第 33 卷第 4 期
2017 年 4 月

无 机 化 学 学 报
CHINESE JOURNAL OF INORGANIC CHEMISTRY

Vol.33 No.4
685-691

两个基于苯并咪唑席夫碱的镍(Ⅱ)配合物的合成、晶体结构和抑菌活性

赵海燕* 杨晓东 李 娜
(河北科技大学理学院,石家庄 050018)

摘要: 在甲醇体系中,分别将苯并咪唑席夫碱 HL^1 和 HL^2 与高氯酸镍进行配位反应得到 2 个结构类似的镍配合物$[Ni(L^1)_2]\cdot 2H_2O$ (**1**) 和 $[Ni(L^2)_2]\cdot 2H_2O$ (**2**) (HL^1 =*N*-(benzimidazol-2-ylethyl)-5-chlorosalicylideneimine, HL^2 =*N*-(Benzimidazol-2-ylethyl)-5-bromosalicylidenei-mine),并用元素分析、红外光谱、紫外-可见光谱和单晶 X 射线衍射对其结构进行了表征。结构分析表明:两个配合物均属于单斜晶系,*C*2/*c* 空间群,Ni(Ⅱ)与来自 2 个席夫碱配体的 4 个氮原子和 2 个氧原子配位,形成八面体结构。配合物中的氢键将配合物 **1** 和配合物 **2** 分别连接成二维和三维网络结构。选取金黄色葡萄球菌和大肠杆菌作为菌种,研究了 2 个席夫碱配体和 2 个配合物的抑菌能力。

关键词: 席夫碱; 镍(Ⅱ)配合物; 晶体结构; 抑菌活性
中图分类号: O614.81+3 **文献标识码**: A **文章编号**: 1001-4861(2017)04-0685-07
DOI: 10.11862/CJIC.2017.064

Two Ni(Ⅱ) Complexes of Schiff Base Ligands Containing Benzimidazole Ring: Syntheses, Crystal Structures and Antibacterial Properties

ZHAO Hai-Yan* YANG Xiao-Dong LI Na
(*College of Science, Hebei University of Science and Technology, Shijiazhuang* 050018, *China*)

Abstract: Two complexes $[Ni(L^1)_2]\cdot 2H_2O$ (**1**) and $[Ni(L^2)_2]\cdot 2H_2O$ (**2**) have been synthesized using the bezimidazole derived tridentate (NNO donor) potential Schiff base ligands HL^1 and HL^2, which are prepared from reaction of 2-aminoethyl-1*H*-benzimidazole with 5-chlorosalicylaldehyde and 5-bromosalicylaldehyde, respectively, and characterized by elemental analysis, FT-IR and UV-Vis spectroscopies and single crystal X-ray crystallography. In **1** and **2**, each Ni(Ⅱ) has a distorted octahedral arrangement with a N_4O_2 donor set in trichelated fashion of the Schiff base ligands. Furthermore, the complex units in **1** and **2** are linked into 2D and 3D supramolecular networks by H-bonding in the solid state, respectively. The bioactivity studies showed that both the two complexes exhibit moderate to strong antibacterial activities against *S. aureus* (Gram-positive) and *E. coli* (Gram-negative) bacteria and were found more active than the corresponding Schiff base ligands. CCDC: 1401182, **1**; 1401183, **2**.

Keywords: Schiff base; Ni(Ⅱ) complex; crystal structure; antibacterial activity

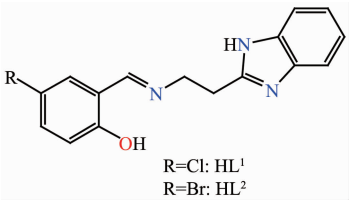
0 Introduction

For decades, Schiff bases and their transition metal complexes have attracted a lot of attention due to their wide biological applications[1-5]. It is obvious that in Schiff bases the azomethine linkage (C=N) is an important structural requirement for biological activity[6]. Metal complexes containing salicylidene

收稿日期:2016-11-07。收修改稿日期:2017-02-04。
2015 年河北科技大学五大平台开放基金课题(No.50)资助。
*通信联系人。E-mail:hbhaiyanzh@163.com;会员登记号:S06N6511M1009。

Schiff bases have been of great interest due to their diverse roles in magnetic, luminescence[7-8] and pharmacological properties[9]. It was also reported that salicylidene Schiff base with halogen atoms in the salicylaldehyde moiety had greater biological activities, like antibacterial and antifungal activities[1,10-11]. Benzimidazole and their derivatives have received considerable attention in recent years due to their wide variety of biological activities including antimicroabial [12], antifungal [13], antitumor [14], antiviral [15] *etc*. However, literature survey shows that study on metal complexes of benzimidazole-derived salicylidene Schiff bases is not rich. Until now, a limited number of Cu(Ⅱ), Ni(Ⅱ) and V (Ⅳ, Ⅴ) complexes with the above type of Schiff base derivatives have been reported[16-24]. On the other hand, much attention has been paid to nickel complexes of Schiff base derivatives because such complexes have various applications, such as, as antibacterial agents, as fungicide agents, in the treatment of cancer and for other biological activities[25-27].

Herein, we report the syntheses, spectral characterizations and crystal structures of two Ni(Ⅱ) complexes by using two benzimidazole-derived Schiff base ligands HL^1 and HL^2 (Scheme 1). Moreover, antibacterial activities of the two ligands and two complexes were also investigated against *S. aureus* (Gram-positive) and *E. coli* (Gram-negative) bacteria.



Scheme 1 Structures of Schiff base ligands HL^1 and HL^2

1 Experimental

1.1 Material and physical measurement

2-Aminoethyl-1*H*-benzimidazole dihydrochloride was prepared by the method reported by Ceson et al.[28]. All of the other reagents were used as received. Microanalyses (C, H, N) were carried out using a Perkin-Elmer 240C analyzer. The infrared spectra in KBr pellets were obtained on a ThermoFisher Nicolet 6700 spectrometer in the 4 000~400 cm^{-1} region. Electronic spectra were carried out in methanol solvent on a Shimadzu UV-2550 spectrophotometer. ^1H NMR spectra were taken in $CDCl_3$ on a Bruker Avance 500MHz spectrometer at room temperature with tetramethylsilane as the internal standard.

1.2 Syntheses of the ligands

1.2.1 Synthesis of *N*-(benzimidazol-2-ylethyl)-5-chlorosalicylideneimine (HL^1)

HL^1 was synthesized by a condensation reaction between 2-aminoethyl-1*H*-benzimidazole dihydrochloride (1.335 g, 5 mmol), previously neutralized with K_2CO_3 (0.83 g, 6 mmol), and 5-chlorosalicylaldehyde (0.605 g, 5 mmol) in 25 mL of methanol. The mixture was stirred at room temperature for two hours and then a yellow precipitate was obtained which was filtered off and washed with cold MeOH and then dried in air. Yield: 96%. m.p. 83~85 ℃. IR (KBr pellet, cm^{-1}): 2 839, 1 637, 1 416, 1 274, 750. ^1H NMR (500 MHz, $CDCl_3$): δ 3.29~3.32 (t, 2H, $-CH_2-$), 4.12~4.15 (t, 2H, $-CH_2-$), 6.86~7.55(m, 7H, Ar-H), 8.28(s, 1H, -CH=N-), 13.12 (b, 1H, OH). UV-Vis (methanol, λ_{max} / nm): 274, 281, 328. Anal. Calcd. for $C_{16}H_{14}ClN_3O$ (%): C, 64.16; H, 4.71; N, 14.03. Found (%): C, 64.30; H, 4.57; N, 14.12.

1.2.2 Synthesis of *N*-(Benzimidazol-2-ylethyl)-5-bromosalicylideneimine (HL^2)

The preparation of HL^2 followed the same procedure described for HL^1 except that 5-bromosalicylaldehyde was used instead of 5-chrolosalicylaldehyde.The ligand precipitated as a yellow solid. Yield: 90%. m.p. 191~193 ℃. IR (KBr pellet, cm^{-1}): 2 840, 1 637, 1 415, 1 273, 752. ^1H NMR (500 MHz, $CDCl_3$,): δ 3.29~3.34 (t, 2H, $-CH_2-$), 4.12~4.17 (t, 2H, $-CH_2-$), 6.82~7.71(m, 7H, Ar-H), 8.29 (s, 1H, -CH=N-), 13.22 (b, 1H, OH). UV-Vis (methanol, λ_{max} / nm): 274, 281, 330. Anal. Calcd. for $C_{16}H_{14}BrN_3O$(%): C, 55.83; H, 4.10; N, 12.21; S, 18.7. Found(%): C, 55.60; H, 4.21; N, 12.34.

1.3 Syntheses of the complexes

1.3.1 Synthesis of $[Ni(L^1)_2]\cdot 2H_2O$ (**1**)

Schiff base HL^1 (0.060 g, 0.2 mmol) was dissolved in MeOH (10 mL) and 0.028 mL NEt_3 was added. A solution $Ni(ClO_4)_2\cdot 6H_2O$, (0.036, 0.1 mmol) in MeOH (10 mL) were then added with stirring at

room temperature. The resulting green solution was stirred for two hours. Green yellow crystals suitable for X-ray structural analysis were obtained by slow evaporation of the solvent after several days. Yield: (0.055 g, 80%). IR (KBr pellet, cm^{-1}): 3 656, 2 901, 1 622, 1 526, 1 458, 1 385, 1 325, 750. Anal. Calcd. for $C_{32}H_{30}Cl_2N_6NiO_4$ (%): C, 55.52; H, 4.37; N, 12.14. Found(%): C, 55.64; H, 4.43; N, 12.35.

1.3.2 Synthesis of $[Ni(L^2)_2]\cdot 2H_2O$ (**2**)

The preparation of complex **2** follows the same procedure as that of **1**, except that HL^2 (0.079 g, 0.2 mmol) was used. Yield: (0.065 g, 84%). IR (KBr pellet, cm^{-1}): 3 649, 2 903, 1 620, 1 523, 1 458, 1 382, 1 327, 748. Anal. Calcd. for $C_{32}H_{30}Br_2N_6NiO_4$ (%): C, 49.20; H, 3.87; N, 10.76. Found(%): C, 49.31; H, 3.63; N, 10.51.

1.4 X-ray crystallography

For the structure determination, suitable single crystals with dimensions of 0.30 mm×0.25 mm×0.17 mm (**1**) and 0.21 mm×0.19 mm×0.15 mm (**2**), respectively, were mounted on a Bruker Smart 1000 CCD diffractometer, fine focus sealed tube equipped with graphite-monochromatized Mo $K\alpha$ radiation (λ= 0.071 073 nm) at 293(2) K. Semi-empirical absorption corrections were applied using SADABS program[29]. All the structures were solved by direct method, followed by full-matrix least-squares refinements on F^2 with anisotropic displacement parameters for all non-hydrogen atoms using the programs SHELXS-97 and SHELXL-97[30]. All the hydrogen atoms were placed in their calculated positions and refined riding with their carrier atoms. The relevant crystal data and structure refinement for **1** and **2** are collected in Table 1. Selected bond lengths and bond angles are presented in Table 2.

CCDC: 1401182, **1**; 1401183, **2**.

1.5 Antibacterial activity test

The *in vitro* antimicrobial activity of Schiff base HL^1 and HL^2 and their respectively complexes **1**~**2** were studied against *Staphylococcus aureus* (as Gram positive bacteria) and *Escherichia coli* (as Gram negative bacteria) by the standard disc diffusion method[31]. The same procedure[32] was followed for the

Table 1　Crystallographic data and refinement summary for the 1 and 2

Complex	1	2
Formula	$C_{32}H_{30}Cl_2N_6NiO_4$	$C_{32}H_{30}Br_2N_6NiO_4$
Formula weight	692.23	781.15
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*
a / nm	1.528 07(9)	1.506 79(14)
b / nm	1.200 26(5)	1.225 39(11)
c / nm	1.770 29(10)	1.786 7(2)
β / (°)	102.389(2)	102.337(2)
Volume / nm^3	3.171 2(3)	3.222 8(6)
Z	4	4
D_c / ($g\cdot cm^{-3}$)	1.450	1.610
Absorption coefficient / mm^{-1}	0.827	3.128
θ range / (°)	2.61~25.02	2.59~25.02
Limiting indices	$-13 \leqslant h \leqslant 18, -14 \leqslant k \leqslant 14, -18 \leqslant l \leqslant 21$	$-17 \leqslant h \leqslant 17, -13 \leqslant k \leqslant 14, -19 \leqslant l \leqslant 21$
Reflections collected	5 718	9 083
Reflections unique (R_{int})	2 810 (0.035 8)	2 848 (0.064 4)
Observed reflections [$I \geqslant 2\sigma(I)$]	1 891	1 724
R_1, wR_2 [$I \geqslant 2\sigma(I)$]	0.045 5, 0.094 7	0.049 8, 0.077 3
R_1, wR_2 (all data)	0.079 4, 0.113 6	0.102 4, 0.094 7
Goodness-of-fit on F^2	1.040	1.035
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / ($e\cdot nm^{-3}$)	383, −306	462, −398

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

1					
Ni1-N1	0.208 6(3)	Ni1-N1^{i}	0.208 6(3)	Ni1-N2	0.208 2(3)
Ni1-N2^{i}	0.208 2(3)	Ni1-O1	0.203 6(2)	Ni1-O1^{i}	0.203 6(2)
O1^{i}-Ni1-O1	94.36(13)	N2^{i}-Ni1-N1^{i}	88.61(10)	O1^{i}-Ni1-N2^{i}	174.77(10)
N2-Ni1-N1^{i}	97.13(10)	O1-Ni1-N2^{i}	87.75(10)	O1^{i}-Ni1-N1	87.77(10)
O1^{i}-Ni1-N2	87.75(10)	O1-Ni1-N1	86.69(10)	O1-Ni1-N2	174.77(10)
N2^{i}-Ni1-N1	97.13(10)	N2^{i}-Ni1-N2	90.55(15)	N2-Ni1-N1	88.61(10)
O1^{i}-Ni1-N1^{i}	86.69(10)	N1^{i}-Ni1-N1	171.85(15)	O1-Ni1-N1^{i}	87.77(10)
2					
Ni1-N1	0.208 0(4)	Ni1-N1^{i}	0.208 0(4)	Ni1-N2	0.208 9(4)
Ni1-N2^{i}	0.208 9(4)	Ni1-O1	0.203 7(3)	Ni1-O1^{i}	0.203 7(3)
O1^{i}-Ni1-O1	94.79(18)	N1^{i}-Ni1-N2^{i}	88.88(14)	O1^{i}-Ni1-N1^{i}	86.57(13)
N1-Ni1-N2^{i}	97.56(10)	O1-Ni1-N1^{i}	87.23(13)	O1^{i}-Ni1-N2	87.43(13)
O1^{i}-Ni1-N1	87.23(13)	O1-Ni1-N2	174.84(14)	O1-Ni1-N1	86.57(13)
N1^{i}-Ni1-N2	97.56(14)	N1^{i}-Ni1-N1	170.8(2)	N1-Ni1-N2	88.88(14)
O1^{i}-Ni1-N2^{i}	174.84(14)	N2^{i}-Ni1-N2	90.7(2)	O1-Ni1-N2^{i}	87.43(13)

Symmetry transformations used to generate equivalent atoms: ^{i} $-x+1, y, -z+3/2$ for **1**; ^{i} $-x+1, y, -z+1/2$ for **2**

determination of zone inhibition of all the compounds against standard controls.

2 Results and discussion

2.1 Syntheses and characterization

The ligands HL^1 and HL^2 were prepared by the direct condensation reaction of 2-aminoethyl-1*H*-benzimidazole dihydrochloride, previously neutralized with K_2CO_3, with 5-chlorosalicylaldehyde and 5-bromosalicylaldehyde (molar ratio 1∶1) in methanol, respectively. The metal complexes **1**~**2** were obtained by the reaction of corresponding ligands with $Ni(ClO_4)_2 \cdot 6H_2O$ in a ratio of 2∶1 (n_{ligand}/n_{Ni}) in methanol medium. The two complexes are air stable and soluble in EtOH, MeOH, DMSO and DMF.

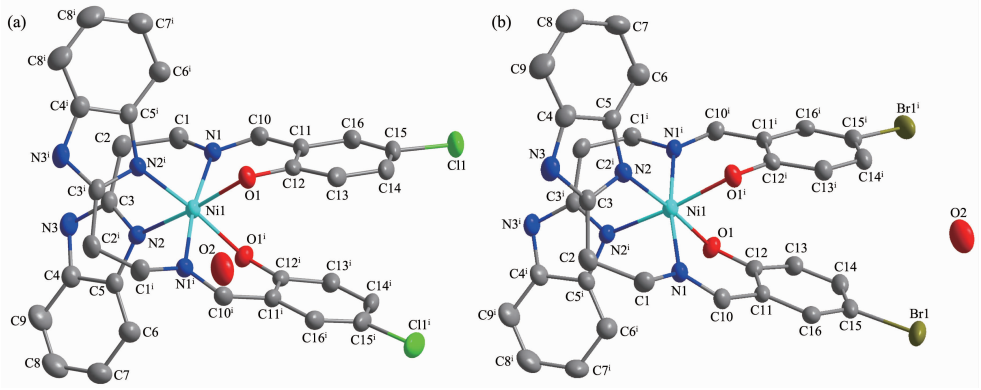
Several medium intensity bands spreading between 3 300 and 2 300 cm^{-1} in the two complexes indicate that the NH groups of the benzimidazole rings are involved in hydrogen bonding with other electronegative atoms[21]. Bands at 3 656 and 3 649 cm^{-1} are assigned as ν(O-H) stretching vibrations of the hydrate water molecules in **1** and **2**, respectively. The IR spectra of the two Schiff bases showed a very sharp and strong C=N stretching vibration around 1 637 cm^{-1}. For the two complexes the same band was observed around 1 622 cm^{-1}, which was shifted towards lower wavelength, suggesting coordination through the azomethine nitrogen atom of the ligands. The electronic spectra of the free Schiff base ligands and the two complexes in methanol were measured at room temperature. UV bands around 275 and 283 nm are observed for the free Schiff bases due to the π-π* transition of the benzimidazole group. In complexes **1** and **2** these bands blue-shift, indicating clear evidence of the ring nitrogen coordination to metal centers[33]. For the free Schiff bases the bands at 326 nm for HL^1 and 330 nm for HL^2, respectively, are characteristic of the n-π* transition of the azomethine linkage. On complexation, this band shifts to a longer wavelength in **1** and **2** (Δ=50 nm for both two complexes)[34]. In the visible region, the two complexes show a broad absorption band appears at λ_{max} value of 640 nm, suggesting a distorted octahedral arrangement around the metal ions.

2.2 Crystal structures of the complexes

X-ray diffraction studies reveal that both complexes **1** and **2** crystallize in monoclinic system with *C*2/*c* space group. As shown in Fig.1, in

complexes **1** and **2**, each complex molecule consists of a monomeric $[Ni(L)_2]$ unit with two solvent water molecules. The hexa-coordinated Ni (Ⅱ) center is bonded to two tridentate Schiff base ligands. Each ligand molecule offers deprotonated phenolic oxygen, imine nitrogen and benzimidazole nitrogen atom as the coordination sites providing a NiN_4O_2 chromophore. The geometry around Ni(Ⅱ) in **1** and **2** can be best described as a distorted octahedron, where the equatorial plane is constructed by two benzimidazole nitrogen atoms and two phenolic oxygen atoms, and the two axial sites being occupied by two imine nitrogen atoms. The average Ni-N and Ni-O distances are 0.208 4 and 0.203 7 nm, respectively, which are comparable to those reported for the similar Schiff base complexes of Ni(Ⅱ)[35]. The three *trans*-angles at nickel(Ⅱ) vary from 170.8(2)° to 174.84(14)° while the *cis*-angles are in the range of 86.57 (13)~97.56 (10)°, being deviating significantly from 180° and 90°, respectively, indicating the coordination geometry in complexes **1** and **2** is distorted from a regular octahedron.

In complexes **1** and **2**, the water molecules are involved in hydrogen bonds acting as both acceptors and donors leading to the formation of intermolecular interaction network. Acting as an acceptor, the O2 atom of the water molecule is engaged in the N3–H3 ⋯ O2$^{\#}$ hydrogen bonds to the H atom on the benzimidazole N atom. On the other hand, as a donor, the O2 atom is engaged with O1 atom of the phenolic group and the N2 atom of the benzimidazole ring through O2–H⋯O1$^{\#}$ and O2–H⋯N2$^{\#}$ hydrogen bonds, respectively, where # refers to the different L ligand. These hydrogen bonds link the complex **1** and **2** into a 2D structure (Fig.2a and 2b). Besides, complex **1** was further linked into a 3D structure by the intermolecular C1–H1B⋯Cl1 hydrogen bonds between a CH_2 group bound to the imino moiety of L^1 ligand and an adjacent Cl1 atom (Fig.3). The bond parameters of



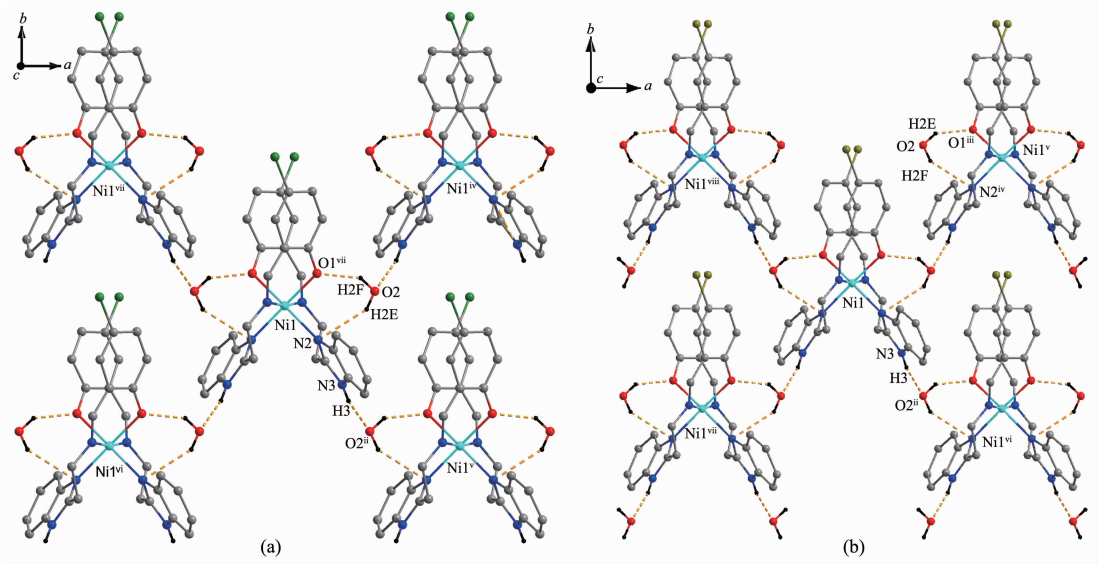
H atoms are omitted for clarity; Symmetry codes: ^{i} $-x+1, y, -z+3/2$ for **1**; ^{i} $-x+1, y, -z+1/2$ for **2**

Fig.1　Molecular structures of **1** (a) and **2** (b) with 30% probability level along with the atom numbering scheme

Table 3　Hydrogen bond parameters in 1 and 2

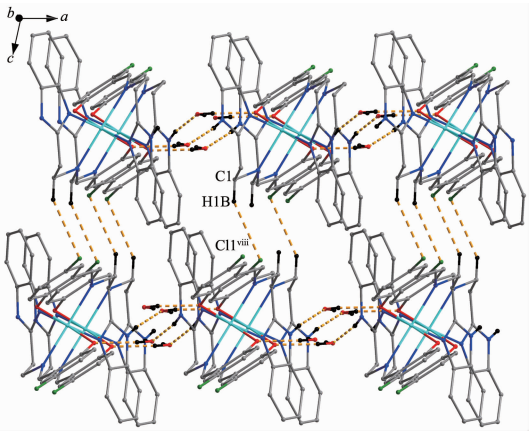
D–H⋯A	*d*(D-H) / nm	*d*(H⋯A) / nm	*d*(D⋯A) / nm	∠DHA / (°)
1				
N3–H3⋯O2^{ii}	0.086	0.185 7	0.270 4	168.11
O2–H2E⋯N2	0.085	0.248 5	0.322 6	146.28
O2–H2F⋯O1^{iii}	0.085	0.191 2	0.264 8	144.09
C1–H1B⋯Cl1^{viii}	0.097	0.292 4	0.379 6	150.00
2				
N3–H3⋯O2^{ii}	0.086	0.185 0	0.269 9	169.07
O2–H2E⋯O1^{iii}	0.085	0.191 9	0.265 3	143.87
O2–H2F⋯N2^{iv}	0.085	0.249 0	0.323 2	146.31

Symmetry codes: ^{ii} $-x+3/2, y-1/2, -z+3/2$; ^{iii} $-x+1, y, -z+3/2$; ^{viii} $-x+1, -y+1, -z+1$ for **1**; ^{ii} $x, y-1, z$; ^{iii} $x+1/2, y+1/2, z$; ^{iv} $-x+3/2, y+1/2, -z+1/2$ for **2**



Symmetry codes: [ii] $-x+3/2, y-1/2, -z+3/2$; [iii] $-x+1, y, -z+3/2$; [iv] $x+1/2, y+1/2, z$; [v] $x+1/2, y-1/2, z$; [vi] $x-1/2, y-1/2, z$; [vii] $x-1/2, y+1/2, z$ in (a); [ii] $x, y-1, z$; [iii] $x+1/2, y+1/2, z$; [iv] $-x+3/2, y+1/2, -z+1/2$, [v] $x+1/2, y+1/2, z$; [vi] $x+1/2, y-1/2, z$; [vii] $x-1/2, y,-1/2\ z$; [viii] $x-1/2, y+1/2, z$ in (b)

Fig.2 Formation of 2D network by hydrogen bonding interactions in **1** (a) and **2** (b)



Symmetry codes: [viii] $-x+1, -y+1, -z+1$

Fig.3 Formation of 3D network by hydrogen bonding interactions in complex **1**

hydrogen bonds are listed in Table 3.

2.3 Antibacterial activity of the compounds

The antibacterial activity of Schiff base ligands, HL^1 and HL^2 and their two Ni(Ⅱ) complexes were studied against one Gram-positive (*S. aureus*) and one Gram-negative (*E. coli*) bacterial strains and the results were showed in Table 4. The two Schiff base ligands are active against *S. aureus* and *E. coli* at different concentrations. HL^1 exhibits greater antibacterial activity against *E. coli* whereas HL^2 shows higher zone against *S. aureus*. The antibacterial activity of Schiff base ligands may be due to the presence of azomethine group as well as the presence of the hydroxyl and benzimidazole rings, all of which may play a significant role in the antibacterial activity[6,10-12].

Table 4 Antibacterial activities of the ligands and the complexes

Compound	Dose / ($\mu g \cdot mL^{-1}$)	Inhibition zone diameter / mm	
		S. aureus	*E. coli*
HL^1	125	9	13
	250	11	14
	500	12	16
HL^2	125	10	11
	250	12	12
	500	13	12
Complex **1**	125	11	15
	250	13	15
	500	14	20
Complex **2**	125	16	13
	250	16	15
	500	18	16
DMSO(AR)		—	—

The two Ni(Ⅱ) complexes have moderate to strong antibacterial activity against *S. aureus* and *E. coli* and exhibit higher activity than the corresponding Schiff bases. It is interesting to note that **1** has stronger activities against *E. coli* than **2** whereas **2** has stronger activities against *S. aureus* than **1**, which is similar to

the correspondin g Schiff bases. The result indicates that chlorine and bromine atoms may have a subtle influence on the antibacterial activities.

References:

[1] Saghatforoush L A, Chalabian F, Aminkhani A, et al. *Eur. J. Med. Chem.*, **2009**,**44**(11):4490-4495

[2] Hranjec M, Starčević K, Pavelić S K, et al. *Eur. J. Med. Chem.*, **2011**,**46**(6):2274-2279

[3] Creaven B S, Devereux M, Foltyn A, et al. *Polyhedron*, **2010**, **29**(2):813-822

[4] ZHANG Qi-Long (张奇龙), WANG Huan-Yu (王焕宇), JIANG Feng(江峰), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2016**,**32**(3):464-468

[5] QIU Xiao-Yang(仇晓阳). *Chinese J. Inorg. Chem.*(无机化学学报), **2014**,**30**(7):1667-1672

[6] Iqbal A, Siddiqui H L, Ashraf C M, et al. *Molecules*, **2007**, **12**(2):245-254

[7] Khatua S, Kang J, Kim K, et al. *Eur. J. Inorg. Chem.*, **2010**, **31**(11):5018-5026

[8] Maxim C, Pasatoiu T D, Kravtsov V C, et al. *Inorg. Chim. Acta*, **2008**,**361**(14/15):3903-3911

[9] Dhahagani K, Kumar S M, Chakkaravarthi G, et al. *Spectrochim. Acta Part A*, **2014**,**117**:87-94

[10]Shi L, Ge H M, Tan S H, et al. *Eur. J. Med. Chem.*, **2007**, **42**(4):558-564

[11]Creaven B S, Devereux M, Karcz D, et al. *J. Inorg. Biochem.*, **2009**,**103**(9):1196-1203

[12]Ates-Alagoz Z, Yildiz S, Buyukbingol E. *Chemotherapy*, **2007**,**53**(2):110-113

[13]Göker H, Kus C, Boykin D W, et al. *Bioorg. Med. Chem.*, **2002**,**10**(8):2589-2596

[14]Hranjec M, Pavlović G, Marjanović M, et al. *Eur. J. Med. Chem.*, **2010**,**45**(6):2405-2417

[15]Starčević K, Kralj M, Ester K, et al. *Bioorg. Med. Chem.*, **2007**,**15**(13):4419-4426

[16]Qiu X H, Tong X L. *Acta Crystallogr. Sect. E*, **2005**,**E61**: m1470-m1471

[17]Qiu X H, Tong X L. *Acta Crystallogr. Sect. E*, **2005**,**E61**: m2302-m2304

[18]Qiu X H, Tong X L. *Acta Crystallogr. Sect. E*, **2006**,**E62**: m841-m842

[19]Qiu X H, Tong X L. *Acta Crystallogr. Sect. E*, **2006**,**E62**: m977-m979

[20]QIU Xiao-Hang(邱晓航), ZHAO Jun(赵君), TONG Xiao-Lan(仝小兰). *Chin. J. Struct. Chem.*(结构化学), **2006**,**25**(11): 1343-1346

[21]Maurya M R, Kumar A, Ebel M, et al. *Inorg. Chem.*, **2006**, **45**(13):5924-5937

[22]Maurya M R, Chandrakar A K, Chand S. *J. Mol. Catal. A: Chem.*, **2007**,**263**(1/2):227-237

[23]ZHAO Hai-Yan(赵海燕), QIU Xiao-Hang(邱晓航), SHEN Pan-Wen(申泮文). *Chinese J. Inorg. Chem.*(无机化学学报), **2010**,**26**(12):2221-2226

[24]Kumar R, Kumar R, Mahiya K, et al. *Transition Met. Chem.*, **2015**,**40**(2):189-195

[25]Patil S A, Prabhakara C T, Halasangi B M, et al. *Spectrochim. Acta Part A*, **2015**,**137**:641-651

[26]Chai L Q, Zhang H S, Huang J J, et al. *Spectrochim. Acta Part A*, **2015**,**137**:661-669

[27]Chandra S, Gautam S, Rajor H K, et al. *Spectrochim. Acta Part A*, **2015**,**137**:749-760

[28]Cescon L A, Day A R. *J. Org. Chem.*, **1962**,**27**(2):581-586

[29]Sheldrick G M. *SADABS, Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany, **1996**.

[30]Sheldrick G M. *SHELXL*-97, *Program for X-ray Crystal Structure Solution*, Göttingen University, Germany, **1997**.

[31]Drew W L, Barry A L, O′Toole R, et al. *Appl. Environ. Microbiol.*, **1972**,**24**(2):240-247

[32]Zhao H Y, Ma J J, Han Z G, et al. *Synth. React. Inorg. Met.-Org. Chem.*, **2015**,**45**(4):621-627

[33]Mohapatra S C, Tehlan S, Hundal M S, et al. *Inorg. Chim. Acta*, **2008**,**361**(7):1897-1907

[34]Golcu A, Tumer M, Demirelli H, et al. *Inorg. Chim. Acta*, **2005**,**358**(6):1785-1797

[35]Demir S, Yazclar T K, Tas M. *Inorg. Chim. Acta*, **2014**,**409** (Part A):399-406