

N-((喹啉-8-基)亚甲基)水杨酰肼 Sn(IV)/Ag(I) 配合物的合成、晶体结构和 DNA 相互作用

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摘要: 合成并通过单晶衍射、元素分析及红外光谱表征了配合物[Sn(L)Ph₂Cl]·0.25CH₃OH (**1**)和[Ag(HL)(NO₃)]·CH₃OH (**2**)(HL=*N*-((喹啉-8-亚甲基)水杨酰肼)的结构。单晶衍射结果表明, 配合物 **1** 的 Sn(IV)与配体中的 1 个 ON₂ 供体, 1 个氯离子, 2 个苯环上的碳原子配位, 形成扭曲的八面体结构。配合物 **2** 的中心金属离子与配体中的 ON₂ 供体和 1 个双齿硝酸根配位, 拥有扭曲的四方锥配位构型。此外, 荧光光谱表明配合物与 DNA 的相互作用强于配体。

关键词: 喹啉; 配合物; 晶体结构; DNA 相互作用

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Sn(IV)/Ag(I) Complexes of *N*-((Quinolin-8-yl)methylene)salicylhydrazide: Syntheses, Crystal Structures and DNA Interaction

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Abstract: Two complexes, namely, [Sn(L)Ph₂Cl]·0.25CH₃OH (**1**) and [Ag(HL)(NO₃)]·CH₃OH (**2**) based on HL (HL=*N*-((quinolin-8-yl)methylene)salicylhydrazide) were synthesized and characterized by X-ray diffraction analyses. The result shows that the Sn(IV) ion in complex **1** coordinates with one anionic hydrazone ligand with ON₂ donor set, one chloride ion and two carbon atoms coming from two phenyl groups, thus giving a distorted octahedral coordination geometry. The Ag(I) ion in complex **2** that displays a distorted square pyramid coordination geometry is surrounded by one tridentate hydrazone ligand and one bidentate nitrate anions. In addition, the fluorescence spectra indicate that the interactions of the complexes with DNA are stronger than ligand HL. CCDC: 1883407, HL; 1892778, **1**; 1883405, **2**.

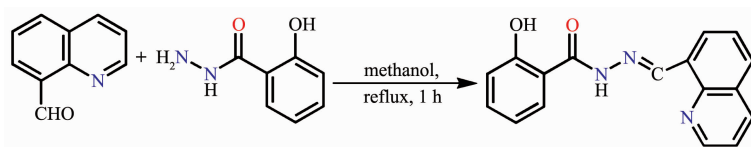
Keywords: quinoline; complex; crystal structure; DNA interaction

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Schiff bases are an important class of ligands in coordination chemistry and have been found extensive application in many different fields^[1-4]. The Schiff base derivatives of acylhydrazone have attracted more attention due to their variable bonding modes towards metal ions and wide range of biological properties, such as antioxidant, anti-inflammatory, antibacterial and antitumor activities^[5]. As one of the most important heterocycles, quinoline is frequently employed for the construction of transition metal complexes with significant pharmacological activities^[6-7]. Our group has reported the structures of several Zn(II)/Cd(II) complexes



Scheme 1 Synthetic route of HL

1 Experimental

1.1 Materials and measurements

Solvents and starting materials for synthesis were purchased commercially and used as received. Elemental analysis was carried out on an Elemental Vario EL analyzer. The IR spectra ($\nu=4\ 000\sim400\text{ cm}^{-1}$) were determined by the KBr pressed disc method on a Bruker V70 FT-IR spectrophotometer. ^1H NMR spectra of HL was acquired with Bruker AV400 NMR instrument in DMSO- d_6 solution with TMS as internal standard. The UV spectra were recorded on a Purkinje General TU-1800 spectrophotometer. The interactions between three compounds and EB-DNA are measured using literature method^[14] via emission spectra on a Varian CARY Eclipse spectrophotometer with the pass width of emission and excitation being 5 nm.

1.2 Preparations of the ligand HL, complexes 1 and 2

As shown in Scheme 1, the ligand HL was prepared by condensation of quinoline-8-carbaldehyde (1.57 g, 10 mmol) and 2-hydroxybenzoyl hydrazine (1.52 g, 10 mmol) in methanol solution (100 mL) under refluxing for 1 h. The white solid was filtered and washed three times by methanol. Yield: 2.01 g (69%). Elemental analysis Calcd. for $\text{C}_{17}\text{H}_{13}\text{N}_3\text{O}_2(\%)$: C 70.09,

with quinoline-containing acylhydrazone^[8]. Nevertheless, the investigation on Ag(I) and Sn(IV) complexes with such type of ligands are relatively scarce. In fact, Ag(I)-based complexes have been known for centuries, especially with respect to medical properties^[9-10], and Sn(IV) compounds are widely used in catalysis, pesticides, polyvinyl chloride stabilizer, preservative, sterilization, anticancer drug and so on^[11-13]. Herein, we report the crystal structures and DNA binding properties of Sn(IV) and Ag(I) complexes with *N*-((quinolin-8-yl)methylene)salicylhydrazide (HL, Scheme 1).

H 4.50, N 14.42; Found (%): C 70.26, H 4.29, N 14.55. FT-IR (cm^{-1}): $\nu(\text{N-H})$ 3 259, $\nu(\text{O=C})$ 1 651, $\nu(\text{C=N})$ 1 604, $\nu(\text{quinoline C=N})$ 1 575. ^1H NMR (400 MHz, DMSO- d_6): δ 12.13 (1H, s, NH-C=O), 12.01 (1H, s, OH), 9.73 (1H, s, CH=N), 8.96~8.98 (1H)/8.36~8.44 (2H)/7.94~8.09 (2H)/7.59~7.72 (2H)/7.40~7.42 (1H)/6.91~6.95 (2H) for Ar-H.

The complexes **1** and **2** were generated by reaction of the ligand HL (5 mmol) with equimolar of Ph_2SnCl_2 and AgNO_3 in methanol solution (10 mL), respectively. Crystals suitable for X-ray diffraction analysis were obtained by evaporating the corresponding reaction solutions at room temperature.

1: Yellow blocks. Anal. Calcd. for $\text{C}_{29.25}\text{H}_{23}\text{ClN}_3\text{O}_{2.25}\text{Sn}(\%)$: C 57.97, H 3.79, N 6.92; Found(%): C 57.76, H 3.82, N 6.75. FT-IR (cm^{-1}): $\nu(\text{N=C-O})$ 1 624, $\nu(\text{C=N})$ 1 589, $\nu(\text{C=N quinoline})$ 1 575.

2: Colorless blocks. Anal. Calcd. for $\text{C}_{18}\text{H}_{17}\text{N}_4\text{O}_6\text{Ag}(\%)$: C 43.83, H 3.47, N 11.36; Found(%): C 43.62, H 3.77, N 11.16. FT-IR (cm^{-1}): $\nu(\text{N-H})$ 3 446, $\nu(\text{N=C-O})$ 1 615, $\nu(\text{C=N})$ 1 586, $\nu(\text{C=N quinoline})$ 1 528, $\nu(\text{NO}_3)$ 1 478 and 1 302.

1.3 X-ray crystallography

The X-ray diffraction measurement for HL, complexes **1** and **2** were performed on a Bruker SMART APEX II CCD diffractometer equipped with

a graphite monochromatized Mo $K\alpha$ radiation ($\lambda = 0.071\ 073\ \text{nm}$) by using $\varphi\text{-}\omega$ scan mode. Semi-empirical absorption correction was applied to the intensity data using the SADABS program^[15]. The structures were solved by direct methods and refined by full matrix least-square on F^2 using the SHELXTL-97 program^[16].

All non-hydrogen atoms were refined anisotropically. All the other H atoms were positioned geometrically and refined using a riding model. Details of the crystal parameters, data collection and refinements for HL, complexes **1** and **2** are summarized in Table 1.

CCDC: 1883407, HL; 1892778, **1**; 1883405, **2**.

Table 1 Selected crystallographic data for HL, complexes **1** and **2**

	HL	1	2
Empirical formula	C ₁₇ H ₁₃ N ₃ O ₂	C _{29.25} H ₂₃ ClN ₃ O _{2.25} Sn	C ₁₈ H ₁₇ N ₄ O ₆ Ag
Formula weight	291.30	606.65	493.22
T / K	296	296	296
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	<i>Pca</i> 2 ₁	<i>P2</i> ₁ / <i>c</i>	<i>Pna</i> 2 ₁
<i>a</i> / nm	1.312 5(2)	1.596 05(12)	2.100 2(13)
<i>b</i> / nm	0.647 38(12)	1.205 79(8)	0.500 5(3)
<i>c</i> / nm	1.661 4(3)	2.804 7(2)	1.793 4(12)
<i>V</i> / nm ³	1.411 6(4)	5.205 4(6)	1.855(2)
<i>Z</i>	4	8	4
<i>D_c</i> / (Mg·m ⁻³)	1.371	1.548	1.738
Unique reflection	2 189	9 172	3 070
<i>R_{int}</i>	0.051	0.036	0.071
GOF	1.021	1.067	1.016
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ =0.043 8, <i>wR</i> ₂ =0.088 7	<i>R</i> ₁ =0.032 1, <i>wR</i> ₂ =0.066 1	<i>R</i> ₁ =0.049 2, <i>wR</i> ₂ =0.095 5
<i>R</i> indices (all data)	<i>R</i> ₁ =0.071 6, <i>wR</i> ₂ =0.102 4	<i>R</i> ₁ =0.051 1, <i>wR</i> ₂ =0.073 9	<i>R</i> ₁ =0.116 6, <i>wR</i> ₂ =0.115 7

2 Results and discussion

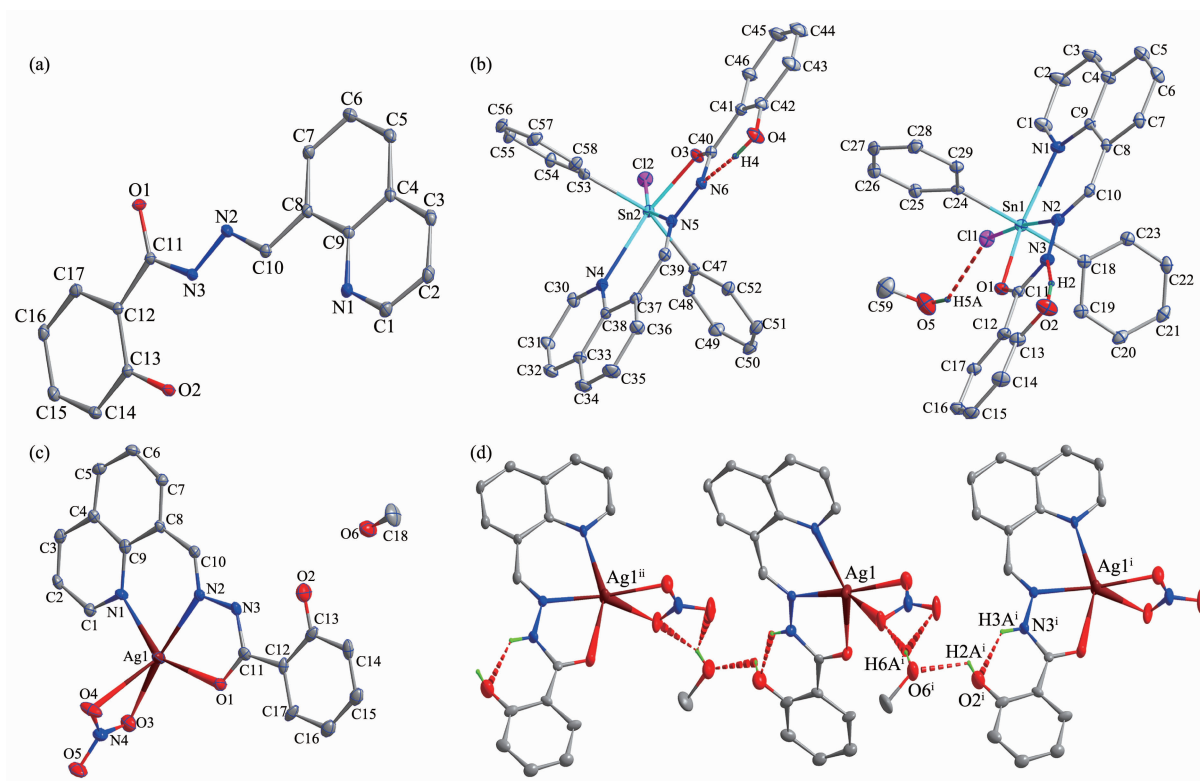
2.1 Crystal structures description

A diamond drawing of HL, complexes **1** and **2** are shown in Fig.1a~c. Selected bond distances and angles are listed in Table 2. The bond length of carbonyl group in HL is 0.122 8(4) nm, which is similar as that in complex **2** (0.124 9(15) nm), while obviously shorter than that in complex **1** (0.128 1(4) and 0.128 9(4) nm). This fact shows that HL is anionic and neutral in complexes **1** and **2**, respectively.

As shown in Fig.1a, the asymmetric unit of complex **1** contains two independent complexes molecules and a half of lattice water molecule. Each six-coordinated Sn(IV) ion is surrounded by two nitrogen atoms coming from quinoline and imine groups, one chloride ion, one oxygen atom coming from carbonyl group and two carbon atoms coming from two phenyl groups, exhibiting a distorted octahedral

coordination geometry. There exist intramolecular O—H···N hydrogen bonds (O2—H2···N3, O4—H4···N6 and O5—H5A···Cl1, with D···A distance being 0.257 8, 0.259 1 and 0.341 0 nm, D—H···A angle being 145°, 144° and 147°, respectively) in the structure.

In complex **2**, the Ag(I) ion is surrounded by one tridentate hydrazone ligand with ON₂ donor set and one bidentate nitrate anions, possessing a distorted square pyramid coordination geometry ($\tau = 0.338$). Furthermore, in the solid structure of **2**, the complex molecules are linked by lattice methanol molecules into chains along *c* axis via various of intermolecular O—H···O hydrogen bonds (O2—H2A···O6, with D···A distance being 0.272 5(18) nm, D—H···A angle being 122.2°; O6—H6A···O4ⁱ, with D···A distance being 0.301 1(17) nm, D—H···A angle being 161.1°; O6—H6A···O5ⁱ, with D···A distance being 0.296 4(18) nm, D—H···A angle being 132.4°, Symmetry codes: ⁱ 1.5−*x*, 0.5+*y*, −0.5+*z*). The intramolecular O—H···O hydrogen



Symmetry codes: ⁱ 1.5-x, 0.5+y, -0.5+z; ⁱⁱ 1.5-x, -0.5+y, 0.5+z

Fig.1 Diamond drawing of HL (a), and complexes **1** (b) and **2** (c) with 10% thermal ellipsoids;
Chain-like structures in complex **2** formed by hydrogen bonds shown in dashed line (d)

Table 2 Selected bond lengths (nm) and angles (°) in HL, complexes **1** and **2**

HL					
C11-O1	0.122 8(4)	C10-N2	0.128 6(5)	C13-O2	0.136 4(5)
1					
Sn1-O1	0.213 2(2)	Sn1-C24	0.214 4(3)	Sn1-C18	0.214 7(3)
Sn1-N2	0.228 2(3)	Sn1-N1	0.236 9(3)	Sn1-Cl1	0.251 47(9)
Sn2-O3	0.208 4(2)	Sn2-C47	0.213 6(3)	Sn2-C53	0.213 7(3)
Sn2-N5	0.232 0(3)	Sn2-Cl2	0.250 34(9)	Sn2-N4	0.252 9(3)
O1-Sn1-C24	89.461(10)	O1-Sn1-C18	90.77(11)	C24-Sn1-C18	178.89(13)
O1-Sn1-N2	72.86(9)	C24-Sn1-N2	93.34(11)	C18-Sn1-N2	87.76(10)
O1-Sn1-N1	151.62(9)	C24-Sn1-N1	88.24(11)	C18-Sn1-N1	92.12(12)
N2-Sn1-N1	79.05(10)	O1-Sn1-Cl1	104.76(7)	C24-Sn1-Cl1	92.29(10)
C18-Sn1-Cl1	86.60(8)	N2-Sn1-Cl1	173.86(7)	N1-Sn1-Cl1	103.59(7)
O3-Sn2-C47	102.63(11)	O3-Sn2-C53	98.77(11)	C47-Sn2-C53	158.47(12)
O3-Sn2-N5	72.34(9)	C47-Sn2-N5	91.34(11)	C53-Sn2-N5	92.94(11)
O3-Sn2-Cl2	88.66(7)	C47-Sn2-Cl2	90.53(9)	C53-Sn2-Cl2	92.27(9)
N5-Sn2-Cl2	160.86(7)	O3-Sn2-N4	147.97(9)	C47-Sn2-N4	78.55(10)
C53-Sn2-N4	82.11(10)	N5-Sn2-N4	75.64(9)	Cl2-Sn2-N4	123.36(7)
2					
Ag1-N2	0.233 0(9)	Ag1-N1	0.238 0(10)	Ag1-O1	0.243 5(9)
Ag1-O3	0.237 4(12)	Ag1-O4	0.266 3(11)		

Continued Table 2

N2-Ag1-O4	142.9(4)	O1-Ag1-O4	108.6(4)	O3-Ag1-N1	103.5(4)
O3-Ag1-O4	48.7(4)	O3-Ag1-O1	107.1(4)	N2-Ag1-O1	69.5(4)
N1-Ag1-O4	98.6(4)	N2-Ag1-O3	168.2(4)	N2-Ag1-N1	78.6(3)
N1-Ag1-O1	147.9(4)				

bonds between amine N atoms and hydroxyl O atoms (N3–H3A···O2, with D···A distance being 0.259 8(15) nm, D–H···A angle being 130.7°) are also present.

2.2 IR spectra

The FT-IR spectral region for both complexes are more or less similar due to the similar coordination modes of the ligands. The $\nu(\text{C}=\text{O})$ of the free ligand was 1 651 cm^{-1} , and it disappeared in the spectra of complexes. Meanwhile, new $\text{N}=\text{C}-\text{O}$ stretching vibration absorption was observed at 1 624 and 1 615 cm^{-1} in complexes **1** and **2**, respectively, revealing that the $\text{C}=\text{O}$ in $\text{O}=\text{C}-\text{N}$ moiety has enolized and the oxygen atom coordinates to the metal ion in both complexes^[8]. The $\nu(\text{C}=\text{N})$ bands of the imine group, quinoline ring in the hydrazone ligand shifted to lower frequency values in the complexes, indicating that the N atoms of such two units take part in the coordination^[17-18]. In addition, the general pattern of the IR spectroscopy for complex **2** supports the normal coordination of bidentate nitrate group^[19]. It is in accordance with the crystal structure study.

2.3 UV spectra

The UV spectra of HL, complexes **1** and **2** were measured in CH_3OH solution ($c=20 \mu\text{mol}\cdot\text{L}^{-1}$) at room temperature (Fig.2). The spectra of HL featured two bands located at 229 nm ($\varepsilon=50\ 168 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) and

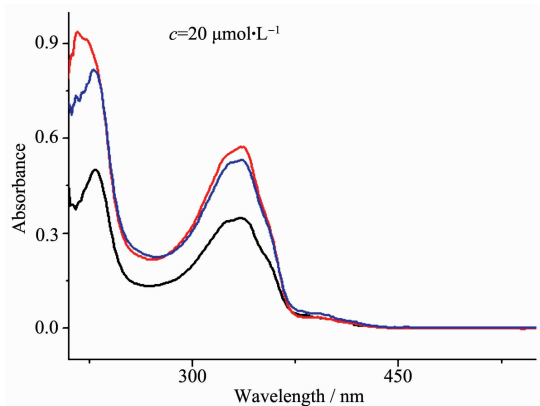
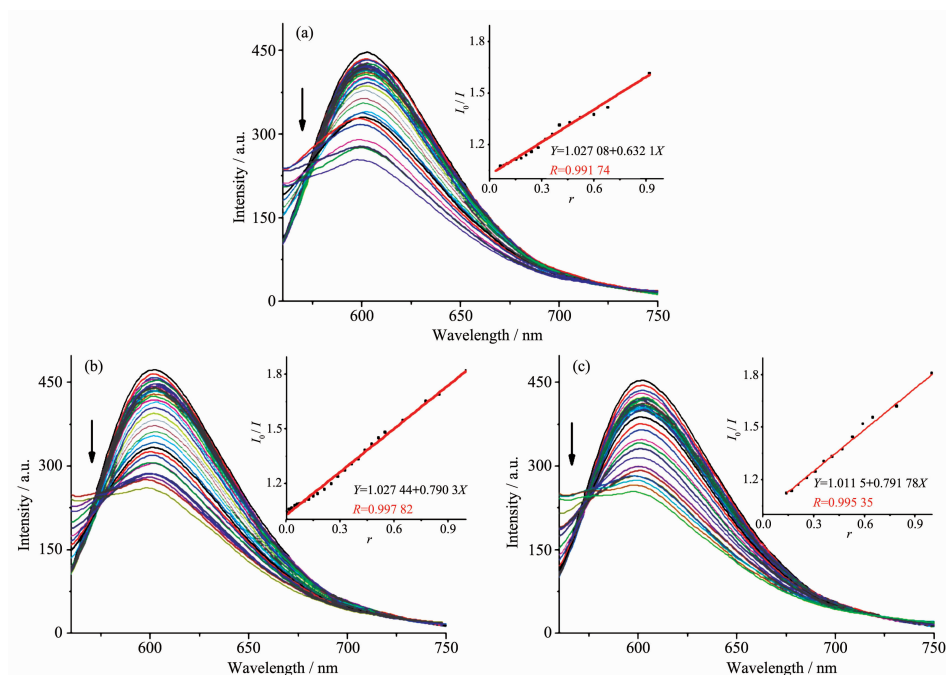


Fig.2 UV spectra of the ligand HL, complexes **1** and **2** in CH_3OH solution at room temperature

336 nm ($\varepsilon=34\ 974 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$), which could be assigned to characteristic $\pi-\pi^*$ transition centered on quinolone ring and the imine moiety^[20], respectively. Both bands exhibited significant hyperchromicity in the spectra of both complexes ($\varepsilon=93\ 738$ and $57\ 310 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ for complex **1**; $\varepsilon=81\ 974$ and $53\ 125 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ for complex **2**), indicating that the ligand HL takes part in the coordination^[21].

2.4 EB-DNA binding study by fluorescence spectra

It is well known that EB can intercalate nonspecifically into DNA, which causes it to fluoresce strongly. Competitive binding of other drugs to DNA and EB will result in displacement of bound EB and a decrease in the fluorescence intensity^[22-23]. The effects of the ligand and complexes on the fluorescence spectra of EB-DNA system are presented in Fig.3. The fluorescence intensities of EB bound to ct-DNA at about 600 nm showed remarkable decreasing trends with the increasing concentration of the tested compounds, indicating that some EB molecules are released into solution after the exchange with the compounds. The quenching of EB bound to DNA by the compounds is in agreement with the linear Stern-Volmer equation: $I_0/I=1+K_{\text{sq}}r$ ^[22], where I_0 and I represent the fluorescence intensities in the absence and presence of quencher, respectively; K_{sq} is the linear Stern-Volmer quenching constant; r is the ratio of the concentration of quencher and DNA. In the quenching plots of I_0/I versus r , K_{sq} values are given by the slopes. The K_{sq} values were 0.632 1, 0.790 3 and 0.791 9 for the ligand HL, complexes **1** and **2**, respectively. The results indicate that interactions of the complexes with DNA are stronger than that of the ligand HL, because the complexes have higher rigidity to bind the base pairs along DNA, thus increasing their binding abilities^[14].



Arrow shows the fluorescence intensities change of EB-DNA system upon increasing tested compound concentration;

Inset: plot of I_0/I versus r , $r=c_{\text{compound}}/c_{\text{DNA}}$

Fig.3 Emission spectra of EB-DNA system in the presence of HL (a) and complexes **1** (b) and **2** (c), respectively

References:

- [1] Beyene B B, Das K, Kerayu B A, et al. *Catal. Commun.*, **2019**,**119**:111-114
- [2] Saghatforoush L, Moeini K, Hosseini-Yazdi S A, et al. *RSC Adv.*, **2018**,**62**:35625-35639
- [3] Yousif E, Ahmed D S, El-Hiti G A, et al. *Polymers*, **2018**: 103-105
- [4] Bourosh P N, Revenko M D, Stratulat E F, et al. *Russ. J. Inorg. Chem.*, **2014**,**59**:545-557
- [5] Bahmudov K T, Kopylovich M N, Pombeiro A J L. *Coord. Chem. Rev.*, **2013**,**257**:1244-1281
- [6] Kasiotis, K M, Fokialakis N, Haroutounian S A. *Synthesis*, **2006**,**11**:1791-1802
- [7] Stringer T, Taylor D, Guzgay H, et al. *Dalton. Trans.*, **2015**, **33**:14906-14917
- [8] XU Zhi-Hong(许志红), WU Wei-Na(吴伟娜), LIU Shu-Yang (刘树阳), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2018**,**34**(2):375-380
- [9] Movahedi E, Rezavani A R. *J. Mol. Struct.*, **2017**,**1139**:407-417
- [10] Písařík P, Jelínek M, Remsa J, et al. *Mater. Sci. Eng. C*, **2017**,**77**:955-962
- [11] Aamal AK, Zhu H B, Harb M, et al. *Catal. Sci. Technol.*, **2017**,**7**:581-586
- [12] Grzeskiewicz A M, Owczarzak A, Kucinska M, et al. *J. Coord. Chem.*, **2017**,**70**:1776-1789
- [13] Attanzio A, Ippolito M, Girasolo M A, et al. *J. Inorg. Biochem.*, **2017**,**7**:36056-36071
- [14] SHEN Wei(沈伟), HU Wei-Ji(胡未极), WU Xiao-Yong(吴小勇), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2016**,**32** (6):1101-1110
- [15] Sheldrick G M. *SADABS*, University of Göttingen, Germany, **1996**.
- [16] Sheldrick G M. *SHELX-97, Program for the Solution and the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.
- [17] Huang Y Q, Zhao W, Chen J G, et al. *Z. Anorg. Allg. Chem.*, **2012**,**638**:679-682
- [18] Huang Y Q, Wan Y, Chen H Y, et al. *New J. Chem.*, **2016**, **40**:7587-7595
- [19] WANG Na(王娜), HE Xin-Qian(贺新前), LIN Qiu-Yue(林秋月), et al. *Journal of the Chinese Rare Earth Society*(中国稀土学报), **2010**,**28**(2):141-146
- [20] Song X Q, Zeng Z P, Liu W S, et al. *J. Solid State Chem.*, **2009**,**182**:841-848
- [21] LI Xiao-Jing(李晓静), WU Wei-Na(吴伟娜), XU Chou-Qing (徐周庆), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2015**,**31**(11):2265-2271
- [22] Yang Z Y, Wang Y, Wang Y. *Bioorg. Med. Chem. Lett.*, **2007**,**17**:2096-2101
- [23] Joseph M, Suni V, Kurup M R P, et al. *Polyhedron*, **2004**, **23**:3069-3080