梯形四核有机锡氧簇合物的合成、表征、量子化学、热稳定性及荧光性质研究

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摘要：在甲醇中三苄基氯化锡与 3,4-二甲氧基苯甲酸发生脱烃基反应，合成了梯形四核有机锡氧簇合物 $[(\mu\text{-O})(\mu\text{-OMe})(L)Sn_2(CH_2Ph)_4]_2$ $(HL=(MeO)_2C_6H_3CO_2H)$，经 UV、IR、元素分析及 X-射线单晶衍射表征结构。该晶体属三斜晶系，空间群 $P\bar{1}$，晶体学参数：$a=1.225\ 6(5)$ nm，$b=1.229\ 4(5)$ nm，$c=1.378\ 0(5)$ nm，$\alpha=69.784(7)°$，$\beta=68.568(7)°$，$\gamma=72.926(7)°$，$V=1.780\ 1(12)$ nm^3，$Z=1$，$D_c=1.549$ g·cm^{-3}，μ(Mo $K\alpha$)$=1.447$ mm^{-1}，$F(000)=832$，$R_1=0.0261$，$wR_2=0.060\ 6$。晶体结构分析表明：整个分子是以 Sn_2O_2 四元环为中心的对称结构，中心锡原子呈五配位畸变三角双锥构型。晶体中，两相邻的配合物分子经 C–H$\cdots\pi$ 作用组成一维带状结构。利用量子化学 G03W 软件，在 LANL2DZ 基组对配合物的稳定性、前沿分子轨道组成及能量进行研究。热重分析表明，配合物在 128 ℃以下能稳定存在。此外，还研究了该配合物的荧光性质。

关键词：有机锡氧簇合物；合成；晶体结构；量子化学；热稳定性

Synthesis, Characterization, Quantum Chemistry, Thermal and Fluorescence Property of a Ladderlike Tetranuclear Organooxotin Cluster

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Abstract: An organooxotin cluster $[(\mu\text{-O})(\mu\text{-OMe})(L)Sn_2(CH_2Ph)_4]_2$ $(HL=(MeO)_2C_6H_3CO_2H)$ has been synthesized by the dealkylation reaction of $(PhCH_2)_3SnCl$ with 3,4-dimethoxybenzoic acid in methanol, and was characterized by UV, IR, elemental analysis and X-ray crystal diffraction. The crystal belongs to triclinic system, space group $P\bar{1}$ with the cell parameters: $a=1.225\ 6(5)$ nm, $b=1.229\ 4(5)$ nm, $c=1.378\ 0(5)$ nm, $\alpha=69.784(7)°$, $\beta=68.568(7)°$, $\gamma=72.926(7)°$, $V=1.7801(12)$ nm^3, $Z=1$, $D_c=1.549$ g·cm^{-3}, μ(Mo $K\alpha$)$=1.447$ mm^{-1}, $F(000)=832$, $R_1=0.026\ 1$ and $wR_2=0.0606$. Crystal structure shows a distorted trigonal bipyramidal configuration with five-coordination for the central tin atom, and the complex has a centrosymmetric structure mode with a four-membered central endocyclic Sn_2O_2 unit. Due to the C-H$\cdots\pi$ interactions between phenyl-H and benzene ring, the adjacent molecules of the complex is linked to generate 1D ribbon structure. A theoretical investigation of one structural unit of the title complex was carried out using Gaussian

03W at LANL2DZ level. The stability and the composition of the frontier molecular orbitals confirmed the coordination geometry of the crystal structure. Thermogravimetric analysis shows that the complex is stable up to 128 ℃. Moreover, its fluorescence spectra was also investigated. CCDC: 841414.

Key words: organooxotin cluster; synthesis; crystal structure; quantum chemistry; thermal stability

0 Introduction

Organotin complexes are an important class of organometallic complexes and have attracted considerable attention for several reasons. Many organotin complexes are used as reagents or catalysts in organic synthesis[1]. Stille reaction utilizes organotin complexes such as R_3SnR' (representative examples include Ph_4Sn, n-$Bu_3SnCH=CH_2$) for the formation of new C-C bonds and is a powerful tool in the synthetic technique of organic chemists[1]. Triorganotin radicals have been used widely in organic synthesis [2], while diorganotin complexes have been used in esterification and transesterification reactions [3-4]. Diorganotin complexes, particularly the di-n-butyl derivatives, are the most effective stabilizers of poly (vinyl chloride)[5]. Moreover, many triorganotin complexes are used as fungicides, acaricides and in antifouling paints [6-8]. Some tri- and diorganotin complexes have shown broad-spectrum antitumour activities[9-10].

Among organotin complexes, organostannoxanes containing four-membered cyclic Sn_2O_2 units are a quite interesting family. Most of the interest in these complexes grows from the fascinating structural diversity which they possess, such as dimer [11], ladder[12-13], cube[14], drum[15], football[16], cage[17], cap[18], crown [19] and butterfly[20] derivatives. And these varied architectures can be gained by varying synthetic methods. In recent years, we also reported a series of organooxotin clusters, including dimer[21], ladder[22], and drum[23] organotin complexes. Generally, it is believed that tetratomic ring is unstable owing to the influence of ring strain, but further studies show that most of which exhibit great stability under normal temperature and pressure conditions. In continuation to our previous work, herein we report the syntheses, characterization, quantum chemistry, thermal and fluorescence property of a new organooxotin cluster $[(\mu\text{-O})(\mu\text{-OMe})(L)Sn_2(CH_2Ph)_4]_2(HL=(MeO)_2C_6H_3CO_2H)$.

1 Experimental Section

1.1 Materials and measurements

Methanol and 3, 4-dimethoxybenzoic acid were of analytical grade obtained from commercial sources and used without further purification. Tribenzyltin chloride was prepared in situ as previously reported[24]. The melting point was obtained on an X-4 microscopic melting point apparatus and is uncorrected. UV-Vis absorption spectrum was recorded on a Shimadzu UV2550 spectrophotometer at room temperature. IR spectra (KBr pellet) was recorded on a Shimadzu IRPrestige-21 spectrometer (4 000~400 cm^{-1} range). Elemental analysis of C, H was performed with a Perkin-Elmer 2400 Ⅱ elemental analyser. Thermal stability was measured on a Netzsch TG 209 F3 thermogravimetric analyzer at a heating rate of 10 ℃·min^{-1} under N_2 atmosphere. Fluorescence (FL) emission spectra were measured using a HITACHI F-7000 fluorescence spectrophotometer.

1.2 Synthesis

A mixture of $(PhCH_2)_3SnCl$ (0.428 g, 1 mmol), 3, 4-dimethoxybenzoic acid (0.182 g, 1 mmol), a few drops of Et_3N and CH_3OH (20 mL) was stirred and heated at reflux for 1 h. After cooling down to room temperature, the solution was filtered. Colorless crystals were obtained by the slow evaporation of methanol solution at room temperature after a week. Yield: 0.297 g (71.6%). m.p. 129~131 ℃. Anal. Calcd. for $C_{76}H_{80}O_{12}Sn_4$ (%): C, 54.98; H, 4.86. Found (%): C, 54.97; H, 4.83. IR (cm^{-1}): 3 022.6 (w, ν_{Ar-H}); 2937.7 (m, ν_{C-H}); 1 600.0 (s, $\nu_{as}COO$); 1 394.6 (m, ν_sCOO); 490.9 (w, ν_{Sn-C}); 452.3 (w, ν_{Sn-O}).

1.3　Determination of crystal structure

　　X-ray diffraction data for the crystal was performed with graphite monochromated Mo $K\alpha$ radiation (λ=0.071 073 nm) on a Bruker Smart Apex Ⅱ CCD diffractometer, and collected by the φ-ω scan technique at 296 (2) K. Multi-scan absorption correction was applied to the data. The crystal structure was solved by direct methods and refined by full-matrix least-squares on F^2. All the non-hydrogen atoms were located in successive difference Fourier syntheses and then refined anisotropically. Hydrogen atoms were placed in calculated positions, and then refined isotropically with the isotropic vibration parameters related to the parent atom. All calculations were performed with SHELXTL-97 programs. Fig.1 was created with Ortep3, Fig.2 was obtained from the DIAMOND 3.1c software package. The crystal data and structure refinement parameters of this complex are listed in Table 1.

　　CCDC: 841414.

Table 1　Crystal data and structure refinement parameters of the complex

Empirical formula	$C_{76}H_{80}O_{12}Sn_4$	D_c / (g·cm^{-3})	1.549
Formula weight	1 660.16	Absorption coefficient / mm^{-1}	1.447
Temperature / K	296(2)	$F(000)$	832
Wavelength / nm	0.071 073	Crystal size / mm	0.43×0.40×0.35
Crystal system	Triclinic	θ range for data collection (°)	1.80 to 25.05
Space group	$P\bar{1}$	Limiting indices	$-14 \leqslant h \leqslant 13$, $-14 \leqslant k \leqslant 14$, $-16 \leqslant l \leqslant 16$
a / nm	1.225 6(5)	Reflections collected/unique	16 597/6 262 (R_{int}=0.024 1)
b / nm	1.229 4(5)	Completeness to θ / %	99.2
c / nm	1.378 0(5)	Data/restraints / parameters	6 262/0/418
α / (°)	69.784(7)	Goodness-of-fit on F^2	1.136
β / (°)	68.568(7)	Final R indices ($I>2\sigma(I)$)	R_1=0.026 1, wR_2=0.060 6
γ / (°)	72.926(7)	R indices (all data)	R_1=0.032 0, wR_2=0.065 7
Volume / nm^3	1.780 1(12)	Largest diff. peak and hole / (e·nm^{-3})	642 and −719
Z	1		
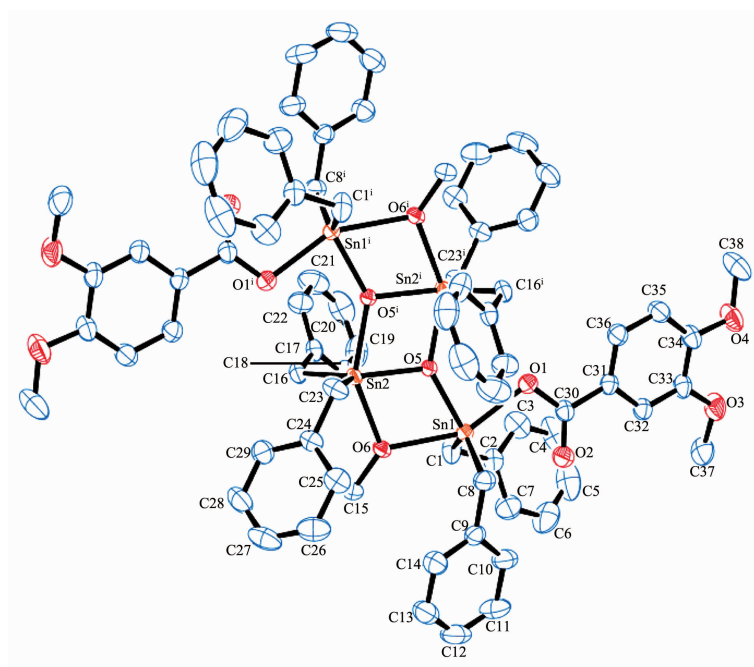
Symmetry code: ^{i} 2−x, 1−y, 1−z; Hydrogen atoms are omitted for clarity

Fig.1　Molecular structure of the complex with 30% probability ellipsoids
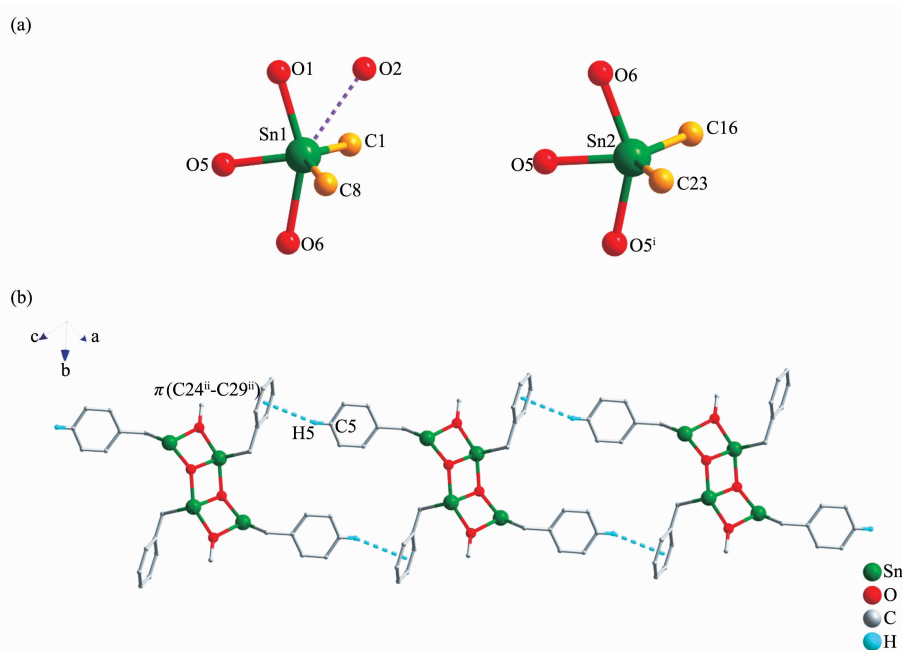
Symmetry codes: ^{i} 2−x, 1−y, 1−z; ^{ii} −1+x, y, 1+z; C5-H5···π(C24^{ii} -C29^{ii}) 0.313 7 nm; carboxylate ligands and some benzyl groups are omitted for clarity

Fig.2　(a) Coordination environment around the two different types of tin centers in the complex; (b) 1D ribbon structure of the complex by C-H···π interactions

1.4　Quantum chemistry calculation

According to the method described in reference[22], quantum chemistry calculation of the complex was performed with Gaussian03W program at B3LYP/LANL2DZ level on a P4 personal computer. For modeling the initial guess of title complex was obtained from the X-ray refinement data. In order to save time, the minimum structural unit of the complex was used in the calculation. The frontier molecular orbital surfaces are visualized by GaussView Molecular Visualization program.

2　Results and Discussion

2.1　IR Spectra

The absorption frequencies of interest are ν (COO), ν(Sn-C) and ν(Sn-O). The absence of a broad band in the range 3 100~2 500 cm^{-1} appearing in the ligand acid, as ν (OH) vibrations, indicating metal-ligand bond formation through this site. Similarly, weak absorption appear at 490.9 and 452.3 cm^{-1}, assigned to Sn-C and Sn-O bonds, respectively, also support the formation of complex [25]. The shift in ν (COO) vibrations to lower frequencies as compare to

ligand acid and magnitude of $\Delta\nu$(COO) (205.4 cm^{-1}) indicating a monodentate nature of the carboxylate towards the Sn atom[26]. The $\Delta\nu$(COO) value of the complex is close to 200 cm^{-1}, which indicates that Sn ···O weak interaction exist between tin atom and non-bonded oxygen atom of carboxyl group. This was confirmed by X-ray diffraction.

2.2　Description of the structure

The molecular structure of the complex is shown in Fig.1. Selected bond lengths and angles are given in Table 2. The molecular of title complex adopts a centrosymmetric structure by virtue of μ_3-oxo (O5, O5^i) (^{i} 2−x, 1−y, 1−z) (Sn2−O5 0.204 7 nm, Sn2-O5^i 0.214 9 nm) which form the central R$_4$Sn$_2$O$_2$ core with planar Sn$_2$O$_2$ ring, resulting in a ladder type structural motif. The two oxygen atoms of this unit are tridentate as they link three Sn atoms, two endo-cyclic (Sn2, Sn2^i) and one exo-cyclic (Sn1 for O5, Sn1^i for O5^i). The distance between the endocyclic and exocyclic tin is 0.343 0 nm and the distance between the two endocyclic tin atoms is 0.334 0 nm. The additional links between the endo- and exo-cyclic Sn are provided by bidentate deprotonated methanol that

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

Sn1-O5	0.204 3(2)	Sn1-C1	0.214 6(4)	Sn1-C8	0.215 5(4)
Sn1-O1	0.217 0(2)	Sn1-O6	0.228 8(2)	Sn2-O5	0.204 7(2)
Sn2-C23	0.213 4(3)	Sn2-O6	0.213 7(2)	Sn2-O5^i	0.214 9(2)
Sn2-C16	0.216 2(3)	O5-Sn2^i	0.214 9(2)		
O5-Sn1-C1	110.38(15)	O5-Sn1-C8	114.54(12)	C1-Sn1-C8	131.12(17)
O5-Sn1-O1	82.74(9)	C1-Sn1-O1	99.85(14)	C8-Sn1-O1	103.84(12)
O5-Sn1-O6	70.61(8)	C1-Sn1-O6	87.76(12)	C8-Sn1-O6	89.60(12)
O1-Sn1-O6	153.26(8)	O5-Sn2-C23	114.33(13)	O5-Sn2-O6	73.73(8)
C23-Sn2-O6	99.87(12)	O5-Sn2-O5^i	74.53(9)	C23-Sn2-O5^i	96.66(11)
O6-Sn2-O5^i	148.01(8)	O5-Sn2-C16	123.91(11)	C23-Sn2-C16	121.76(14)
O6-Sn2-C16	97.02(12)	O5^i-Sn2-C16	97.25(12)	Sn1-O5-Sn2	114.00(10)
Sn1-O5-Sn2^i	140.49(10)	Sn2-O5-Sn2^i	105.47(9)	Sn2-O6-Sn1	101.59(9)

Symmetry code: ^{i} 2−x, 1−y, 1−z

form the asymmetrical bridges (Sn2-O6 0.213 7 nm, Sn1-O6 0.228 8 nm). Each exo-cyclic Sn atom is also coordinated by a monodentate carboxylate ligand (Sn1-O1 0.217 0 nm). The Sn1⋯O2 distance 0.280 3 nm is considered long for primary Sn-O bonding, but represent a type of secondary interaction[27]. The bond angles are O5-Sn2-O5^i 74.53° and Sn2-O5-Sn2^i 105.47° at the μ_3-O atom and O5-Sn2-O6 73.73°, Sn2-O6-Sn1 101.59°, O6-Sn1-O5 70.61°, Sn1-O5-Sn2 114.00° at the μ_2-OMe group.

For the complex, all of the tin atoms are five-coordinated by two Bn-C (Bn: benzyl) atoms and three O atoms, resulting in C_2SnO_3 trigonal bipyramidal coordination environments with two Bn-C atoms (C1 and C8 for Sn1, C16 and C23 for Sn2) and one O atom (O5) in equatorial positions and the other two O atoms (O1 and O6 for Sn1, O6 and O5^i for Sn2) in axial positions (shown in Fig.2a). The axial O-Sn-O angles are not 180° but 153.26° for O1-Sn1-O6 of Sn1, 148.01° for O6-Sn2-O5^i of Sn2, which indicate that the structures are distorted trigonal bipyramidal. The distortions may be related to the rigid framework of the ladder. If the weak Sn1⋯O2 interaction is taken into account, the geometry of Sn1 atom is best described as distorted octahedron.

The formation of the distannoxanes represents an example of ladder-type carboxylates in which the insertion of μ_2-OMe group occurs. Crystal structure of

the complex features a μ_2-coordination of -OMe. This result can be interpreted in terms of donor strength competition, in which the -OMe groups show higher donor capacity than the carboxylate group of the ligand[28-29].

In addition, for the complex, intermolecular C-H⋯π interactions between 4-Ph-H of benzyl groups and benzene ring of benzyl groups in a adjacent molecule (C5-H5⋯π(C24^{ii}-C29^{ii}) 0.313 7 nm, ^{ii} −1+x, y, 1 +z) result in the formation of a 1D ribbon structure (shown in Fig.2b).

2.3 Quantum chemistry study

The calculation covered 86 atoms, 492 basis functions, 1 284 primitive gaussians, 162 α electrons and 162 β electrons. For this complex, the total molecular energy is −1 929.273 641 50 a.u., the energies of HOMO and LUMO are −0.188 13 and −0.088 40 a.u., respectively. The $\Delta E(E_{LUMO}-E_{HOMO})$ value is 0.099 73 a.u., which shows the complex is stable in the ground state.

In order to explore the bonding characteristics of the complex, the molecular orbitals were investigated systematically. The sum of the square of atomic orbital coefficient was used to represent the contribution of each type of atom to molecular orbital and normalized. The atoms of the complex were divided into four groups (Sn; O; C; H).
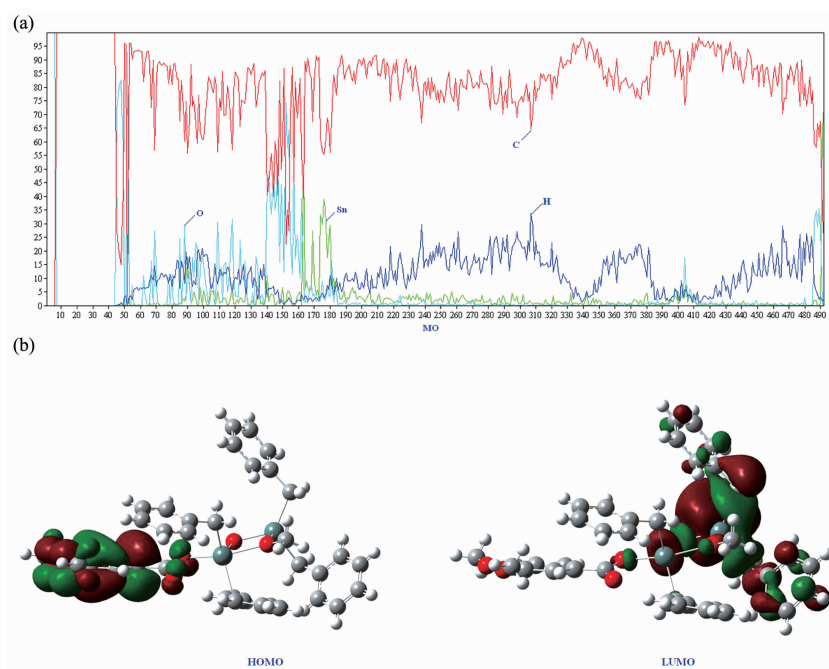
Molecular orbitals composition of the complex is

Fig.3　(a) Molecular orbitals composition of the complex at LANL2DZ level; (b) Schematic diagram of frontier MO for the complex

Table 3　Calculated some frontier molecular orbitals composition (%) of the complex at LanL2DZ level

MO	E / a.u.	Sn	O	C	H
162_{HOMO}	−0.188 13	0.16	39.28	56.33	4.20
163_{LUMO}	−0.088 40	51.38	7.32	39.36	1.93

shown in Fig.3a, the frontier molecular orbitals component of the complex is shown in Fig.3b, the contribution of C, H, O and Sn atoms to HOMO and LUMO are listed in Table 3. We can see that the HOMO is composed chiefly of O and C atoms (the sum of the two is 95.61%), while the LUMO is mainly formed by Sn and C atoms　(the sum is 90.74%). Certainly when electron transfer occurs from ground state to excited state, electrons mainly transfer from O and C atoms to Sn atom to generate a charge transfer complex.

2.4　Thermal analysis

　　Thermogravimetric analyse was carried out for the complex, in order to investigate its thermal stability　(see Fig.4). The thermogravimetric curve shows that the complex is stable up to 128 ℃, and then a noticeable weight loss up to 361 ℃ is seen (nearly 56.5%). After this, no weight loss occurs. Assuming that the residue corresponds to SnO_2, the
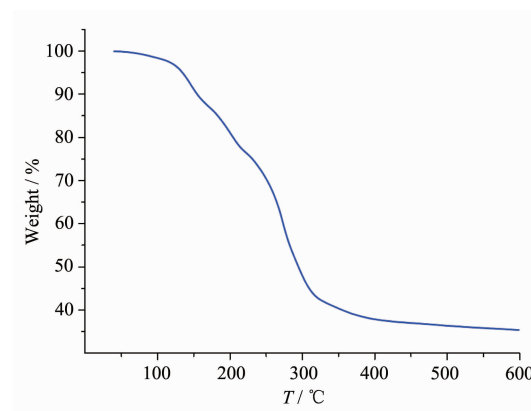

Fig.4　Thermogravimetric analysis curve of the complex

observed weight of residue is basically in agreement with the calculated value　(Calcd. 36.3%). Thus, the organotin complex described herein show good thermal stability.

2.5　UV-Vis spectrum analysis

　　The optical property of the ligand $(2.0 \times 10^{-5}$ mol· $L^{-1})$ and complex　$(1.0 \times 10^{-5}$ mol·$L^{-1})$ were

characterized by UV-Vis spectrum in methanol at room temperature (Fig.5). As can be seen that the absorption spectra of the complex is similar to the ligand. The well-defined absorption peaks at 254 nm and 288 nm for the ligand are assigned to E_2-bands and B-bands[30], respectively. While the peak intensity at 288 nm for the complex obviously decreased and the other absorption band appeared at 248 nm with enhanced intensity and blue-shift (6 nm).
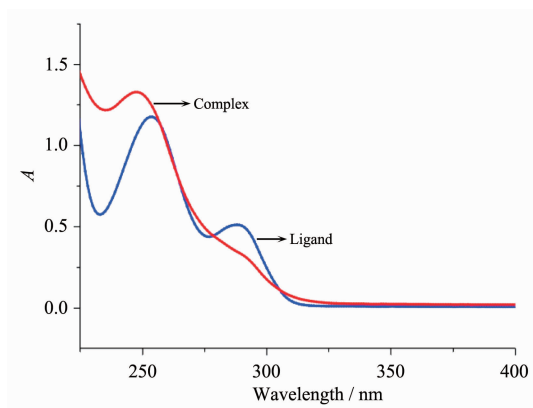

Fig.5　Absorption spectra of the complex and ligand

2.6　Fluorescence Property

Fluorescence behaviours of the ligand and complex have been studied in methanol at room temperature with sample concentration of 2.0×10^{-5} mol·L^{-1} and 1.0×10^{-5} mol·L^{-1}, respectively. The results show the emission spectrum of the complex is a broad band peaking at 340 nm with the excitation wavelength of 290 nm, which is similar to that of the ligand (shown in Fig.6). This could be due to intraligand π_1-π_1* transitions [31]. Compared to luminescence spectrum of the free ligand, the complex
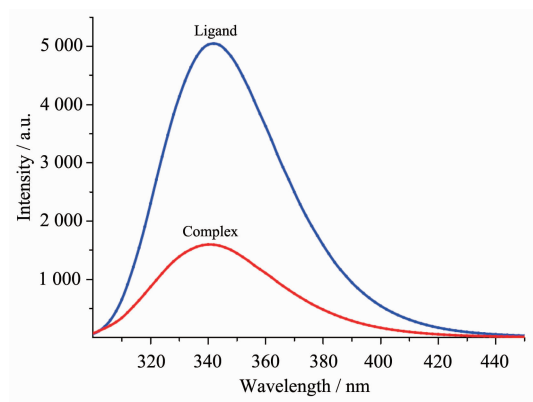

Fig.6　Emission spectra of the complex and ligand

showed a slight blue-shift (2 nm) and the fluorescence intensity in the complex decreased.

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