaction *in situ* between cyano and azido groups in the presence of water. As expected, we successfully achieve such Ag tetrazole coordination polymer as shown in Scheme 3, Herein we report the synthesis, X-ray crystal structures and fluorescent property of [mono(5-(3-pyridyl) tetrazolato)Ag], [(3-PTZ)Ag] (**1**).



Scheme 1



Scheme 2



Scheme 3

1 Experimental

1.1 Synthesis of [mono(5-(3-pyridyl) tetrazolato) Ag] **1**

Complex **1** was prepared under hydrothermal reaction condition. (Scheme 3) A heavy-walled Pyrex tube containing a mixture of $\text{Ag}(\text{3-cyanopyridine})\text{NO}_3$ (0.274 g, 0.1 mmol), NaN_3 (0.065 g, 0.1 mmol), water (0.5 mL) and ethanol (1.0 mL) was frozen and sealed

under vacuum, then placed inside an oven at 140 °C. The pale yellow block-like crystals were obtained after 24 hours of heating. Yield: 0.066 3 g (72 %) on the basis of 3-cyanopyridine. Calc. for **1**: C 28.35, H 1.57, N 27.56; Found for **1**: C 27.56, H 1.50, N 27.12, IR (KBr, cm^{-1}) 3 422(s), 2 924(w), 1 637(w), 1 603(w), 1 581(w), 1 458(w), 1 422(m), 1 366(w), 1 123(m), 1 013(m), 818(w), 754(w), 700(m), 640(w), 459(w).

1.2 X-ray data collection and structure determination of **1**

A single crystal of **1** was prepared as described above; a pale yellow block crystal with a dimension of 0.15 mm \times 0.15 mm \times 0.30 mm was employed for structural analysis. Suitable single crystals of **1** were selected under a polarizing microscope and fixed with epoxy cement on fine glass fibres which were then mounted on a Bruker P4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) for

Table 1 Crystal data and structure refinement for **1**

Empirical formula	$\text{C}_6\text{H}_4\text{N}_5\text{Ag}$
F_w	254.01
T / K	296(2)
Wavelength / nm	0.071 073
Crystal system	Triclinic
Space group	$P\bar{1}$
a / nm	0.626 08(10)
b / nm	0.784 98(13)
c / nm	0.805 84(12)
$\alpha / (^\circ)$	75.171(4)
$\beta / (^\circ)$	76.653(3)
$\gamma / (^\circ)$	68.332(3)
V / nm^3	0.351 67(10)
Z	2
$\rho(\text{calc}) / (\text{g} \cdot \text{cm}^{-3})$	2.399
$\mu(\text{Mo } K\alpha) / \text{mm}^{-1}$	2.803
$F(000)$	244
Crystal size / mm	0.15 \times 0.15 \times 0.3
θ range for data collection $/ (^\circ)$	2.7–33.5
Index ranges	$-9 \leq h \leq 9$, $-12 \leq k \leq 10$, $-11 \leq l \leq 12$
Reflections collected	3 391
Independent reflections	2 497 [$R(\text{int})=0.022$]
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	0.98
Final R indices [$I > 2\sigma(I)$]	$R_1=0.0528$, $wR_2=0.1760$

cell determination and the subsequent data collection. The crystal structures were solved using direct methods with the help of the SHELXS-97 program^[4]. Subsequent difference Fourier syntheses enabled all heavier atoms to be located. After several cycles of refinement, all hydrogen atoms were located from the successive difference Fourier syntheses. All non-hydrogen atoms were finally refined with anisotropic

displacement parameters by full-matrix least-squares techniques. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. Detailed information about the crystal data and structure determination are summarized in Table 1. Selected inter atomic distances and bond angles are given in Table 2.

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Table 2 Selected bond distances (nm) and angles (°) for **1**

Ag(1)-N(4)#1	0.223 6(4)	Ag(1)-N(5)#2	0.231 5(4)	Ag(1)-N(1)3	0.235 3(5)
Ag(1)-N(3)	0.246 7(4)	N(3)-N(4)	0.133 6(5)		
N(4)#1-Ag(1)-N(5)#2	110.55(15)	N(4)#1-Ag(1)-N(1)#3	133.62(17)	N(5)#2-Ag(1)-N(1)#3	101.39(16)
N(4)#1-Ag(1)-N(3)	105.03(14)	N(5)#2-Ag(1)-N(3)	121.28(16)	N(1)3-Ag(1)-N(3)	84.71(15)
C(2)-N(3)-Ag(1)	125.9(3)	N(4)-N(3)-Ag(1)	111.5(3)	C(3)-N(1)-Ag(1)#3	120.2(4)
C(9)-N(1)-Ag(1)#3	117.6(3)	N(4)-N(5)-Ag(1)#4	127.8(3)	N(2)-N(5)-Ag(1)#4	122.0(3)
N(5)-N(4)-N(3)	109.2(4)	N(5)-N(4)-Ag(1)#1	120.8(3)	N(3)-N(4)-Ag(1)#1	129.7(3)

Symmetry transformations used to generate equivalent atoms: 1: $-x, -y+1, -z+1$; 2: $x+1, y, z$; 3: $-x, -y+2, -z$; 4: $x-1, y, z$.

2 Results and discussion

IR spectrum of **1** shows that typical peaks ($\sim 2\ 100\ \text{cm}^{-1}$) of the cyano group in the 3-cyanopyridine ligand disappeared and the appearance of a peak (at *ca.* $1\ 600\ \text{cm}^{-1}$ associated with three peaks at $1\ 581(\text{w}), 1\ 458(\text{w}), 1\ 422(\text{m})\ \text{cm}^{-1}$, respectively) suggests the formation of the tetrazole group.

Crystallographic data of **1** indicates that [(3-PTZ) Ag] (**1**) belongs to crystal system, triclinic, space group $P\bar{1}$ and $Z=2$. The local coordination geometry around each Ag center in **1** (Fig.1) is a slightly distorted tetrahedron defined four N atoms from three different tetrazole and one pyridyl group. Thus, each 3-pyridyl tetrazole (3-PTZ) as a tetradentate ligand coordinates to four different silver centers leads to the formation of the 2D layered network. It is worth noting that two silver atoms, four nitrogen atoms from two different tetrazole rings, for example, Ag1, N3, N4, N4C, N3C, Ag1B, consist of a stable six-membered ring as shown in Fig.1 and each six-membered ring is connected together through side-sharing to 1D infinite chain in which each six-membered ring is not an equal-sided hexagonal with two short side N-N and four long sides Ag-N as shown in Fig.2b. Each such 1D chain is connected by pyridyl group to result in the formation of 2D network containing a six-membered

ring as connecting node as shown in Fig.2c. At the same time, the nearest pyridyl group of 3-PTZ ligand displays weak π - π stacking in ABAB sequence with a distance of pyridine ring stacking of about $0.379\ 7\ \text{nm}$ (X1A-X2B) (Fig.2a). Such 2-D layered structure stack together with ABAB sequence to extend in three-dimension direction (Fig.3). The Ag-N bond distances range from $0.223\ 6(4)$ to $0.246\ 7(4)\ \text{nm}$, and the Ag-Ntetrazole bond lengths are comparable to those found in catena- $(\mu_4\text{-tetrazolato})(\mu_3\text{-tetrazolato})\text{-di-silver(I)}$ ($0.216\ 1\sim 0.238\ 2\ \text{nm}$) and catena-bis- $(\mu_4\text{-tetrazolato})\text{-tri-silver(I)}$ nitrate ($0.219\ 7\sim 0.240\ 9\ \text{nm}$)^[8], while the bond distances of C-N, N-N, C-H are normal and unexceptional. To the best of our knowledge, compound **1** is the third crystallographically characterized Ag-tetrazole coordination polymer^[5].

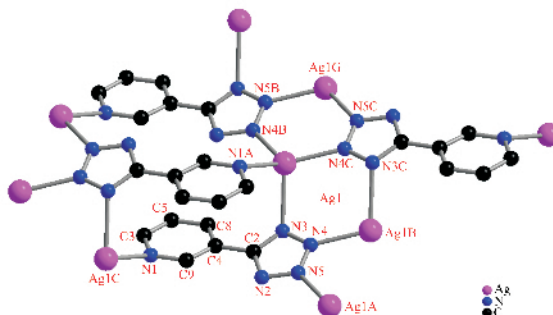


Fig.1 Asymmetry structure of compound **1**

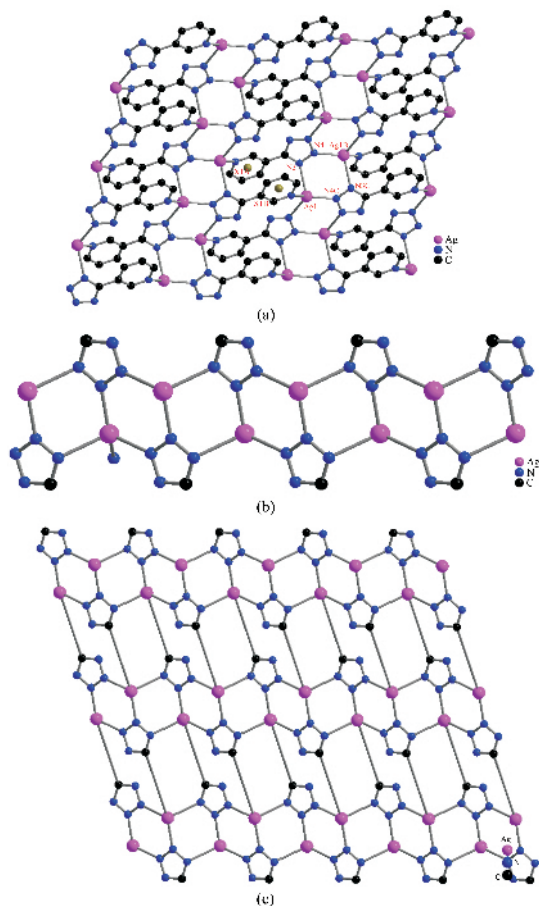


Fig.2 A 2D square grid representation of **1** (a) X1A, X2B is the centers of two different pyridine ring; (b) 1 D chain form from side-sharing six-membered rings (c) 2D layered structure, the long line representation of pyridine ring

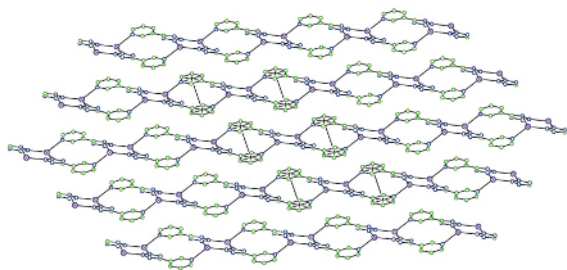


Fig.3 A crystal packing perspective view of **1** (along *a* axis) in which the relationship between layers is in ABAB staggered mode

Interestingly, the solid-state fluorescence spectrum (a Perkin-Elmer LS50B was used for measurement) of powdered **1** at room temperature shows that maximal emission peaks occur in 495 and 521 nm (Fig.4), suggesting **1** may be good blue-light emitted material. **1** have a 2-D condensed polymeric structure;

this unique structure perhaps leads to significant enhancement of the fluorescent intensities, which are approximately two to three times larger than that of free ligand. The enhancement are perhaps a result of coordination of the ligand to Ag, which increases the conformational rigidity of ligand, thereby reducing the non-radiative decay of the intraligand **1** (π - π^*) excited state^[2a,6].

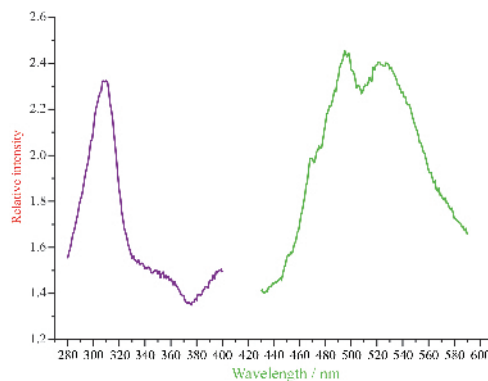


Fig.4 Solid state fluorescent emission spectrum of **1** at room temperature (λ_{ex} =309 nm)

In conclusion, apart from affording a new insight into the nature of the solid formed in the Demko-Sharpley reaction, the work described here demonstrates the value of hydrothermal approaches in the generation of novel coordination polymers. At the same time, this work will enlighten how to synthesize indirectly the tetrazole complex with metals that are easy to reduce or oxidize in synthesis process, and explore functional coordination polymers with novel structure.

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