Scientific paper

Synthesis, Crystal Structures and Antibacterial Activities of Trifluoromethylsulfonate Salts of 2-[(3-Chloropyridinium-2-yl)hydrazonomethyl]-6-methoxyphenol and its Copper(II) and Cobalt(III) Complexes

Ya-Li Sang,* Xue-Song Lin and Wei-Dong Sun

Department of Chemistry and Chemical Engineering, Chifeng University, Chifeng 024001, P. R. China

* Corresponding author: E-mail: sangyali0814@126.com

Received: 05-08-2016

Abstract

A new trifluoromethylsulfonate salt of 2-[(3-chloropyridinium-2-yl)hydrazonomethyl]-6-methoxyphenol, (HL)CF₃SO₃, and its copper(II) and cobalt(III) complexes, [CuL(OH₂)]CF₃SO₃ \cdot 0.5H₂O (1) and [CoL₂]CF₃SO₃ \cdot CH₃OH (2), were prepared and characterized by physico-chemical methods and single crystal X-ray analysis. A trifluoromethylsulfonate anion is present in each of the compounds. The Cu atom in complex 1 is coordinated by the phenolate O, imino N and pyridine N atoms of L ligand, giving square planar geometry. The Co atom in complex 2 is coordinated by two phenolate O, two imino N and two pyridine N atoms from two L ligands, giving octahedral geometry. The three compounds were tested *in vitro* for their antibacterial activities.

Keywords: Schiff base; Copper; Cobalt; Synthesis; Crystal structure; Antibacterial activity

1. Introduction

Schiff bases are readily synthesized by the condensation reaction of carbonyl compounds with primary amines.¹ Schiff bases have been widely investigated for their biological activities, such as antibacterial and antitumor activities,² biomimetic catalytic properties, *etc.*⁵ Metal complexes of Schiff bases have also received much attention. These complexes not only play an important role in the development of coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures,⁴ but also exhibit interesting biological activities.⁵

In recent years, a number of Schiff bases and their complexes have been reported.⁶ Most of the compounds show versatile biological properties especially antibacterial activities.⁷ It was reported that the compounds bearing halo-atoms on the aromatic ring have improved antibacterial and antifungal activities.⁸ In the present work, a new trifluoromethylsulfonate salt of 2-[(3-chloropyridinium-2-yl)hydrazonomethyl]-6-methoxyphenol, (HL)CF₃SO₃, and its copper(II) and cobalt(III) complexes, [Cu-

 $L(OH_2)$]CF₃SO₃ · 0.5H₂O (1) and [CoL₂]CF₃SO₃ · CH₃OH (2), are prepared and characterized. The antibacterial activities against *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli*, and *Pseudomonas fluorescens*, were evaluated.



Scheme 1. The Schiff base ligand L

2. Experimental

2. 1. Materials and Measurements

3-Methoxysalicylaldehyde and (3-chloropyridin-2yl)hydrazine with AR grade were obtained from Aldrich and used as received. Copper trifluoromethylsulfonate and cobalt trifluoromethylsulfonate were prepared by the reaction of trifluoromethylsulfonic acid with $[Cu_2(OH)_2CO_3]$ and $CoCO_3$, respectively. Elemental analyses were performed using a Perkin-Elmer 240C analytical instrument. Infrared spectra were recorded on a Nicolet 5DX FT-IR spectrophotometer with KBr pellets. ¹H NMR spectra were recorded on a Bruker instrument at 400 MHz. Molar conductance was measured with a Shanghai DDS-11A conductometer.

2. 2. Synthesis of (HL)CF₃SO₃

3-Methoxysalicylaldehyde (1.52 g, 0.010 mol) and (3-chloropyridin-2-yl)hydrazine (1.43 g, 0.010 mol) were mixed in methanol (30 mL). The mixture was stirred at room temperature and then evaporated to give vellow powder of L, which was washed three times with methanol and dried in air. Yield: 91%. Anal. Calcd. for C₁₃H₁₂ClN₃O₂ (%): C, 56.2; H, 4.4; N, 15.1. Found: C, 56.4; H, 4.3; N, 15.2. ¹H NMR (*d*⁶-DMSO): δ: 8.72 (s, 1H, CH=N), 8.18 (d, 1H, NH), 7.98 (d, 1H, PyH), 7.49 (d, 1H, PyH), 7.23 (d, 1H, ArH), 7.03-6.94 (m, 2H, ArH), 6.87 (t, 1H, PyH), 3.82 (s, 3H, OCH₃). Single crystals were formed by addition of equimolar quantity of trifluoromethylsulfonic acid to the methanol solution of L. IR data (KBr, cm⁻¹): 3439w, 3300w, 1644m, 1594m, 1518m, 1456s, 1407s, 1358s, 1253m, 1157s, 1073s, 949s, 858s, 733w, 629w, 543s, 526s, 470m.

2. 3. Synthesis of [CuL(OH₂)]CF₃SO₃ · 0.5H₂O (1)

To a methanolic solution (10 mL) of L (27.7 mg, 0.10 mmol), an aqueous solution (2 mL) of copper trifluoromethylsulfonate (36.2 mg, 0.10 mmol) was added with stirring. The mixture was stirred for half an hour and filtered. The filtrate was kept undisturbed at room temperature to slow evaporate for seven days, generating blue crystals suitable for X-ray diffraction. Crystals were isolated by filtration and dried in air. Yield 38% with respect to L. Anal. Calcd. for $C_{28}H_{28}Cl_2Cu_2F_6N_6O_{13}S_2$ (%): C, 32.6; H, 2.7; N, 8.1. Found: C, 32.8; H, 2.8; N, 8.0. IR data (KBr, cm⁻¹): 3453m, 1622m, 1538m, 1449m, 1253s, 1157s, 1066s, 956s, 858s, 782w, 741w, 636m, 576s.

2. 4. Synthesis of $[CoL_2]CF_3SO_3 \cdot CH_3OH(2)$

To a methanolic solution (10 mL) of L (27.7 mg, 0.10 mmol), an aqueous solution (2 mL) of cobalt trifluoromethylsulfonate (35.7 mg, 0.10 mmol) was added with stirring. The mixture was stirred for half an hour and filtered. The filtrate was kept undisturbed at room temperature to slow evaporate for seven days, generating brown crystals suitable for X-ray diffraction. Crystals were isolated by filtration and dried in air. Yield 45% with respect to L. Anal. Calcd. for $C_{28}H_{26}Cl_2CoF_3N_6O_8S$ (%): C, 42.4; H, 3.3; N, 10.6. Found: C, 42.5; H, 3.4; N, 10.4. IR data (KBr, cm⁻¹): 3467m, 1615m, 1538m, 1449m, 1365w, 1295w, 1247w, 1164s, 1073s, 949s, 858s, 734w, 637w, 533s.

Table 1. Crystallographic and experimental data for the compounds

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	2
Formula weight427.81032.779crystal systemmonoclinictriclinictricspace group P_{2_1}/c $P-1$ F a (Å) $6.9336(8)$ $6.7377(4)$ 11.5 b (Å) $14.2452(12)$ $10.7336(7)$ 11.53 c (Å) $18.0427(17)$ $14.1830(9)$ 13.30 α (°) 90 $79.579(2)$ 72.0 β (°) 90 $89.838(2)$ 68.9	CoF ₃ N ₆ O ₈ S
$\begin{array}{ccc} \mbox{crystal system} & \mbox{monoclinic} & \mbox{triclinic} & \mbox{tricl} \\ \mbox{space group} & P_{2_1/c} & P_{-1} & P_{-1} \\ a({\rm \AA}) & 6.9336(8) & 6.7377(4) & 11.5 \\ b({\rm \AA}) & 14.2452(12) & 10.7336(7) & 11.5 \\ c({\rm \AA}) & 18.0427(17) & 14.1830(9) & 13.30 \\ \alpha(^{\circ}) & 90 & 79.579(2) & 72.0 \\ \beta(^{\circ}) & 90 & 89.838(2) & 68.9 \end{array}$	3.4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	linic
$\begin{array}{cccc} a(\mathring{A}) & 6.9336(8) & 6.7377(4) & 11.5 \\ b(\mathring{A}) & 14.2452(12) & 10.7336(7) & 11.5 \\ c(\mathring{A}) & 18.0427(17) & 14.1830(9) & 13.30 \\ \alpha(^{\circ}) & 90 & 79.579(2) & 72.0 \\ \beta(^{\circ}) & 90 & 89.838(2) & 68.9 \end{array}$	-1
$\begin{array}{ccccc} b({\rm \AA}) & 14.2452(12) & 10.7336(7) & 11.5\\ c({\rm \AA}) & 18.0427(17) & 14.1830(9) & 13.30\\ \alpha(^{\circ}) & 90 & 79.579(2) & 72.0\\ \beta(^{\circ}) & 90 & 89.838(2) & 68.9 \end{array}$	33(8)
c (Å)18.0427(17)14.1830(9)13.30 α (°)9079.579(2)72.0 β (°)9089.838(2)68.9	327(6)
$\begin{array}{cccc} \alpha (^{\circ}) & 90 & 79.579(2) & 72.0 \\ \beta (^{\circ}) & 90 & 89.838(2) & 68.9 \end{array}$	08(10)
β (°) 90 89.838(2) 68.9	15(2)
	64(2)
γ ^(°) 90 82.976(2) 84.1	73(2)
$V(Å^3)$ 1782.1(3) 1001.0(1) 1574	1.5(2)
Z 4 1	2
ρ (g/cm ³) 1.594 1.713 1.	574
<i>F</i> (000) 872 520 8	08
Measured reflections 6386 6951 11	854
Unique reflections 2895 3582 55	336
Observed reflections 1913 2791 4:	539
Parameters/restraints 253/1 275/7 45	2/2
$R_{\rm int}$ 0.0504 0.0287 0.0	432
$\begin{array}{c} \text{Goodness of fit on } F^2 \\ 1.021 \\ 1.028 \\ 1.$)78
$R_1, wR_2 [I \ge 2\sigma(I)]^a$ 0.0508, 0.0986 0.0636, 0.1618 0.0561	, 0.1548
R_1, wR_2 (all data) ^a 0.0877, 0.1177 0.0816, 0.1804 0.0727	, 0.1720

 ${}^{a}R_{I} = \sum |F_{o}| - |F_{c}| / \sum |F_{o}|, wR_{2} = [\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o}^{2})^{2}]^{1/2}.$

2. 5. X-ray Crystallography

Suitable single crystals of the compounds were selected and mounted on a Bruker Smart 1000 CCD area-detec-

Table 2. Selected bond lengths $({\rm \AA})$ and angles $(^{\circ})$ for the compounds

1.276(4)	N1-N2	1.399(3)
1.280(6)	N1-N2	1.382(5)
1.878(3)	Cu1–N1	1.938(4)
1.950(4)	Cu1-N3	1.972(4)
92.99(15)	O1-Cu1-O3	89.29(17)
175.22(17)	O1-Cu1-N3	172.63(15)
82.26(17)	O3-Cu1-N3	95.87(18)
1.300(5)	N1-N2	1.392(4)
1.872(3)	Co1–O1	1.878(3)
1.879(3)	Co1-O3	1.895(3)
1.938(3)	Co1-N3	1.952(3)
94.49(12)	N1-Co1-N4	175.44(13)
88.84(12)	N1-Co1-O3	88.95(12)
90.53(12)	N4-Co1-O3	94.15(12)
94.68(13)	01-Co1-N6	89.94(12)
82.19(13)	O3-Co1-N6	176.29(12)
82.68(13)	O1-Co1-N3	176.39(12)
93.86(13)	O3-Co1-N3	91.65(12)
88.06(13)		
	1.276(4) 1.280(6) 1.878(3) 1.950(4) 92.99(15) 175.22(17) 82.26(17) 1.300(5) 1.872(3) 1.879(3) 1.938(3) 94.49(12) 88.84(12) 90.53(12) 94.68(13) 82.19(13) 82.68(13) 93.86(13) 88.06(13)	$\begin{array}{c cccc} 1.276(4) & N1-N2 \\ \hline 1.280(6) & N1-N2 \\ \hline 1.878(3) & Cu1-N1 \\ 1.950(4) & Cu1-N3 \\ \hline 92.99(15) & O1-Cu1-O3 \\ 175.22(17) & O1-Cu1-N3 \\ \hline 82.26(17) & O3-Cu1-N3 \\ \hline 1.300(5) & N1-N2 \\ \hline 1.872(3) & Co1-O1 \\ \hline 1.879(3) & Co1-O3 \\ \hline 1.938(3) & Co1-O3 \\ \hline 1.938(3) & Co1-N3 \\ \hline 94.49(12) & N1-Co1-N4 \\ \hline 88.84(12) & N1-Co1-N4 \\ \hline 88.84(12) & N1-Co1-O3 \\ \hline 90.53(12) & N4-Co1-O3 \\ \hline 94.68(13) & O1-Co1-N6 \\ \hline 82.19(13) & O3-Co1-N6 \\ \hline 82.68(13) & O1-Co1-N3 \\ \hline 93.86(13) & O3-Co1-N3 \\ \hline 88.06(13) \\ \hline \end{array}$

tor diffractometer with graphite monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å) at 298(2) K. Data reduction and cell refinement were performed by the SMART and SAINT programs.⁹ Empirical absorption correction was applied by using SADABS.¹⁰ The structures were solved by direct methods and refined with the full-matrix least-squares technique using SHELXL97.¹¹ The non-H atoms in the structures were subjected to refined anisotropic refinement. The amino hydrogen atoms were located from difference Fourier maps and refined isotropically. The remaining hydrogen atoms were located in geometrically and treated with the riding mode. Crystallographic data and experimental details for the compounds are summarized in Table 1. Selected bond lengths and angles for the compounds are listed in Table 2.

2. 6. Antibacterial Test

Antibacterial activities of the compounds were tested in vitro against Bacillus subtilis, Staphylococcus aureus, Escherichia coli, and Pseudomonas fluorescens using MH medium (Mueller-Hinton medium: casein hydrolysate 17.5 g, soluble starch 1.5 g, beef extract 1000 mL). The minimum inhibitory concentrations (MIC) of the test compounds were determined by a colorimetric method using the dye MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide).¹² A solution of the compound (50 μ g mL⁻¹) in DMSO was prepared and graded quantities of the test compounds were incorporated in specified quantity of sterilized liquid MH medium. A specified quantity of the medium containing the compound was poured into microtitration plates. Suspension of the microorganism was prepared to contain about 10⁵ colony forming units cfu mL⁻¹ and applied to microtitration pla-

Table 3. Distances (Å) and angles (°) involving hydrogen bonding of the compounds

D-Н…А	<i>d</i> (<i>D</i> -H)	<i>d</i> (H··· <i>A</i>)	<i>d</i> (<i>D</i> … <i>A</i>)	Angle(D-H…A)
(HL)CF ₃ SO ₃				
N3-H3-O3 ⁱ	0.86(3)	2.00(4)	2.797(4)	156(4)
N2-H2-O5	0.90(1)	1.97(2)	2.847(4)	164(4)
O1-H1…O2	0.82	2.23	2.678(3)	114
O1-H1····O4 ⁱⁱ	0.82	2.14	2.814(4)	140
1				
O3-H3A…O4 ⁱⁱⁱ	0.85	2.27	2.726(7)	114
O3-H3B…O7	0.85	1.80	2.629(9)	164
N2-H2···O6 ^{iv}	0.90(1)	1.97(2)	2.852(6)	167(7)
O7-H7A···O3 ^v	0.85	2.44	3.230(9)	155
O7-H7B…O2	0.85	2.31	2.916(9)	128
2				
N5-H5····O7 ^{vi}	0.89(2)	2.02(3)	2.853(5)	156(5)
N2-H2···O3 ^{vii}	0.89(2)	2.61(4)	3.348(4)	141(5)
N2-H2···O4 ^{vii}	0.89(2)	2.14(5)	2.803(5)	130(5)
O8-H8····S1 ^{viii}	0.82	3.03	3.797(5)	157
O8-H8…O5 ^{viii}	0.82	2.13	2.923(7)	163

Symmetry codes: i) x, $\frac{1}{2} - y$, $-\frac{1}{2} + z$; ii) -1 + x, y, z; iii) 1 - x, 2 - y, 1 - z; iv) 1 - x, 1 - y, 1 - z; v) -x, 2 - y, 1 - z; vi) x, 1 + y, z; vii) 1 - x, 1 - y, 1 - z; viii) x, y, 1 + z.

Sang et al.: Synthesis, Crystal Structures and Antibacterial ...

tes with serially diluted compounds in DMSO to be tested and incubated at 37 °C for 24 h. After the MICs were visually determined on each of the microtitration plates, 50 μ L of PBS (Phosphate Buffered Saline 0.01 mol L⁻¹, pH 7.4: Na₂HPO₄ · 12H₂O 2.9 g, KH₂PO₄ 0.2 g, NaCl 8.0 g, KCl 0.2 g, distilled water 1000 mL) containing 2 mg of MTT was added to each well. Incubation was continued at room temperature for 4–5 h. The content of each well was removed, and 100 μ L of isopropyl alcohol containing 5% 1.0 mol L⁻¹ HCl was added to extract the dye. After 12 h of incubation at room temperature, the optical density (OD) was measured with a microplate reader at 550 nm. The observed MICs are presented in Table 3.

3. Results and Discussion

The Schiff base L was readily prepared by condensation reaction of 3-methoxysalicylaldehyde and (3-chloropyridin-2-yl)hydrazine in methanol. Single crystals were formed by the addition of trifluoromethylsulfonic acid, followed by slow evaporation. The copper and cobalt complexes were prepared by the reaction of the Schiff base with copper trifluoromethylsulfonate and cobalt trifluoromethylsulfonate, respectively, in methanol/water solution. As usually observed for the preparation of cobalt complexes, Co^{II} underwent aerial oxidation to Co^{III} in the synthetic route of complex **2**. The molar conductivities of the trifluoromethylsulfonate salts of the Schiff base ligand, complex **1** and complex **2** measured in methanol at concentration of 10^{-3} M are 253, 227 and 208 Ω^{-1} cm² mol⁻¹, indicating the 1:1 electrolytic nature of the compounds in solution.¹³

3. 1. Crystal Structure Description of (HL)CF₃SO₃

Figure 1 gives perspective view of the compound. The asymmetric unit contains a protonated Schiff base ca-



Figure 1. Crystal structure of (HL)CF₃SO₃. Displacement is drawn at the 30% probability level. Hydrogen bonds are shown as dashed lines.



Figure 2. Packing diagram of (HL)CF₃SO₃ viewed along the *a* axis. Hydrogen bonds are shown as dashed lines.

tion, HL and a trifluoromethylsulfonate. The anion is linked to the cation through intermolecular N–H···O hydrogen bonds (Table 3). There are two intramolecular O–H···O and N–H···N hydrogen bonds in the Schiff base cation. The dihedral angle between the benzene and pyridine rings is $2.0(3)^{\circ}$. The torsion angles of C1–C7–N1–N2 and C7–N1–N2–C8 are 0.5(3) and $0.8(3)^{\circ}$, respectively. The bond values of the compound are within normal ranges.¹⁴ In the crystal structure of the compound, the Schiff base cations are linked by trifluoromethylsulfonate anions through hydrogen bonds (Table 3), giving 2D sheets parallel to the *ac* plane (Figure 2).

3. 2. Crystal Structure Description of 1

Figure 3 gives perspective view of complex 1. The asymmetric unit contains a mononuclear Schiff base copper complex cation, a trifluoromethylsulfonate and half water molecule. The water molecule is linked to the cation

through intermolecular O–H···O hydrogen bonds (Table 3). The dihedral angle between the benzene and pyridine rings is 3.6(5)°. The torsion angles of C1–C7–N1–N2 and C7–N1–N2–C8 are 0.6(5) and 1.6(5)°, respectively. The Cu atom is coordinated by the phenolate O, imino N and pyridine N atoms of the Schiff base ligand and one water molecule, giving a square planar geometry. The coordinate bond values of the complex are within normal ranges.¹⁵ In the crystal structure of the complex, the Schiff base copper complex cations are linked by trifluoromethylsulfonate anions and water molecules through hydrogen bonds (Table 3), giving 2D sheets parallel to the *ab* plane (Figure 4).

3. 3. Crystal Structure Description of 2

Figure 5 gives perspective view of complex **2**. The asymmetric unit contains a mononuclear Schiff base cobalt complex cation, a trifluoromethylsulfonate and a methanol molecule. The dihedral angles between the benzene



Figure 3. Crystal structure of 1. Displacement is drawn at the 30% probability level. Hydrogen bonds are shown as dashed lines.



Figure 4. Packing diagram of 1 viewed along the *a* axis. Hydrogen bonds are shown as dashed lines.

and pyridine rings are $17.7(4)^{\circ}$ for Co1 molecule and 22.4(4)° for Co2 molecule. The torsion angles of C1–C7–N1–N2, C7–N1–N2–C8, C13–C19–N4–N5 and C19–N4–N5–C20 are 6.3(4), 3.8(4), 6.0(4) and 14.5(5)°, respectively. The Co atom is coordinated by two phenolate O, two imino N and two pyridine N atoms from two Schiff base ligands giving an octahedral geometry. The coordinate bond values of the complex are within normal ranges.¹⁶ In the crystal structure of the complex, adjacent

two Schiff base cobalt complex cations are linked through hydrogen bonds (Table 3) giving a dimer (Figure 6).

3. 2. IR Spectra

The weak and broad absorptions centered in the region of 3400–3500 cm⁻¹ are assigned to the stretching vibration of the O–H groups of the methanol or water molecules. In the spectrum of (HL)CF₃SO₃, the sharp band at



Figure 5. Crystal structure of 2. Displacement is drawn at the 30% probability level.



Figure 6. Packing diagram of 2 viewed along the c axis. Hydrogen bonds are shown as dashed lines.

3300 cm⁻¹ is attributed to the vibration of the N–H group of the ligand. This absorption is absent in the spectra of the complexes, indicating the coordination through pyridine nitrogen atom. Several other bands in the range of 2900–3150 cm⁻¹ are assigned to the characteristic absorption of CH groups. The phenolic i(C-O) in the spectra of the compounds are observed as medium or weak bands at about 1250 cm⁻¹. The medium band at 1644 cm⁻¹ of (HL)CF₃SO₃ is assigned to the azomethine group, v_{C=N}, which is observed at low wave numbers of 1622 cm⁻¹ for 1 and 1615 cm⁻¹ for **2**, indicating the coordination of the imino nitrogen atoms to the metal atoms. The spectra of the compounds exhibit strong absorption bands at about 1160 and 1070 cm⁻¹, corresponding to the stretching vibrations of the trifluoromethylsulfonate anions.

3. 3. Antibacterial Activities

The compounds were screened *in vitro* for antibacterial activities against *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli*, and *Pseudomonas fluorescens* by the MTT method. The MICs of the compounds against the bacteria are presented in Table 4. Penicillin was used as a reference.

The Schiff base L and the trifluoromethylsulfate salt of L show equal activities against the bacterial. In general, both complexes have stronger activities against the bacteria than L and (HL)CF₃SO₃. Complexes **1** and **2** show equal activities against *Staphylococcus aureus*, while for the other bacteria, complex **1** has stronger activities than complex **2**. Even though both complexes have effective activities against *Bacillus subtilis*, they are much weak than penicillin. However, as for the remaining bacteria, the complexes have stronger activities than penicillin. The trends in the present work are in accordance with those in the literature that metal complexes usually have stronger antibacterial activities than their corresponding ligands.¹⁷

4. Conclusions

A new trifluoromethylsulfonate salt of 2-[(3-chloropyridinium-2-yl)hydrazonomethyl]-6-methoxyphenol and its copper(II) and cobalt(III) complexes have been prepared and characterized. The Schiff base ligand coordinates to the metal atoms through phenolate oxygen, imino nitrogen and pyridine nitrogen atoms. Structures of the compounds are confirmed by infrared spectra and single crystal X-ray determination. The antibacterial activities of the Schiff base and the complexes were assayed. The results indicated that the complexes are potential antibacterial material.

5. Supplementary Material

CCDC reference numbers 1497251 for (HL)CF₃SO₃, 1497251 for **1** and 1497254 for **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk, or from Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk.

6. Acknowledgements

We gratefully acknowledge the financial support by the Research Program of Science and Technology at Universities of Inner Mongolia Autonomous Region (NJZY238 and NJZY239) and the Inner Mongolia Key Laboratory of Photoelectric Functional Materials.

7. References

- 2. (a) S. Sumathi, P. Tharmaraj, C. D. Sheela, R. Ebenezer. J. Coord. Chem. 2011, 64, 1707–1717; http://dx.doi.org/10.1080/00958972.2011.580844
 (b) Z. H. Chohan, M. UI-Hassan, K. M. Khan, C. T. Supuran. J. Enzym. Inhib. Med. Chem. 2005, 20, 183–188. http://dx.doi.org/10.1080/14756360500043257

Table 4. Antibacterial activities

	$MIC (\mu g m L^{-1})$					
	Bacillus subtilis	Escherichia coli	Pseudomonas fluorescens	Staphylococcus aureus		
L	50	> 100	25	12.5		
(HL)CF ₃ SO ₃	50	> 100	25	12.5		
1	6.25	12.5	3.12	1.56		
2	12.5	25	12.5	1.56		
Penicillin	1.3	> 100	> 100	2.1		

Sang et al.: Synthesis, Crystal Structures and Antibacterial ...

- M. A. Vazquez-Fernandez, M. I. Fernandez-Garcia, G. Gonzalez-Riopedre, M. Maneiro, M. J. Rodriguez-Douton. J. Coord. Chem. 2011, 64, 3843–3858. http://dx.doi.org/10.1080/00958972.2011.633164
- 4. (a) A. Lalehzari, J. Desper, C. J. Levy. *Inorg. Chem.* 2008, 47, 1120–1126; http://dx.doi.org/10.1021/ic702015u
 (b) N. Raman, S. Johnson Raja, A. Sakthivel. *J. Coord. Chem.* 2009, 62, 691–709; http://dx.doi.org/10.1080/00958970802326179
 (c) A. D. Garnovskii, I. S. Vasilchenko, D. A. Garnovskii, B. I. Kharisov. *J. Coord. Chem.* 2009, 62, 151–204. http://dx.doi.org/10.1080/00958970802398178
- 5. (a) R. S. Joseyphus, M. S. Nair. J. Coord. Chem. 2009, 62, 319–327; http://dx.doi.org/10.1080/00958970802236048
 (b) N. Nishat, Rahis-Ud-Din, S. Dhyani. J. Coord. Chem. 2009, 62, 996–1004; http://dx.doi.org/10.1080/00958970802339651
 (c) M. S. Refat, I. M. El-Deen, Z. M. Anwer, S. El-Ghol. J. Coord. Chem. 2009, 62, 1709–1718;
 - http://dx.doi.org/10.1080/00958970802684205
 - (d) R. Vafazadeh, A. C. Willis, M. M. Heidari, N. Hasanzade. *Acta Chim. Slov.* **2015**, *62*, 122–129;
 - http://dx.doi.org/10.17344/acsi.2014.797
 - (e) S.-S. Qian, X. Zhao, J. Wang, Z. You. *Acta Chim. Slov.* **2015**, *62*, 828–833.
- (a) H. Li, Z.-J. Zhong, X.-Z. You, W. Chen. J. Coord. Chem. 1997, 42, 271–281;
- http://dx.doi.org/10.1080/00958979708022857 (b) V. Mougel, P. Horeglad, G. Nocton, J. Pecaut, M. Mazzanti. *Angew. Chem. Int. Ed. Engl.* **2009**, *48*, 8477–8480; http://dx.doi.org/10.1002/anie.200903457 (c) X.-L. Ma, Z.-L. You, *Transit. Met. Chem.* **2008**, *33*, 961–
- 965. http://dx.doi.org/10.1007/s11243-008-9136-1
 7. (a) J. Gao, Y.-G. Liu, Y. Zhou, L. M. Boxer, F. R. Woolley, R. A. Zingaro. *ChemBioChem* 2007, *8*, 332–340; http://dx.doi.org/10.1002/cbic.200600299
 (b) T. W. Failes, T. W. Hambley. *J. Inorg. Biochem.* 2007, *101*, 396–403.
 - http://dx.doi.org/10.1016/j.jinorgbio.2006.11.003
- M. Zhang, D.-M. Xian, H.-H. Li, J.-C. Zhang, Z.-L. You. Aust. J. Chem. 2012, 65, 343–350.

- SMART and SAINT. Area Detector Control and Integration Software, Siemens Analytical X-Ray Systems, Inc., Madison, Wisconsin, USA, 1996.
- G. M. Sheldrick, SADABS. Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, 1996.
- 11. G. M. Sheldrick. SHELXTL V5.1 Software Reference Manual, Bruker AXS, Inc., Madison, Wisconsin, USA, 1997.
- J. Meletiadis, J. F. G. M. Meis, J. W. Mouton, J. P. Donnelly, P. E. Verweij. J. Clin. Microbiol. 2000, 38, 2949–2954.
- 13. W. J. Geary. *Coord. Chem. Rev.* **1971**, *7*, 81–122. http://dx.doi.org/10.1016/S0010-8545(00)80009-0
- 14. (a) T. Tunc, M. Sari, R. Yagbasan, H. Tezcan, E. Sahin. *Acta Crystallogr.* 2003, *C59*, o192–o193;
 (b) M. Chang, A. Kobayashi, K. Nakajima, H.-C. Chang, M. Kato. *Inorg. Chem.* 2011, *50*, 8308–8317. http://dx.doi.org/10.1021/ic2008396
- 15. (a) K. Ghosh, P. Kumar, V. Mohan, U. P. Singh, S. Kasiri, S. S. Mandal. *Inorg. Chem.* 2012, *51*, 3343–3345; http://dx.doi.org/10.1021/ic2016676
 (b) K. Ghosh, P. Kumar, N. Tyagi, U. P. Singh, V. Aggarwal, M. C. Baratto. *Eur. J. Med. Chem.* 2010, *45*, 3770–3779. http://dx.doi.org/10.1016/j.ejmech.2010.05.026
- 16. (a) J. M. Holland, C. A. Kilner, M. Thornton-Pett, M. A. Halcrow. *Polyhedron* 2001, *20*, 2829–2840; http://dx.doi.org/10.1016/S0277-5387(01)00892-0
 (b) C. W. G. Ansell, J. Lewis, P. R. Raithby. *J. Chem. Soc. Dalton Trans.* 1982, 2557–2559. http://dx.doi.org/10.1039/dt9820002557
- 17. (a) A.-G. Xie, Y. Qu, M.-M. Wang, G.-Q. Gan, H. Chen, Z.-D. Lin, D. Zhen. J. Coord. Chem. 2009, 62, 2268–2275; http://dx.doi.org/10.1080/00958970902822127
 (b) M. A. Phaniband, S. D. Dhumwad. J. Coord. Chem. 2009, 62, 2399–2410; http://dx.doi.org/10.1080/00958970902803341
 (c) S. Sumathi, P. Tharmaraj, C. D. Sheela, R. Ebenezer, P. S. Bhava. J. Coord. Chem. 2011, 64, 1673–1682; http://dx.doi.org/10.1080/00958972.2011.579116
 (d) M. Ghosh, M. Fleck, B. Mahanti, A. Ghosh, G. Pilet, D. Bandyopadhyay. J. Coord. Chem. 2012, 65, 3884–3894. http://dx.doi.org/10.1080/00958972.2012.727990

Povzetek

Pripravili smo novo trifluorometilsulfonatno sol 2-[(3-kloropiridin-2-il)hidrazonometil]-6-metoksifenola, (HL)CF₃SO₃, in njena bakrova(II) in kobaltova(III) kompleksa [CuL(OH₂)]CF₃SO₃ · 0.5H₂O (1) in [CoL₂]CF₃SO₃ · CH₃OH (2) ter jih okarakterizirali s fizikalno-kemijskimi metodami in monokristalno rentgensko analizo. Trifluorometilsulfonatni anion je prisoten v vseh treh spojinah. Cu atom v kompleksu 1 je koordiniran preko fenolatnega O, imino N in piridinskega N atoma liganda L in ima kvadratno-planarno geometrijo. Co atom v kompleksu 2 je koordiniran preko dveh fenolatnih O, dveh imino N in dveh piridinskih N atomov dveh L ligandov in ima oktaedrično geometrijo. Vsem triem spojinam smo določili *in vitro* antibakterijsko aktivnost.