2-苯基-4-硒唑甲酸铜(Ⅱ)配合物的合成、晶体结构和生物活性

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摘要: 采用溶液法合成了一种新型铜(Ⅱ)配合物$[Cu_2(NO_3)_2L(phen)_2(H_2O)]NO_3$(HL=2-苯基-4-硒唑甲酸,phen=1,10-邻菲啰啉)。用元素分析、红外光谱等表征手段确定了配合物的组成;用单晶 X-射线衍射测定了配合物的晶体结构。配合物 $C_{34}H_{24}Cu_2N_8O_{12}Se$ 属于三斜晶系,空间群 $P\bar{1}$。用溴化乙锭荧光探针法研究了配合物与 DNA 的相互作用。分别考察了配体和配合物对五种细菌:大肠埃氏杆菌(*E.coli*), 表皮葡萄球菌(*S.epidermidis*), 草绿色链球菌(*S.viridans*),金黄色葡萄球菌(*S. aureus*),鲍曼不动杆菌(*A.baumanii*)的抗菌活性。同时也考察了配体和配合物对人类胰腺癌 PANC-28 细胞和人类肝癌 HuH7 细胞的体外增殖抑制作用。实验结果表明配合物具有良好的生物活性。

关键词: 铜(Ⅱ)配合物; 2-苯基-4-硒唑甲酸; 1,10-邻菲啰啉; 晶体结构; 生物活性
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A Copper(Ⅱ) Complex Constructed by 2-Phenyl-4-selenazole Carboxylic Acid: Synthesis, Crystal Structure and Biological Activity

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Abstract: A copper(Ⅱ) complex $[Cu_2(NO_3)_2L(phen)_2(H_2O)]NO_3$, (HL=2-phenyl-4-selenazole carboxylic acid, phen=1,10-phenanthroline), was synthesized and characterized by elemental analysis and IR spectra. Its crystal structure was determined by single crystal X-ray diffraction method. The complex, $C_{34}H_{24}N_8Cu_2O_{12}Se$, crystallized in the triclinic system, space group $P\bar{1}$. The interaction of the complex with DNA was studied by ethidium bromide (EB) fluorescence spectroscopy. The antibacterial activities of the ligand and the complex against five species of bacteria, Escherichia coli (*E. coli*), Staphylococcus epidermidis (*S. epidermidis*), Streptococcus viridans (*S. viridans*), Staphylococcus aureus (*S. aureus*) and Acinetobacter baumanii (*A. baumanii*), were tested respectively. The anticancer activities of the ligand and the complex against human pancreatic cancer line PANC-28 and human hepatocarcinoma line HuH7 were also studied by employing MTT assay. The results revealed that the complex possessed significant biological activity. CCDC: 804066.

Key words: copper(Ⅱ) complex; 2-phenyl-4-selenazole carboxylic acid; 1,10-phenanthroline; crystal structure; biological activity

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Selenium is one of the necessary microelements for vital movement. It plays a significant role [1-3] in anti-oxidation, anti-aging, protecting the heart, tumour prevention and treatment, relieving side reaction caused by chemotherapy drugs, increasing drug tolerance, reducing cisplatin nephrotoxicity and ototoxicity, maintaining normal endocrine function and so on. Since the 1980s, a large number of bioactive organoselenium compounds have been synthesized, and selenazole derivatives exhibit favorable antitumor and antibacterial activity. This indicates they possess potential function which can be used as drugs and drug intermediates. Srivastava and Boritzk [4-5] found selenazofurin was a highly efficient antiviral and antitumor drug, which exhibited significant *in vitro* inhibitory activity against lymphoblastic leukemia diseased cells P338 and L1210, Kumar[6-7] also found some selenazole derivatives exhibited in vitro antiproliferative activity against cell L1210. Copper is also an important life element. The interaction between polypyridine (such as phen and its derivatives) transition metal (such as Cu, Ru, Co and so on) complexes and DNA has drawn extensive attention [8-12]. Numerous studies concluded that polypyridine copper complexes possessed plentiful potential biological activities due to the intercalation of the complexes into DNA, such as Sigman [13] confirmed some polypyridine copper complexes exhibited nuclease activity; researches conducted by Thomas [14] and Reddy [15] revealed some polypyridine copper complexes possessed photocleavage activity. So it′s significant to carry out the research concerning mechanisms and bonding abilities between copper (Ⅱ) selenazole carboxylic acid polypyridine complexes and DNA, which can help us to design and synthesize DNA secondary structure probes, nucleic acid location reagents and anti-cancer drugs.

As yet, the research about selenazole complexes is still very rare. There are a few reports [16-20] just concerning the synthesis and structural study. We have reported some selenazole derivative complexes [21-22] containing 2-phenyl-4-selenazole carboxylic acid (HL) before, so as a continued and innovative work, a novel mixed ligand copper (Ⅱ) complex ($[Cu_2(NO_3)_2L(phen)_2(H_2O)]NO_3$) have been synthesized and characterized, and its crystal structure was also determined. The interaction intensity and mode between the complex and DNA were studied by ethidium bromide (EB) fluorescent probe. The antibacterial activity and the anticancer activity were also studied.

1 Experimental

1.1 Materials and methods

Calf thymus DNA (CT-DNA) was prepared with 0.1 mol·L^{-1} NaCl. The concentration of CT-DNA was 200 μg·mL^{-1} (c_{DNA}=3.72×10^{-4} mol·L^{-1}). The CT-DNA solutions were stored at 4 ℃ and gave a ratio of UV-Vis absorbance at 260 and 280 nm, A_{260}/A_{280} of 1.8, indicating that DNA was sufficiently free of protein. The buffer solution, 0.0l mol·L^{-1} Tris-HCl (tris (hydroxymethyl) aminomethane hydrochloride (pH 7.4)), was prepared with double-distilled water. *E.coli*, *S. epidermidis*, *S. aureus*, *A. baumanii* and *S. viridans* were supplied by Jinhua municipal hospital of Zhejiang province. Human cancer lines PANC-28 and HuH7 were purchased from Shanghai Institute of Cellular Biology of Chinese Academy of Sciences. All the other solvents and reagents were purchased as analytical grade from commercial sources and used without further purification.

Elemental analyses of C, H and N were carried out on a Vario EL III elemental analyzer. The metal contents were determined by EDTA complexometric titration after decomposing a konown amount of the complexes with concentrated nitric acid. IR spectra with KBr pellets were recorded on a Nicolet NEXUS-670 FTIR spectrometer in the range of 400 ~ 4 000 cm^{-1}. X-ray single-crystal determination was performed on a Bruker Smart APEXII-CCD diffractometer. The optical density (OD) was measured by using a Perkin-Elmer LS55 spectrophotometer.

1.2 Synthesis of the complex

$Cu(NO_3)_2·3H_2O$ (0.121 g, 0.5 mmol) in 10 mL 50% ethanol was added dropwise into the solution of 2-phenyl-4-selenazole carboxylic acid (0.252 g, 1 mmol) and 1,10-phenanthroline (0.100 g, 0.5 mmol) in

absolute ethanol (20 mL) with continuous stirring, then the pH value of mixture solution was adjusted to 5~6 by adding NaOH (0.5 mol·L^{-1}) and refluxed at 80 ℃ for 4 h. Few solid precipitates were filtered, blue block single crystals of complex suitable for X-ray diffraction were obtained from above filter solutions by slow evaporation of the solvent at room temperature after 4 weeks, then washed by ethanol and dried. Yield 40% (based on $Cu(NO_3)_2 \cdot 3H_2O$). IR (KBr, cm^{-1}): 3 423 (m), 3 059 (w), 1 627 (s), 1 560 (s), 1 512(m), 1 503 (m), 1 464 (s), 1 428 (m), 1 380 (s), 1 336(s), 1 269(s), 1 146(w), 1 109(w), 1 034(w), 907(w), 850 (m), 813(w), 767(m), 722(s), 626(w). Anal. Calcd. for $Cu_2C_{34}H_{24}N_8O_{12}Se$ (%): C, 43.32; H, 2.57; N, 11.89; Found (%): C, 43.21; H, 2.55; N, 11.79.

1.3 Fluorescence quenching experiments

EB was used as fluorescence probe for studying the mode and intensity of the interaction of complexes and DNA. Fluorescence quenching experiments were carried out by adding different volumes of complex solution (10^{-4} mol·L^{-1}) to a 10 mL colorimetric cylinder prepared 2 h in advance, which contained 2.0 mL 100 μg·mL^{-1} EB, 1.0 mL 200 μg·mL^{-1} CT-DNA and 2.0 mL Tris-HCl buffer solution (pH 7.4), then the mixed solutions were diluted with double-distilled water. The final solutions were incubated for 12 h at 4 ℃. Then fluorescence was recorded at excitation wavelength of 251 nm and emission wavelength between 520 and 700 nm.

1.4 Antimicrobial and anticancer activity assays

Growth of the cultures was monitored on a spectrophotometer by measuring the OD of bacterium suspensions at 600 nm. The inhibition ratio of compounds against bacteria was calculated as follows: inhibition ratio (%)=(1−OD_a/OD_b)×100%, where OD_a and OD_b represent the optical density of bacterium suspensions in the absence and presence of compounds. Benzylpenicillin sodium and ciprofloxacin were used as the comparison. All experiments were performed in triplicate and data were showed as mean values ±standard deviation (SD). The anticancer activity of the complexes against human pancreatic cancer line PANC-28 and human hepatocarcinoma line HuH7 were also studied by employing MTT assay in this work following the standard procedure [23], each experiment was carried out on at least three separate occasions and data were showed as mean values±SD. Cis-platinum(Cis-Pt) was used as the comparison.

1.5 Crystallographic study

The single crystal of the complex with approximate dimensions of 0.38 mm×0.25 mm×0.17 mm was mounted on a Bruker Smart Apex CCD diffractometer. The diffraction data were collected using a graphite monochromated Mo Kα radiation (λ= 0.071 073 nm) at 296 (2) K. Absorption corrections were applied using SADABS [24]. The structure was solved by using the program SHELXS-97 [25] program package and refined with the full-matrix least-squares technique based on F^2 using the SHELXTL-97 [26] program package. Hydrogen atoms were placed in geometrically calculated positons and refined as riding atoms with a common fixed isotropic thermal parameter. H atoms on water molecules were located in a difference Fourier map and included in the subsequent refinement using restrains (d(O−H)=0.085 nm, d(H···H)=0.130 nm) with U_{iso}(H)=1.5 U_{eq}(O). Other hydrogen atoms were added theoretically. All pertinent crystallographic data for the complex is summarized in Table 1. The select bond distances and bond angles are listed in Table 2.

CCDC: 804066.

2 Results and discussion

2.1 IR spectra

Two absorption peaks at 1 627 ($\nu_{as\ (COO^-)}$) and 1 428 cm^{-1} ($\nu_{a\ (COO^-)}$) appearing in the spectra of complex show the coordination of the carboxylate oxygen atoms with the central Cu^{2+} ions [27]. Three bands occurring at 1 512 ($\delta_{C=N}$), 850 (δ_{C-C}) and 722 cm^{-1} (δ_{C-H}), support the coordination of nitrogen atoms from phen[28]. The broad absorption band at 3 423 cm^{-1} may be assigned to the hydroxy group of water, which shows the present of water in the complex, while the absorption peaks at 907 and 626 cm^{-1} indicate the coordination of water. Three absorption peaks at 1 464, 1 269 and 1 039 cm^{-1} are assigned to two

Table 1 Crystllographic data for the complex

Empirical formula	$C_{34}H_{24}Cu_2N_8O_{12}Se$	D_c / (g·cm^{-3})	1.788
Formula weight	942.65	Absorption coefficient / mm^{-1}	2.333
Temperature / K	296(2)	Crystal size / mm	0.38×0.25×0.17
Crystal system	Triclinic	F(000)	944
Space group	$P\bar{1}$	Reflections collected	25 323
a / nm	1.037 71(6)	Unique reflections	6 155
b / nm	1.272 45(8)	Observable reflections ($I>2\sigma(I)$)	5 163
c / nm	1.406 66(9)	θ_{min}, θ_{max} / (°)	1.50, 25.00
α / (°)	97.333(3)	Data/restraints/parameters	6 155/814/514
β / (°)	100.414(4)	Goodness-of-fit (on F^2)	1.076
γ / (°)	103.172(3)	Final R indices ($I>2\sigma(I)$)	R_1=0.039 8 ,wR_2=0.110 1
V / nm^3	1.750 88(19)	R indices (all data)	R_1=0.049 1, wR_2=0.114 7
Z	2	$\Delta\rho_{max}$, $\Delta\rho_{min}$ / (e·nm^{-3})	1 009, −932

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

Cu(2)-O(2)	0.1960(2)	O(1)-C(21)	0.1256(4)	Cu(1)-O(6)	0.2293(4)
Cu(2)-O(3)	0.1987(3)	O(1)-Cu(1)	0.1980(3)	O(2)-C(21)	0.1263(5)
Cu(2)-N(1)	0.1990(3)	Cu(1)-N(3)	0.1990(3)	Se(1)-C(23)	0.1835(4)
Cu(2)-N(2)	0.2018(3)	Cu(1)-O(1W)	0.2000(3)	Se(1)-C(24)	0.1894(4)
Cu(2)-N(5)	0.2416(3)	Cu(1)-N(4)	0.2009(3)		
O(2)-Cu(2)-O(3)	92.49(12)	N(1)-Cu(2)-N(5)	113.50(11)	O(1W)-Cu(1)-N(4)	165.04(12)
O(2)-Cu(2)-N(1)	168.87(12)	N(2)-Cu(2)-N(5)	101.34(11)	O(1)-Cu(1)-O(6)	82.44(12)
O(3)-Cu(2)-N(1)	93.23(13)	C(21)-O(1)-Cu(1)	128.0(3)	N(3)-Cu(1)-O(6)	101.36(13)
O(2)-Cu(2)-N(2)	91.64(12)	O(1)-Cu(1)-N(3)	172.61(12)	O(1W)-Cu(1)-O(6)	94.65(14)
O(3)-Cu(2)-N(2)	173.34(12)	O(1)-Cu(1)-O(1W)	95.10(11)	N(4)-Cu(1)-O(6)	99.79(14)
N(1)-Cu(2)-N(2)	81.85(12)	N(3)-Cu(1)-O(1W)	90.93(12)	C(21)-O(2)-Cu(2)	123.1(2)
O(2)-Cu(2)-N(5)	76.54(10)	O(1)-Cu(1)-N(4)	90.69(12)	C(23)-Se(1)-C(24)	85.59(18)
O(3)-Cu(2)-N(5)	84.72(11)	N(3)-Cu(1)-N(4)	82.44(13)		

coordinated nitrate anions which behave as monodentate ligand. The appearance of three bands at 1 380, 813 and 767 cm^{-1} is expected due to the existence of the uncoordinated nitrate anion[29-31]. These results are consistent with the X-ray diffraction analysis.

2.2 Crystal structure

X-ray diffraction analysis reveals that the basic asymmetric unit of the complex contains two Cu^{2+} ions, two phen ligands, one 2-phenyl-4-selenazole carboxylic acid anion (L^-), one uncoordinated nitrate anion, two coordinated nitrate anions and one coordinated water molecule, in which the two Cu^{2+} ions are bridged by two carboxylic oxygen atoms from L^- (Fig.1). Cu1 and Cu2 are both five-coordinated, but in different coordination environments. The five atoms coordinated to Cu1 are two nitrogen atoms (N3, N4) from one phen ligand and three oxygen atoms (O1, O1W, O6) from L^-, coordinated water molecule, one nitrate ion, respectively. However, Cu2 is coordinated with five atoms (N1, N2, N5, O2, O3) from the other phen ligand, L^- and another nitrate ion. That is to say, three coordination sites (NO2) from L^- are coordinated atoms in the complex, which is similar to the coordination modes of 2, 2-bipyridine-6, 6-dicarboxylic acid reported by Bünzli [32] and 2-

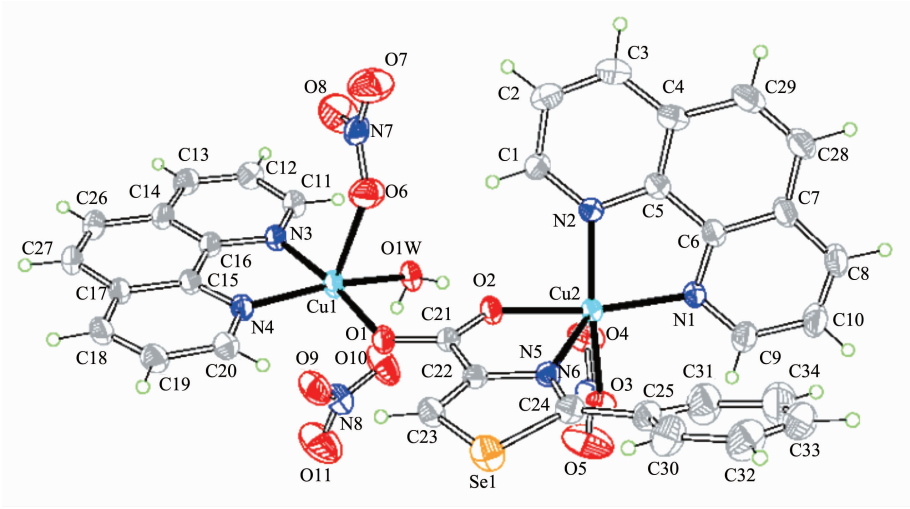
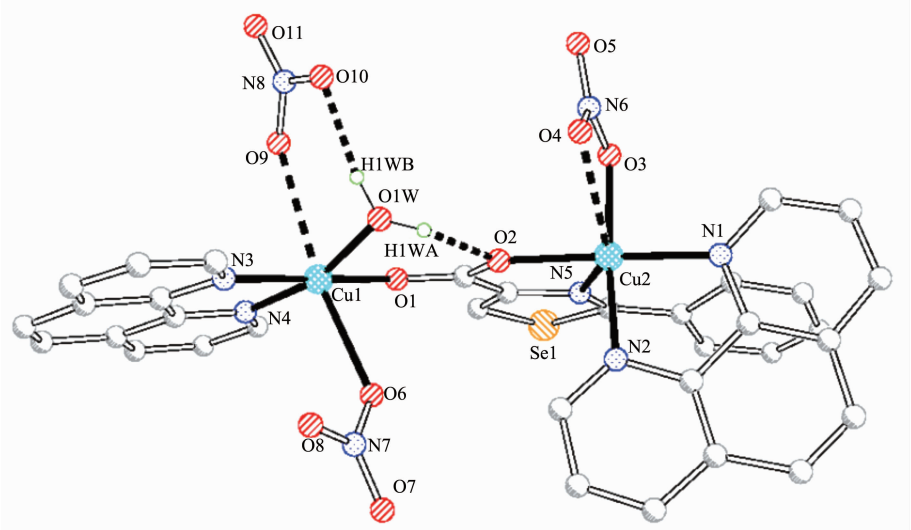


Fig.1　Molecular structure of complex, ellipsoids are shown at the 30% probability level

(hydroxymethyl)pyridine derivatives reported by Weber[33].

There are persistent weak bonding interactions between copper atoms and oxygen atoms. The distances of Cu1⋯O9 and Cu2⋯O4 are 0.262 6(37) and 0.255 6 (43) nm. These are longer than the Cu-O binding distances (Cu1-O1 0.197 9 (28) nm; Cu1-O6 0.229 3 (37) nm; Cu2-O2 0.196 0 (31) nm; Cu2-O3 0.198 7(26) nm) and much shorter than the sum of the van der waals radii between Cu and O (0.384 0 nm), which indicates the existence of strong weak bonding interactions of Cu1 ⋯ O9 and Cu2 ⋯ O4. These interactions enhance the stability of the complex and make each Cu^{2+} ion exhibiting a slightly distorted octahedral geometry (Fig.2). What´s more, through the hydrogen binding interaction of O1W-H1WB ⋯ O10, the nitrate anion is further fixed and a six numbered ring (Cu1, O1W, H1WB, O10, N8, O9) is formed. Another six numbered ring (Cu1, O1W, H1WA, O2, C21, O1) is also formed as the result of the hydrogen binding interaction of O1W –H1WA ⋯ O2. These interactions make the complex connected more closely and enhance the stability of the molecular structure in some degree. The hydrogen bond lengths and angles



Hydrogen bonds and weak bonds are described as dash lines

Fig.2　Structure of the complex formed via hydrogen bonds and weak bonds

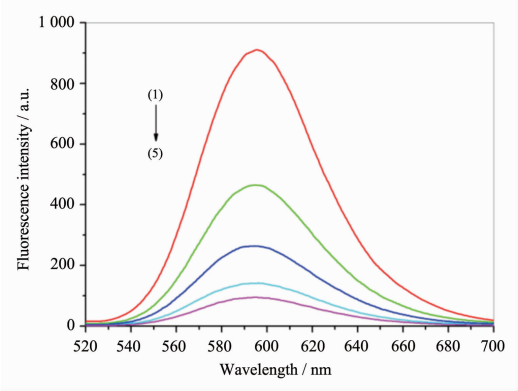
Table 3 Hydrogen bond geometry of the complex

D-H···A	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D···A) / nm	∠DHA / (°)
O(1W)-H(1WA)···O(2)	0.085	0.187	0.268 6(4)	161.6
O(1W)-H(1WB)···O(10)	0.085	0.183	0.265 9(5)	163.9
O(1W)-H(1WB)···O(9)	0.085	0.234	0.300 8(5)	136
O(1W)-H(1WB)···N(8)	0.085	0.242	0.325 1(5)	166.1

are listed in Table 3.

2.3 Fluorescence quenching studies

Fluorescence quenching experiments results (Fig. 3) revealed the fluorescence intensities of EB bound to CT-DNA at 592 nm showed remarkable decreasing trends with the increasing concentration of the complex, which indicated the evident intercalation of the complex into CT-DNA. According to the classical Stern-Volmer equation[34]: $I_0/I=1+K_{sq}r$, where I_0 and I are the emission intensity in the absence and presence of the complex, respectively, K_{sq} is the quenching constant, and r is the concentration ratio of the compound to DNA. The K_{sq} value can be obtained as a slope from the plot of I_0/I versus r linear plot. The K_{sq} value is 2.144 for the complex, indicating the strong intercalation of the complex into CT-DNA[35-36].



From (1) to (5): $r=c_{compound}/c_{DNA}=0, 0.27, 0.54, 0.81, 1.08$, respectively

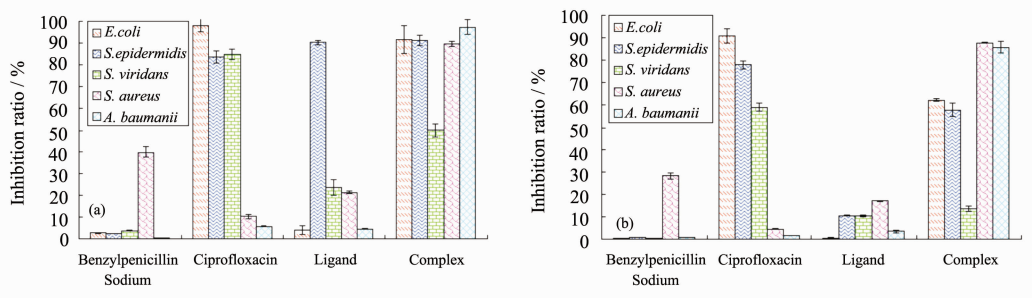
Fig.3 Emission spectra of EB-DNA system in the absence and presence of the complex

2.4 Antimicrobial activity

The antimicrobial activity results (Fig.4) of four compounds (benzylpenicillin sodium, ciprofloxacin, ligand and complex) in the concentrations of 1.0×10^{-3} and 1.0×10^{-4} mol·L^{-1} against *E. coli*, *S. epidermidis*, *S. viridans*, *S. aureus* and *A. baumanii* were presented. In both concentrations, the complex possessed stronger antibacterial activity than the ligand; the complex strongly inhibited the growth of five above tested bacteria in comparison with benzylpenicillin sodium; when compared to ciprofloxacin, the complex exhibited weaker antibacterial activity against *E. coli*, *S. epidermidis*, and *S. Viridans*, but stronger activity against *S. Aureus* and *A. Baumanii*.

2.5 Anticancer activity

The ligand and the complex were examined for *in vitro* anticancer activities against human cancer lines PANC-28 and HuH7. The IC_{50} values of the above two tested compounds, as well as *Cis*-Pt, included as positive control, were listed in Table 4. The results revealed that the ligand didn't show better inhibiting effect against above two cancer lines, however, the complex exhibited much stronger inhibiting effect than



(a) $c_{compound}=1.0\times10^{-3}$ mol·L^{-1}; (b) $c_{compound}=1.0\times10^{-4}$ mol·L^{-1}.

Fig.4 Inhibition ratio of compounds against five species of bacteria (%, x±SD)

Table 4　Inhibitory effects of compounds on cancer cells proliferation in vitro (x±SD)

Compound	Cell lines IC_{50} / (μg·mL^{-1})	
	PANC-28	HuH7
Ligand	863.572±0.012	1 563.570±0.032
Complex	0.717±0.001	3.590±0.010
Cis-Pt	10.240±0.002	19.220±0.001

Cis-Pt, which indicated the complex possessed significant anticancer activity and was a potential and highly active anti-cancer drug.

3　Conclusions

In conclusion, a novel mixed ligand copper(Ⅱ) complex, which contains 2-phenyl-4-selenazole carboxylic acid and phen, has ben synthesized and characterized. The interaction of the complex with CT-DNA has been investigated via the fluorescence spectroscopy, and the results indicate the intercalation of complex into CT-DNA is very strong. This maybe due to that the large rigid aromatic ring plane of phen increases the insertion ability of its compounds. The biological activities of the complex have been evaluated by antimicrobial and anticancer assay, the complex exhibits stronger antimicrobial activities than benzylpenicillin sodium. The anticancer activities of the complex are much higher than *Cis*-Pt, which provides clues for the research and development of this potential and highly active anti-cancer drug in the future.

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