Synthesis, Crystal Structure, Fluorescence Property and Antibacterial Activity of Two Unprecedented One-dimensional Chain Metal-organic Coordination Polymers: $Zn(H\text{-}SSA)(Phen)(H_2O)_2$ and $Cu(H\text{-}SSA)(Phen)(H_2O)_2$

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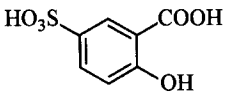
The reaction of 5-sulfosalicylic acid (H_3-SSA) with *o*-phenanthroline (Phen), NaOH, and MCl_2(M = Zn, Cu) affords Zn(H-SSA)(Phen)$(H_2O)_2$(1) and Cu(H-SSA)(Phen)$(H_2O)_2$(2), respectively. Compounds 1 and 2 are characterized by elemental analysis, IR, fluorescence spectra and single crystal X-ray diffraction analysis. The X-ray diffraction analyses reveal that compounds 1 and 2 are isostructure. The 5-sulfosalicylic acid ligand loses two protons at the sulfo-group and carboxylic group during the reaction. The Zn(II) and Cu(II) ions are six-coordinated and adopt distorted octahedral geometry, which are surrounded by two N atoms from Phen, two O atoms from two water molecules, one O atom from $-SO_3$ group and one oxygen from carboxylic group of the other H-SSA. Compounds 1 and 2 have unprecedented one-dimensional linear chain formed by a repeating mononuclear structural unit, which is bridged by H-SSA. The fluorescence intensity of 1 and 2 is stronger than that of Phen and H_3-SSA at 400 nm. The lowest excited single states of these complexes are assigned as mainly Phen localized $^1(\pi,\pi^*)$. The antibacterial activity test shows that compounds 1 and 2 strongly inhibit the growth of *Streptococcus haemolyticus*, *Straphylococcus aureus* and *Escherichia coli*.

Keywords Zn(II) complex, Cu(II) complex, 5-sulfosalicylic acid, crystal structure, chain, fluorescence property, antibacterial activity

Introduction

Salicylic acid (2-oxybenzoic acid, H_2Sal) and its derivatives have been known for a long time to possess anti-inflammatory activity,[1] while it has been found that the biological activity of a wide variety of organic drugs is enhanced upon their metal complexation.[2,3] For example, bis(salicylato)copper(II) is a stronger analgesic and anti-inflammatory agent for animals than salicylic acid itself,[4] and the copper(II) complex of aspirin, Cu_2(aspirin)$_4$, is a more effective anti-inflammatory and anti-rheumatoid agent than aspirin itself.[5,6] In addition, it has been found to have anti-ulcer activity[7,8] and inhibit the rate of tumor growth.[9] As one of salicylic acid derivatives, 5-sulfosalicylic acid (H_3-SSA) (Scheme 1) has been found to have biological activity, its metal complexes with Cu(II), Ni(II), Co(II), Mn(II), Fe(II), Zn(II), and V(IV)O exhibit stronger antimicrobial activity than that of the free ligand,[10] and the antifungal activity is in the order: Cu(II) > Ni(II) > Co(II) > Fe(II) > Mn(II) > V(IV)O.[11] Mohan *et al*. investigated the anti-inflammatory activity of the cupric complexes of pyridine-2, 6-dicarboxylic acid with sulfosalicylic acid.[12] Pang and co-workers studied the rare earth sulfosalicylate complexes and their antibacterial effect and found that all rare earth complexes showed strong antifungal activity against *Eubacteria*.[13,14] Besides, similar to 1,4-benzenedicarboxylate,[15] 1,3-benzenedicarboxylate[16] and 3,3′-azodibenzoate[17] ligands, 5-sulfosalicylic acid possesses polydentate function and is very interesting in supramolecular architecture. Thus the crystal structure studies on 5-sulfosalicylate metal complexes have aroused much interest, in particular, their rare earth element complexes[18-24] and copper(II) complex.[25]

Scheme 1 5-Sulfosalicylic acid



Although there are many reports with regard to the bioinorganic chemistry focused on the 5-sulfosalicylate metal complexes, their crystal structure data and antibacterial activity information are still absent, especially, the relationship between the structure and antibacterial activity. Herein, we report the synthesis, crystal structure, fluorescence property and antibacterial activity of two one-

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dimensional chain metal-organic coordination polymers: $Zn(H\text{-}SSA)(Phen)(H_2O)_2$ (**1**) and $Cu(H\text{-}SSA)(Phen)(H_2O)_2$ (**2**).

Experimental

Synthesis

Materials and physical measurements All reagents were purchased and used as received. Elemental analysis for C, H, and N were performed on a Varlo ERBA 1106EL elemental analyzer. Infrared spectra were measured on a Nicolet FT-IR 170SX spectrophotometer using KBr pellets in the range of 400—4000 cm^{-1}. The UV-vis data were recorded on a Varian CARY 100 Conc type Violet-visible spectrophotometer. The fluorescence intensity measurements were carried out on a Shimdazu RF-540 fluorescence spectrometer at room temperature.

Preparation of $Zn(H\text{-}SSA)(Phen)(H_2O)_2$ (**1**)
5-Sulfosalicylic acid (0.5 mmol) was dissolved in 10 mL of distilled water, and Phen (0.5 mmol) was dissolved in 10 mL of ethanol. Two solutions were mixed, and the resultant solution was adjusted to pH = 8—9 using 1 mol/L NaOH, then the aqueous solution (10 mL) of zinc chloride (1 mmol) was added, and yellow precipitate occurred by refluxing and stirring for 4 h. The reaction mixture was filtered and the precipitate was washed with ethanol and dried in air. The filtrate was stayed at ambient temperature. After two weeks, the yellow block crystal was obtained. Yield 47%; UV-vis (DMSO) λ_{max}: 272.6, 293.8 nm; IR (KBr) ν: 3410 (ms), 3037 (ms), 1622 (s), 1590 (s), 1566 (s), 1478 (w), 1383 (s), 1046 (w), 856 (w), 768 (ms), 703 (ms) cm^{-1}. Anal. calcd for $C_{19}H_{16}ZnN_2O_8S$: C 45.94, H 3.25, N 5.64; found C 46.12, H 3.32, N 5.88.

Preparation of $Cu(H\text{-}SSA)(Phen)(H_2O)_2$(**2**)
Except using copper chloride replacing zinc chloride, the procedure is same to that for compound **1**. Blue block crystal was obtained. Yield 50%; UV-vis (DMSO) λ_{max}: 274.2, 294.7 nm; IR (KBr) ν: 3422 (ms), 3166 (ms), 1627 (ms), 1588 (ms), 1431 (ms), 1343 (w), 1251 (ms), 1226 (ms), 1151 (s), 1027 (ms), 853 (w), 724 (w), 677 (w), 600 (w) cm^{-1}. Anal. calcd for $C_{19}H_{16}CuN_2O_8S$: C 46.10, H 3.26, N 5.66; found C 45.84, H 3.33, N 5.77.

X-*Ray structure determination*

Crystallographic data and refinement parameters for **1** and **2** are given in Table 1. Data collection was performed on a Bruker CCD area detector with MoKα radiation (λ = 0.071073 nm) using the ω-2θ scan technique at 294(2) K. The structure was solved by direct methods and refined by full matrix least-squares and difference Fourier techniques with SHELXTL-97 program. All non-hydrogen atoms were refined anisotropically. The position of hydrogen atoms was refined based on calculation in ideal positions using ride model.

Table 1 Crystallographic data and refinement parameters for **1** and **2**

Complex	**1**	**2**
Empirical formula	$C_{19}H_{16}ZnN_2O_8S$	$C_{19}H_{16}CuN_2O_8S$
M_r	497.77	495.94
Crystal size (mm^3)	0.30×0.28×0.26	0.28×0.20×0.16
Crystal system	Monoclinic	Monoclinic
Space group	*P*2(1)/*c*	*P*2(1)/*c*
μ (mm^{-1})	1.430	1.297
a (nm)	1.43088(19)	1.4107(4)
b (nm)	0.76512(11)	0.7769(2)
c (nm)	1.8597(3)	1.8553(6)
β (°)	108.076(3)	108.839(6)
V (nm^3)	1.9355(5)	1.9245(10)
Z	4	4
D_c(Mg/m^3)	1.708	1.7078
F(000)	1016	1008
T (K)	294(2)	294(2)
$R_1[I>2\sigma(I)]$	0.0304	0.0358
wR_2	0.0822	0.0926
Max./min. peaks ($e\cdot nm^{-3}$)	492 and −505	590 and −441

$w = 1/[\sigma^2(F_o^2) + (0.0550P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

Antibacterial activity test

The complexes were suspended into distilled water, and orbicular filter scrip method was used for testing all samples. The process is similar to that of antibacterial tests of bismuth(III)-quinolone against *Helicobacter pylori* and some other bacteria.[26]

All tested strains (*Streptococcus haemolyticus*, *Straphylococcus aureus*, *Escherichia coli and Pseudomonas aeruginosa*) were freshly isolated from clinical material and dissolved in 15 mL of sterilized agar culture media in 40 ℃, respectively, which were inoculated to sterilizedculture dish. After being stirred to homodisperse, stayed horizontally, and cooled the culture medium of strains were obtained.

The suspensions of complexes and orbicular filter scrip with the diameter of 6 mm were sterilized at 120 ℃ and under high pressure. Then minimum of suspensions were dropped in filter scrip, and put into culture dish containing culture medium of strains after drying in room temperature. Then the culture dish was placed into culture box of biochemistry at 37 ℃ for 72 h. The comparison experiments by using penicillin, *Streptomyces griseus*, gentamycin and normal saline were carried out.

Results and discussion

Description of the structure

The selected bond lengths and bond angles for compounds **1** and **2** are listed in Table 2. The ORTEP drawings of **1** and **2** are shown in Fig. 1. The one-dimensional linear chains of **1** and **2** are given in Fig. 2. Packing perspective views of **1** and **2** are shown in Fig. 3.

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

$Zn(C_7H_4SO_6)(C_{12}H_8N_2)(H_2O)_2$ (**1**)		$Cu(C_7H_4SO_6)(C_{12}H_8N_2)(H_2O)_2$ (**2**)	
Zn(1)—O(1)	0.21754(13)	Cu(1)—O(1)	0.23791(17)
Zn(1)—O(6)	0.20373(13)	Cu(1)—O(6A)	0.19529(17)
Zn(1)—N(1)	0.21288(16)	Cu(1)—N(1)	0.2010(2)
Zn(1)—N(2)	0.21438(16)	Cu(1)—N(2)	0.2017(2)
Zn(1)—O(1W)	0.20361(14)	Cu(1)—O(1W)	0.19537(19)
Zn(1)—O(2W)	0.21615(14)	Cu(1)—O(2W)	0.2418(2)
S(1)—O(1)	0.14563(13)	S(1)—O(1)	0.14497(17)
S(1)—O(2)	0.14643(13)	S(1)—O(2)	0.14704(17)
S(1)—O(3)	0.14489(14)	S(1)—O(3)	0.14474(18)
S(1)—C(17)	0.17632(17)	S(1)—C(17)	0.1762(2)
C(19)—O(6)	0.1282(2)	C(19)—O(5)A	0.1285(3)
C(14)—O(4)	0.1349(2)	C(19)—O(6)	0.1230(3)
C(13)—C(19)	0.1492(3)	C(13)—C(19)	0.1500(3)
C(19)—O(5)	0.1232(2)	C(14)—O(4)	0.1345(3)
O(6)-Zn(1)-O(1W)	94.80(6)	O(5A)-Cu(1)-O(1W)	91.44(8)
O(6)-Zn(1)-O(1)	80.57(5)	O(5A)-Cu(1)-O(1)	79.01(7)
O(6)-Zn(1)-N(2)	173.35(6)	O(5A)-Cu(1)-N(2)	172.65(8)
O(6)-Zn(1)-N(1)	97.46(6)	O(5A)-Cu(1)-N(1)	95.52(8)
N(1)-Zn(1)-N(2)	77.81(6)	N(1)-Cu(1)-N(2)	81.95(8)
O(1W)-Zn(1)-N(2)	89.66(6)	O(1W)-Cu(1)-N(2)	90.63(8)
O(1W)-Zn(1)-N(1)	167.17(6)	O(1W)-Cu(1)-N(1)	171.89(9)
O(1W)-Zn(1)-O(1)	87.34(5)	O(1W)-Cu(1)-O(1)	88.15(7)
N(1)-Zn(1)-O(1)	90.92(6)	N(1)-Cu(1)-O(1)	89.10(7)
N(2)-Zn(1)-O(1)	94.74(5)	N(2)-Cu(1)-O(1)	94.01(7)
O(6)-Zn(1)-O(2W)	91.50(5)	O(5A)-Cu(1)-O(2W)	94.76(7)
O(1W)-Zn(1)-O(2W)	94.77(5)	O(1W)-Cu(1)-O(2W)	96.56(7)
N(1)-Zn(1)-O(2W)	88.71(6)	N(1)-Cu(1)-O(2W)	87.02(8)
N(2)-Zn(1)-O(2W)	93.04(5)	N(2)-Cu(1)-O(2W)	92.01(7)
O(1)-Zn(1)-O(2W)	171.95(5)	O(1)-Cu(1)-O(2W)	172.32(6)

$-x, y+1/2, -z+1/2; -x, -y, -z; x, -y-1/2, z-1/2.$

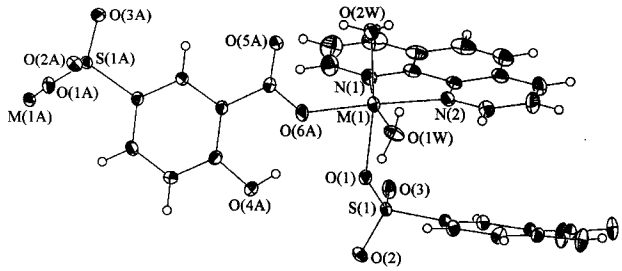

Fig. 1 ORTEP drawing of **1** and **2** [M = Zn(II), Cu(II)].

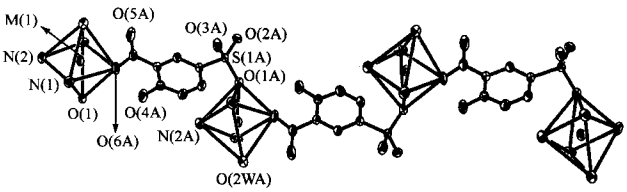

Fig. 2 One-dimensional linear chain highlighting. The C atoms of phen and the H atoms are omitted for clarity.

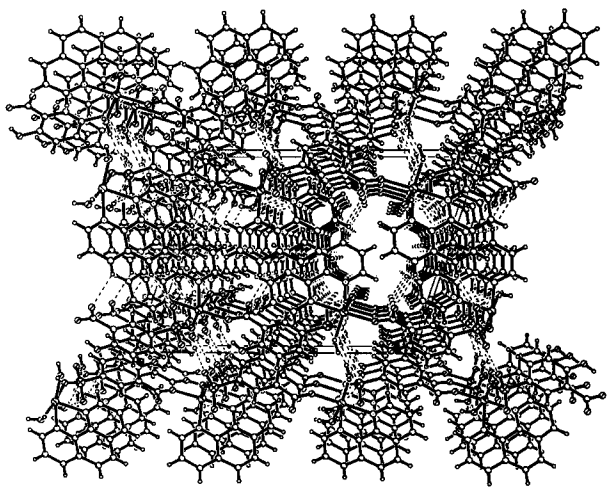

Fig. 3 Paking perspective view of **1** and **2** showing three-dimensional supramolecular strong hydrogen-bonding interactions along *b*-axis.

The 5-sulfosalicylate anion ($H\text{-}SSA^{2-}$), which loses its two protons at carboxylate and sulfonate groups, coordinates bidentately to metal ion through the carboxylate and sulfonate groups giving rise to an unprecedented one-dimensional linear chain. But the phenolic proton remains unchanged, which is distinguished from that of sodium [triaqua(5-sulfosalicylato)copper(II)]$_2$ hemihydrate[25] and $\{Na_3TbLa_2(C_7H_3SO_6)_4 \cdot 26H_2O\}_n$.[18] The coordination geometry around the Zn(II) or Cu(II) center in **1** or **2** can be best described as a distorted octahedron (Fig. 1) because of the adjacent angles deviating greatly. The metal center is six-coordinated through bonding to two oxygen atoms supplied by the carboxylate group of 5-sulfosalicylate ligand and the sulfonate group of the other H-SSA, respectively, two N atoms from Phen, and two terminal water molecules. Two O atoms from one terminal water molecule and one carboxylate of H-SSA, and two N atoms from Phen, bind to Zn(II) or Cu(II) equatorially, in which N(1), N(2) and M(1) [M = Zn(II) or Cu(II)] is co-planar with the Phen ring, while the O atom from one terminal water molecule and the O atom from the other H-SSA bind to the metal center in axial positions. The bond lengths and angles of compounds **1** and **2** are in normal range, but the Cu—O_{carb} [0.19529(17) nm] and Zn—O_{sulf} [0.21754(13) nm] distances are slightly longer than those of sodium [triaqua(5-sulfosalicylato)copper(II)]$_2$ hemihydrate [Cu—O_{carb} 0.1915(3) nm][25] and zinc(II) 2-sulfanilamidopyrimidine [Zn—O_{sulf}0.2017(13) nm],[27] respectively. Owing to Jahn-Teller Effect, the axial bond distances of Cu(1)—O(1) [0.23791(17) nm] and Cu(1)—O(2W) [0.2418(2) nm] are longer than those of the equatorial bond distances (the average bond distance is 0.19834 nm) in compound **2**, which is common for the Cu(II) d^9 configuration. As shown in Fig. 2, the $H\text{-}SSA^{2-}$ anion acts as a bidentate bridging ligand and links the polyhedron forming one-dimensional linear chain. Such coordination mode for 5-sulfosalicylate is rare in other SSA metal complexes[18,21,25] and different from that of lanthanum(III) sulfosalicylate monohydrate,[23] but resembles that of the metal complex with 1,4-benzenedicarboxylate[15] and 1,3-benzenedicarboxylate[16] and 3,3′-azodibenzoate[17] ligands.

From above discussion, it is easy to find that 5-sulfosalicylate anion as a polydentate ligand is able to form a polymeric structure through covalent bonding interaction. However, if taking into consideration the noncovalent bonding interaction, compounds **1** and **2** can be depicted as three-dimensional networks formed by strong hydrogen bonding (C—H$\cdots O_{car}$ and O_W—H$\cdots O_{sulf}$) (Table 3) and weak π-π stacking interaction (Fig. 3), which may play very important role in their antibacterial activity.

IR *spectra*

Comparing the IR spectra of H_3-SSA and Phen with that of the complexes, the characteristic vibration absorption peak of free carboxylic acid (H_3-SSA) at 1676 cm^{-1} is absent in the complexes, but is split into 1590 cm^{-1}[ν_{as}(COO)] and 1383 cm^{-1}[ν_{as}(COO)] for compound **1** with $\Delta\nu$ = 207 cm^{-1}, and spilt into 1627 and 1431 cm^{-1} for compound **2** with $\Delta\nu$ = 196 cm^{-1}. They are all larger than the value of NaSSA ($\Delta\nu$ = 157 cm^{-1}), indicating that the carboxylic group of H-SSA is coordinated to metal ions in a monodentate mode for the two complexes.[28] The characteristic peaks of Phen ν(C—N) (1420 cm^{-1}) and δ(C—H) (851, 737 cm^{-1}) shift to 1383, 768, and 703 cm^{-1} for compound **1**, respectively, and shift to 1343, 724, and 677 cm^{-1} for compound **2**, respectively. The asymmetric vibration peak of the sulfonate group at 1229 cm^{-1} for SSA is split into 1295 and 1046 cm^{-1} for compound **1**, and split into 1251 and 1226 cm^{-1} for compound **2**, demonstrating that the sulfonate group has taken part in coordination.[18] The appearance of two wide peaks at 3410 and 3037 cm^{-1} for compound **1**, which were assigned

Table 3 Selected hydrogen bonding in compound **1**

	D—H (nm)	H···A (nm)	D···A (nm)	∠(DHA) (°)
O(1W)—H(1WA)···O(2)	0.082	0.191	0.27047(18)	162.7
O(1W)—H(1WB)···O(2)	0.084	0.189	0.27200(19)	170.5
O(2W)—H(2WA)···O(5)	0.082	0.195	0.2689(2)	149.5
O(2W)—H(2WB)···O(3)	0.084	0.201	0.28276(19)	163.5
O(4)—H(4A)···O(6)	0.082	0.186	0.2576(2)	144.8

to the asymmetric and symmetric O—H stretching vibrations respectively, may indicate the presence of coordinated water molecules. Identically, the IR spectrum of compound **2** exhibits two broad peaks at 3422 and 3166 cm^{-1}, which may indicate the existence of coordinated H_2O in compound **2**.[25]

UV-vis *and fluorescence spectroscopy*

The UV-vis spectra of compounds **1** and **2** show that, for compound **1**, there are two strong absorption bands at 272.6 and 293.8 nm, and for compound **2**, two similar absorption bands appear at 274.2 and 294.7 nm. In contrast to that of free ligand Phen (λ_{max} = 300 nm) and 5-sulfosalicylic acid (λ_{max} = 310.1 nm), they are all blue-shifted, which are ascribed to the 0-0 band of the Phen and H-SSA localized $S_0 \rightarrow S_1$ transition, respectively.[29]

5-Sulfosalicylic acid (H_3-SSA), Phen, compounds **1** and **2** were dissolved in DMSO with the same molar concentration of 1×10^{-5} mol · L^{-1}. Their excitation and emission spectral measurements were performed on Shimadzu RF-540 fluorescence spectrometer at room temperature. The luminescence data of **1**, **2**, H_3-SSA and Phen are summarized in Table 4. The emission spectra of compounds **1** and **2** are shown in Fig. 4. It should be pointed out that there are a group of double peaks in the long wave region in their fluorescence spectra. Herein, we only consider the main peaks. Table 4 and Fig.4 indicate that the emission of **1** or **2** is neither MLCT (metal-to-ligand charge transfer) nor LMCT (ligand-to-metal charge transfer) in nature, and is mainly from Phen localized $^1(\pi,\pi^*)$ states since a similar weak emission is also observed for free Phen. However, the maximum emissions of **1** and **2** are red-shifted by 40 nm from that of Phen because they are somewhat influenced by the weak fluorescent emission of H_3-SSA.[18,29,30] This assignment is consistent with that of the $S_0 \rightarrow S_1$ absorption. The fluorescence intensity of **1** or **2** is stronger than that of Phen and H_3-SSA and is enhanced when the ligands (Phen, H_3-SSA) coordinate to Zn(II) and Cu(II). From the structures of **1** and **2** we can explain the fluorescence enhancement as follows: first, the crystal structure analyses reveal that the complexes **1** and **2** are relatively rigid one-dimensional molecules, the H-SSA^{2-} anion acts as a bidentate bridging ligand via two monodentate $-SO_3$ groups and links the metal building block chelated by Phen to form one-dimensional linear chain, which prevents the energy loss by molecular vibration.[18,31] Second, Phen chelates the center metal ion and forms six-membered ring which enlarges the conjugated system of the molecule, and makes the π conjugated system not completely localized on Phen moiety but is somewhat extended to aromatic ring of H-SSA ligands, which results in the emission overlapping.[29] Third, the strong intermolecular hydrogen bonding is advantageous to the fluorescence enhancement, which makes the energy transfer from ligand to ligand more effective.[32]

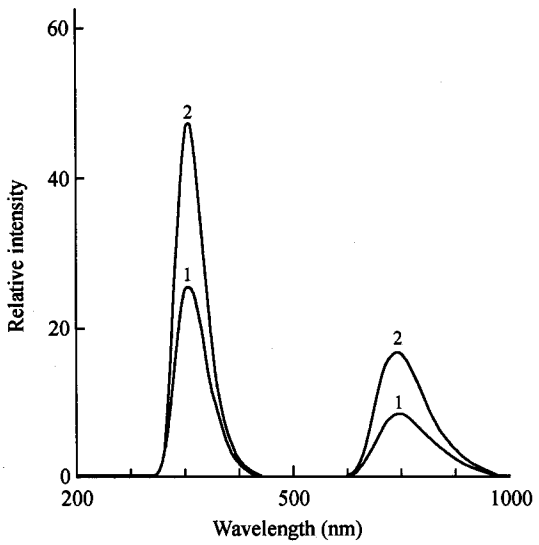

Fig. 4 Emission spectra of **1** and **2** in DMSO at room temperature.

Table 4 Luminescence data of **1**, **2**, H_3-SSA and Phen

Compound	Excitation λ_{max}(nm)	Assignment	Emission λ_{max}(nm) (intensity)	Assignment
1	320	$S_0 \rightarrow S_1$	400 (25), 800 (8)	From $^1(\pi,\pi^*)$
2	310	$S_0 \rightarrow S_1$	400 (47), 800 (17)	From $^1(\pi,\pi^*)$
H_3-SSA	310	$S_0 \rightarrow S_1$	450 (5), 800 (2)	From $^1(\pi,\pi^*)$
Phen	300	$S_0 \rightarrow S_1$	360 (20), 720 (5)	From $^1(\pi,\pi^*)$

Antibacterial activity studies

Using agar cultivated radix, adopting the method of orbicular filter scrip pervasion,[33] we carried out antibacterial activity testing against the common bacteria (such as *Escherichia coli* and *Pseudomonas aeruginosa* of Gram-negative bacteria, and *Straphylococcus aureus* and *Streptococcus haemolyticus* of Gram-positive bacteria). The comparison experiments were accomplished by using penicillin, *Streptomyces griseus*, gentamycin and normal saline. The experiment results are shown in Table 5.

Table 5 indicates that compounds **1** and **2** exhibit strong antibacterial activity against *Streptococcus haemolyticus*, *Straphylococcus aureus* and *Escherichia coli*, of which the diameters of antibacterial ring are bigger than 8 mm. The results show that the antibacterial activities against *Escherichia coli* of compounds **1** and **2** all exceed that of the antibiotic, *Streptomyces griseu*, the antibacterial activity against *Streptococcus haemolyticus* of compound **1** surpasses that of penicillin, but that of **2** is close to penicillin. The antibacterial activity against *Straphylococcus aureus* of **2** is approximately equal to that of penicillin. However, compounds **1** and **2** are not able to inhibit the *Pseudomonas aeruginosa*. As to the antibacterial mechanism of this type of complex, it is still unclear. Generally, it is assumed that the complex can enter the bacteria cell and target the bacterial type II DNA topoisomerase (gyrase) leading to double-stranded DNA breaks and cell death.[33-35]

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 187140 and CCDC No. 187141 for **1** and **2**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: + 44-1223-336033; E-mail: deposit @ ccdc.cam.ac.uk or www: http://www.ccdc.cam.au.uk).

Table 5 Test of the antibacterial activity of **1** and **2**[a]

Bacteria	Diameter of antibacterial ring (mm)					
	1	**2**	Penicillin	*Streptomyces griseus*	Gentamycin	Normal saline
Streptococcus haemolyticus	32	28	30	–	–	–
Staphylococcus aureus	15	31	35	–	–	–
Escherichia coli	30	23	–	21	–	–
Pseudomonas aeruginosa	–	7	–	–	20	–

[a] "–" denoting that the complexes have no antibacterial activity.

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