Scientific paper

Syntheses, Crystal Structures and Antimicrobial Activity of Zinc(II) Complexes Derived from 5-Bromo-2-(((2-piperazin-1-yl)ethyl)imino)methyl)phenol

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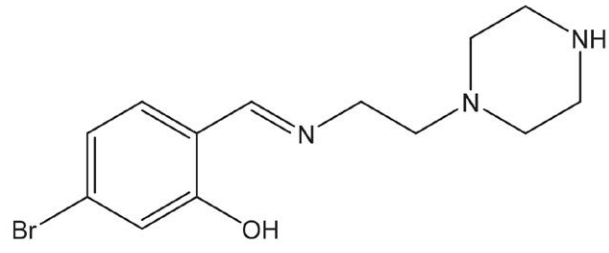
Abstract

Three new zinc(II) complexes, $[ZnCl_2L]\cdot CH_3OH$ (**1**), $[ZnClL(NCS)]\cdot 2CH_3OH\cdot 0.5H_2O$ (**2**), and $[ZnL(NCS)_2]\cdot CH_3OH\cdot H_2O$ (**3**), where L is the zwitterionic form of 5-bromo-2-(((2-piperazin-1-yl)ethyl)imino)methyl)phenol, NCS is thiocyanate anion, were facile prepared by reaction of different molar ratio of L, zinc chloride and ammonium thiocyanate in methanol. The complexes were characterized by IR and UV-Vis spectroscopy. Detailed structures of the three complexes were confirmed by single crystal X-ray determination. The Zn atoms in the complexes are in tetrahedral coordination. The Schiff base ligand coordinates to Zn atom through phenolate oxygen atom and amino and imino nitrogen atoms. The remaining two sites are occupied by two Cl for **1**, one Cl and one NCS for **2**, and two NCS for **3**. The compounds show significant antimicrobial activities.

Keywords: Schiff base, zinc complex, crystal structure, antimicrobial activity

1. Introduction

The preparation of metal complexes with new structures and biological activities is a hot topic in bioinorganic and coordination chemistry. Among various ligands, Schiff bases due to their facile synthesis and interesting biological activities, have received particular attention in the construction of metal complexes.[1] Zinc complexes with Schiff base ligands are reported to have various biological activities, and are used as excellent alternatives for classic organic type antifungal, antibacterial and antitumor agents.[2] Despite the large number of metal complexes with antibacterial activities, it is necessary to prepare new zinc complexes with high activity. It has been reported that compounds with electron-withdrawing groups can improve their antimicrobial ability.[3] The compounds with chloro, fluoro, iodo and bromo groups have shown remarkable antimicrobial activities.[4] Thiocyanate anion is readily coordinate to metal atoms to form complexes with interesting structures.[5] Recently, we have reported some Schiff base complexes with interesting biological activities.[6] Moreover, the complexes with ligands containing piperazine group have effective antibacterial activities.[7] In pursuit of new Schiff base complexes with potential antimicrobial activity, three new zinc complexes $[ZnCl_2L]\cdot CH_3OH$ (**1**), $[ZnClL(NCS)] \cdot 2CH_3OH \cdot 0.5H_2O$ (**2**), and $[ZnL(NCS)_2] \cdot CH_3OH \cdot H_2O$ (**3**), where L is the zwitterionic form of 5-bromo-2-(((2-piperazin-1-yl)ethyl)imino)methyl)phenol (Scheme 1), NCS is thiocyanate anion, and their antimicrobial activities are present. The compounds show significant antimicrobial activities.



Scheme 1. The Schiff base L.

2. Experimental

2. 1. Materials and Methods

4-Bromosalicylaldehyde, *N*-(2-aminoethyl)piperazine, zinc chloride and ammonium thiocyanate were obtained from Sigma-Aldrich. All other chemicals were commercial obtained from Xiya Chemical Co. Ltd. The Schiff base L was prepared according to the literature method.[8] Elemental analyses of C, H and N were carried out in a Perkin-Elmer automated model 2400 Series II CHNS/O analyzer. FT-IR spectra were obtained on a Perkin-Elmer 377 FT-IR spectrometer with samples prepared as KBr pellets. UV-Vis spectra were obtained on a Lambda 35 spectrometer. Molar conductivities of the complexes in DMSO solutions (10^{-3} M) at room temperature were measured using a Systronic model 303 direct reading conductivity meter.

2. 2. Synthesis of $[ZnCl_2L]\cdot CH_3OH$ (1)

HL (0.10 mmol, 31 mg) and zinc chloride (0.10 mmol, 14 mg) were mixed in methanol (20 mL). The mixture was stirred at 25 °C for 20 min to give a colorless solution. Block single crystals were formed upon slow evaporation. The crystals were obtained by filtration. Yield: 32 mg (67%). Anal. calc. for $C_{14}H_{22}BrCl_2N_3O_2Zn$: C, 34.99; H, 4.61; N, 8.74; found: C, 35.12; H, 4.55; N, 8.66%. Characteristic IR data (cm^{-1}): 1633 ($\nu_{C=N}$), 1577, 1529, 1452, 1406, 1351, 1289, 1268, 1185, 1141, 1070, 1019, 910, 855, 805, 763, 733, 610, 596, 534, 479, 449. UV-Vis data (MeOH, λ_{max} (nm), ε (L mol^{-1} cm^{-1})): 227, 2.32×10^3; 245, 1.91×10^3; 267, 1.23×10^3; 366, 6.35×10^2. Molar conductance (10^{-3} mol L^{-1} in DMSO): 32 Ω^{-1} cm^2 mol^{-1}.

2. 3. Synthesis of $[ZnClL(NCS)]\cdot 2CH_3OH\cdot 0.5H_2O$ (2)

HL (0.10 mmol, 31 mg), zinc chloride (0.10 mmol, 14 mg) and ammonium thiocyanate (0.10 mmol, 7.6 mg) were mixed in methanol (20 mL). The mixture was stirred at 25 °C for 20 min to give a colorless solution. Block single crystals were formed upon slow evaporation. The crystals were obtained by filtration. Yield: 35 mg (64%). Anal. calc. for $C_{16}H_{27}BrClN_4O_{3.5}SZn$: C, 35.31; H, 5.00; N, 10.29; found: C, 35.22; H, 5.11; N, 10.20%. Characteristic IR data (cm^{-1}): 2088 (ν_{NCS}), 1632 ($\nu_{C=N}$), 1581, 1523, 1471, 1452, 1411, 1352, 1293, 1247, 1187, 1139, 1065, 1049, 1021, 915, 843, 788, 760, 730, 677, 620, 606, 585, 532, 465. UV-Vis data (MeOH, λ_{max} (nm), ε (L mol^{-1} cm^{-1})): 227, 2.41×10^3; 245, 2.09×10^3; 273, 1.03×10^3; 367, 6.96×10^2. Molar conductance (10^{-3} mol L^{-1} in DMSO): 28 Ω^{-1} cm^2 mol^{-1}.

2. 4. Synthesis of $[ZnL(NCS)_2]\cdot CH_3OH\cdot H_2O$ (3)

HL (0.10 mmol, 31 mg), zinc chloride (0.10 mmol, 14 mg) and ammonium thiocyanate (0.20 mmol, 15 mg) were mixed in methanol (20 mL). The mixture was

Table 1. Crystallographic and refinement data for the complexes

Complex	1	2	3
Formula	$C_{14}H_{22}BrCl_2N_3O_2Zn$	$C_{16}H_{27}BrClN_4O_{3.5}SZn$	$C_{16}H_{24}BrN_5O_3S_2Zn$
Formula weight	480.53	544.21	543.80
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a (Å)	7.7284(12)	9.3833(13)	9.5085(12)
b (Å)	21.3267(16)	20.2828(18)	20.7468(15)
c (Å)	11.4218(13)	11.7620(15)	11.8697(13)
α (°)	90	90	90
β (°)	90.00(2)	95.904(2)	97.085(1)
γ (°)	90	90	90
V (Å^3)	1882.6(4)	2226.7(5)	2323.7(4)
Z	4	4	4
D_{calc} (g cm^{-3})	1.695	1.623	1.554
μ(Mo Kα) (mm^{-1})	3.721	3.137	2.981
F(000)	968	1108	1104
Measured reflections	6661	11590	12096
Unique reflections	2533	4155	4325
Observed reflections ($I \geq 2\sigma(I)$)	1512	2292	2329
Parameters	210	260	258
Restraints	0	15	12
GOOF	0.0878	1.048	1.032
R_1, wR_2 [$I \geq 2\sigma(I)$][a]	0.0470, 0.1021	0.0746, 0.1676	0.0536, 0.1290
R_1, wR_2 (all data)[a]	0.0840, 0.1109	0.1461, 0.1996	0.1224, 0.1558

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

methanol (20 mL). The mixture was stirred at 25 °C for 20 min to give a colorless solution. Block single crystals were formed upon slow evaporation. The crystals were obtained by filtration. Yield: 27 mg (50%). Anal. calc. for $C_{16}H_{24}BrN_5O_3S_2Zn$: C, 35.34; H, 4.45; N, 12.88; found: C, 35.43; H, 4.37; N, 12.75%. Characteristic IR data (cm^{-1}): 2073 (ν_{NCS}), 1634 ($\nu_{C=N}$), 1579, 1527, 1469, 1402, 1349, 1289, 1257, 1196, 1185, 1139, 1072, 1017, 910, 839, 795, 760, 730, 610, 543, 485, 447. UV-Vis data (MeOH, λ_{max} (nm), ε (L mol^{-1} cm^{-1})): 228, 2.45 × 10^3; 245, 2.41 × 10^3; 277, 1.10 × 10^3; 367, 7.13 × 10^2. Molar conductance (10^{-3} mol L^{-1} in DMSO): 25 Ω^{-1} cm^2 mol^{-1}.

2. 5. X-ray Crystallography

X-ray diffraction was done with a Bruker APEX II CCD area diffractometer equipped with Mo-K_α radiation (λ = 0.71073 Å). The collected data were reduced with SAINT.[9] Multi-scan absorption correction was performed with SADABS.[10] Structures of the three zinc complexes were solved by direct method, and refined against F^2 by full-matrix least-squares method with SHELXTL.[11] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. The crystallographic data and refinement parameters for the complexes are listed in Table 1.

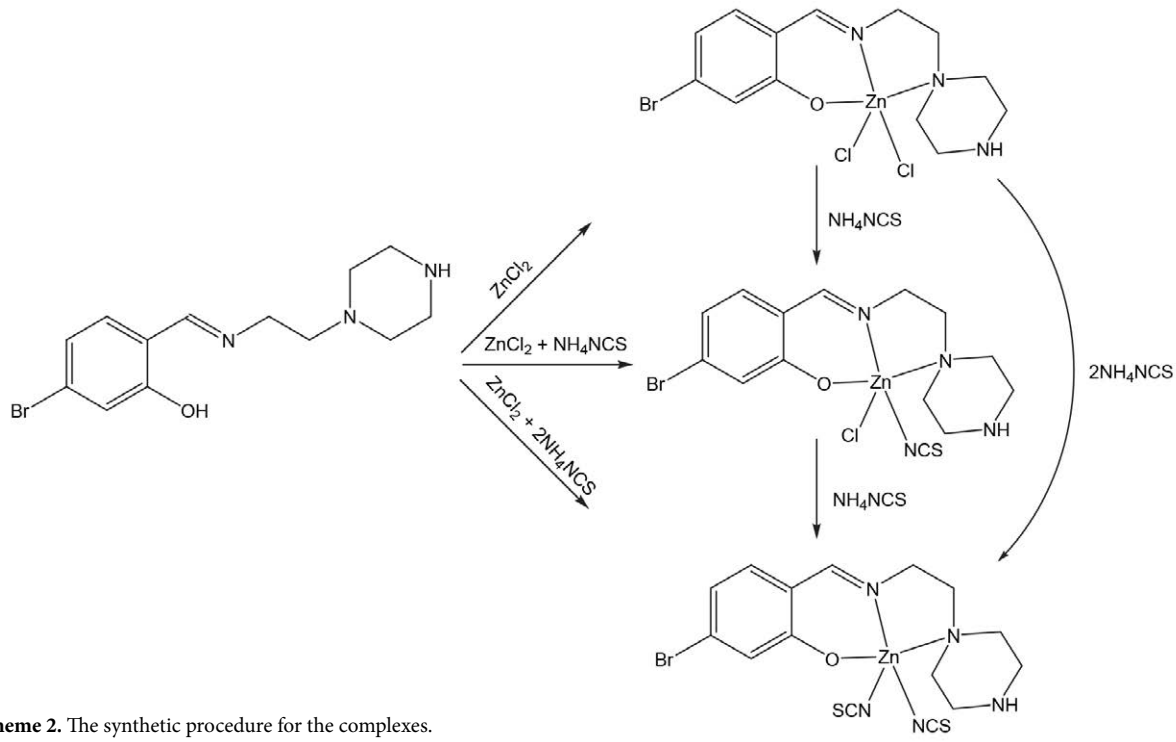
2. 6. Antimicrobial Aassay

The three zinc complexes were assayed against bacteria strains *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli*, and *Pseudomonas fluorescence* using MH (Mueller-Hinton) medium. The compounds were also assayed against fungi *Candida albicans* and *Aspergillus niger* using RPMI-1640 medium. The MIC values were determined by a colorimetric method using MTT.[12] A stock solution of the compound at concentration of 150 μg mL^{-1} in DMSO was prepared and graded quantities (75, 37.5, 18.8, 9.4, 4.7, 2.3, 1.2, and 0.59 μg mL^{-1}), which were incorporated in specified quantity of the corresponding sterilized liquid medium. A specified quantity of the medium containing the compound was poured into micro-titration plates. Suspension of the microorganism was prepared to contain 1.0 × 10^5 cfu mL^{-1} and applied to micro-titration plates with serially diluted compounds in DMSO to be tested and incubated at 37 °C for 24 h and 48 h for bacteria and fungi, respectively. Then the MIC values were visually determined on each of the microtitration plates, 50 μL of PBS (phosphate buffered saline 0.01 mol L^{-1}, pH = 7.4) containing 2 mg of MTT mL^{-1} was added to each well. Incubation was continued at room temperature for 4–5 h. The content of each well was removed and 100 μL solution of 95% isopropanol and 1 mol L^{-1} 5% HCl was added to extract the dye. After 12 h of incubation at room temperature, the optical density was measured with a microplate reader at 550 nm.

3. Results and Discussion

3. 1. Synthesis and Characterization

The three zinc complexes were facile prepared by reaction of the Schiff base ligand, zinc chloride and ammonium thiocyanate in molar ratio of 1:1:0, 1:1:1 and



Scheme 2. The synthetic procedure for the complexes.

1:1:2, respectively in methanol (Scheme 1). Interestingly, complex **2** can be prepared by reaction of equimolar quantities of complex **1** with ammonium thiocyanate. Complex **3** can be prepared by reaction of equimolar quantities of complex **2** with ammonium thiocyanate, or 1:2 molar ratio of complex **1** with ammonium thiocyanate. Single crystals of the three complexes were obtained from their methanolic solution. Elemental analyses of the complexes are in accordance with their molecular structures determined by single crystal X-ray analysis.

3. 2. Spectroscopic Studies

The intense absorptions at 1632–1634 cm^{-1} for the complexes are generated by the vibrations of the C=N bonds of the Schiff base ligands which are formed from the condensation reaction of 4-bromosalicylaldehyde and *N*-(2-aminoethyl)piperazine.[13] The strong bands at 2088 cm^{-1} for complex **2** and 2073 cm^{-1} for complex **3** can be assigned to thiocyanate ligands.[14]

In the electronic spectra of the three complexes, the bands at 360–370 nm are attributed to azomethine chromophore $\pi \rightarrow \pi^*$ transition.[15] The bands at higher energies (220–230 and 240–280 nm) are associated with benzene $\pi \rightarrow \pi^*$ transition.[15]

3. 3. Structure Description of the Complexes

The bond lengths and angles related to the Zn atoms for the three compounds are listed in Table 2. Molecular structures of the compounds are shown in Figures 1, 2 and 3, respectively. Compound **1** contains a $[ZnCl_2L]$ complex molecule and a methanol molecule of crystallization. Compound **2** contains a [ZnClL(NCS)] complex molecule, two methanol molecules and half water molecule of crystallization. Compound **3** contains a $[ZnL(NCS)_2]$ complex molecule, a methanol molecule and a water molecule of crystallization. The Zn atom in each complex is in trigonal bipyramidal coordination, with the equatorial plane defined by the imino nitrogen (N1) of the Schiff base ligand and two Cl or N atoms of the thiocyanate ligands, *viz.* Cl1 and Cl2 for **1**, Cl1 and N4 for **2**, N4 and N5 for **3**. The two axial positions are occupied by the phenolate oxygen (O1) and amino nitrogen (N2) of the Schiff base ligands. The definition of the trigonal bipyramidal coordination is based on index facor τ (0.55 for **1** and **2**, 0.66 for **3**).[16] The Schiff base acts as a tridentate ligand, chelating the Zn atom by generating one five and one six-membered rings with bite angles of 77.24(16)° and 90.00(16)° (**1**), 75.4(3)° and 90.2(3)° (**2**), and 75.9(2)° and 91.19(17)° (**3**). The bond angles in the equatorial planes are 110.60(14)-134.01(14)° (**1**), 106.8(3)-132.4(2)° (**2**) and 109.5(3)-127.7(2)° (**3**), and those between the apical donor atoms are 167.09(14)° (**1**), 165.5(3)° (**2**) and 167.0(2)° (**3**), indicating slight distortion of the coordination from ideal square pyramidal geometry. The coordinate bond lengths and angles in the three complexes are similar to each other, and are comparable to those in reported Schiff base zinc(II) complexes.[17]

In the crystal structures of the three complexes, the methanol and water molecules are linked to complex molecules through intermolecular hydrogen bonds (Table 3), The molecules are linked through hydrogen bonds (Table 3) to form three dimensional networks (Figures 4, 5 and 6).

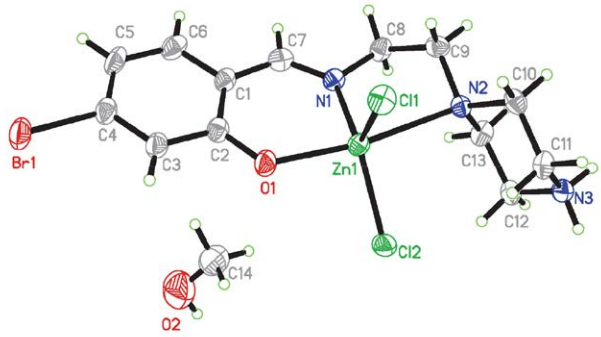


Figure 1. A perspective view of complex **1** with the atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level.

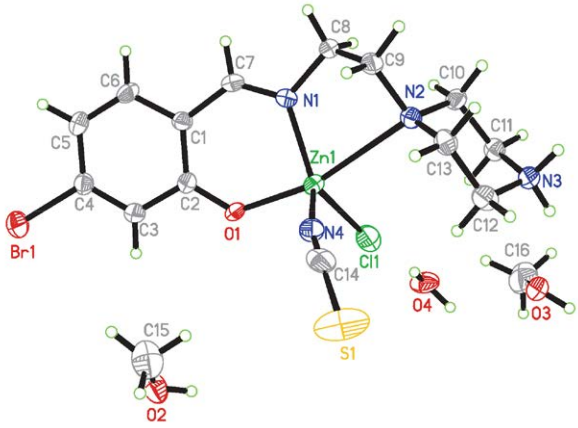


Figure 2. A perspective view of complex **2** with the atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level.

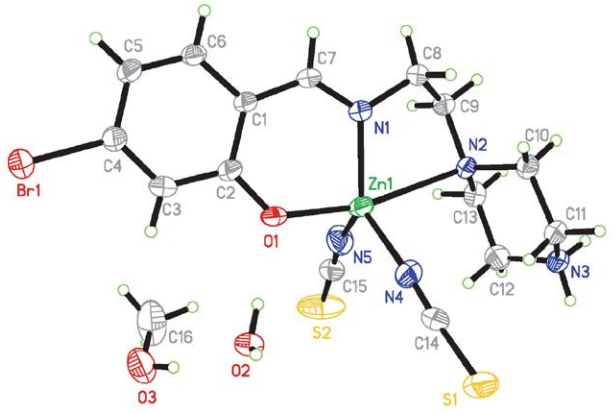


Figure 3. A perspective view of complex **3** with the atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level.

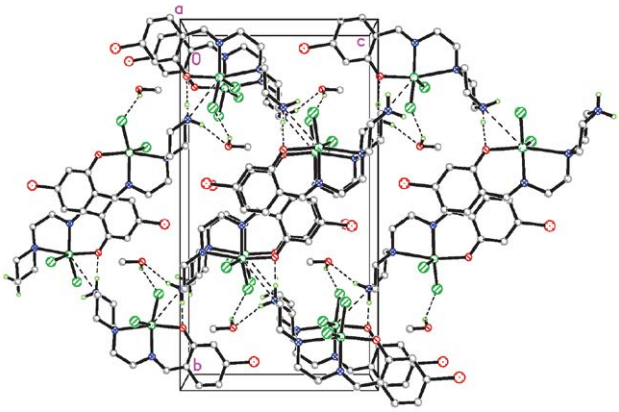


Figure 4. The crystal structure of complex **1**, viewed along the *a* axis. Hydrogen bonds are shown as dashed lines.

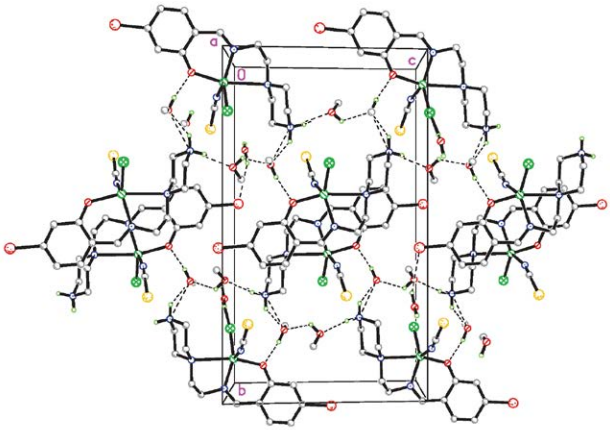


Figure 5. The crystal structure of complex **2**, viewed along the *a* axis. Hydrogen bonds are shown as dashed lines.

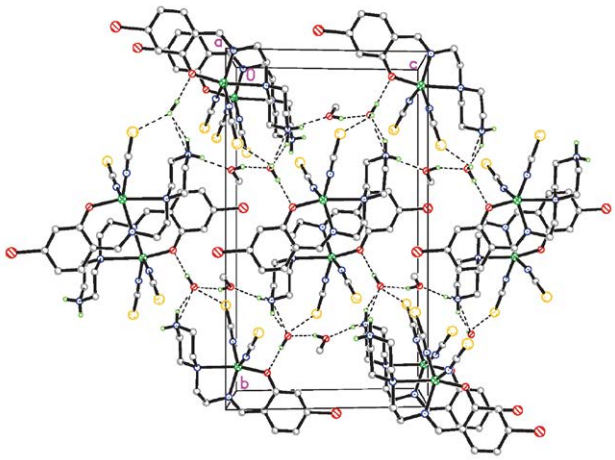


Figure 6. The crystal structure of complex **3**, viewed along the *a* axis. Hydrogen bonds are shown as dashed lines.

Table 2. Selected bond distances (Å) and angles (°) for the complexes

1			
Zn1–N1	2.032(4)	Zn1–O1	2.063(4)
Zn1–N2	2.580(5)	Zn1–Cl1	2.2726(16)
Zn1–Cl2	2.2643(16)		
N1–Zn1–O1	90.00(16)	N1–Zn1–Cl2	134.01(14)
O1–Zn1–Cl2	93.82(12)	N1–Zn1–Cl1	110.60(14)
O1–Zn1–Cl1	95.66(14)	Cl2–Zn1–Cl1	114.56(6)
N1–Zn1–N2	77.24(16)	O1–Zn1–N2	167.09(14)
Cl2–Zn1–N2	93.69(11)	Cl1–Zn1–N2	90.74(10)
2			
Zn1–N1	1.999(7)	Zn1–O1	2.001(6)
Zn1–N2	2.685(6)	Zn1–Cl1	2.209(3)
Zn1–N4	2.009(9)		
N1–Zn1–O1	90.2(3)	N1–Zn1–N4	118.6(4)
O1–Zn1–N4	98.3(4)	N1–Zn1–Cl1	132.4(2)
O1–Zn1–Cl1	97.0(2)	N4–Zn1–Cl1	106.8(3)
N2–Zn1–N1	75.4(3)	N2–Zn1–O1	165.5(3)
N2–Zn1–N4	87.8(3)	N2–Zn1–Cl1	93.7(3)
3			
Zn1–N1	2.008(4)	Zn1–O1	2.008(4)
Zn1–N4	1.961(6)	Zn1–N5	1.984(7)
Zn1–N2	2.674(6)		
N4–Zn1–N5	109.5(3)	N4–Zn1–N1	127.7(2)
N5–Zn1–N1	120.0(2)	N4–Zn1–O1	97.3(2)
N5–Zn1–O1	98.9(2)	N1–Zn1–O1	91.19(17)
N2–Zn1–O1	167.0(2)	N2–Zn1–N1	75.9(2)
N2–Zn1–N4	91.5(2)	N2–Zn1–N5	87.0(2)

Table 3. Hydrogen bond distances (Å) and angles (°) for the complexes

D*–H···*A	***d*(*D*–H)**	***d*(H···*A*)**	***d*(*D*···*A*)**	**Angle (*D*–H···*A*)**
1				
N3–H3A···O2$^{\#1}$	0.90	2.12	2.994(10)	163(6)
N3–H3B···O1$^{\#2}$	0.90	1.85	2.736(6)	168(6)
O2–H2···Cl2$^{\#3}$	0.82	2.62	3.349(8)	150(6)
2				
O2–H2A···O3$^{\#4}$	0.82	2.15	2.702(10)	125(5)
O3–H3C···O1$^{\#5}$	0.82	1.79	2.589(9)	165(5)
O4–H4A···Br1$^{\#6}$	0.85	2.79	3.563(13)	151(6)
O4–H4B···Cl1	0.85	1.65	2.435(14)	151(6)
N3–H3A···O2$^{\#1}$	0.90	1.88	2.752(10)	162(5)
N3–H3B···O3	0.90	2.06	2.827(10)	143(6)
N3–H3B···Cl1$^{\#5}$	0.90	2.97	3.529(8)	122(7)
3				
N3–H3A···O2$^{\#7}$	0.90	2.02	2.827(7)	148(6)
N3–H3B···O3$^{\#8}$	0.90	1.93	2.799(7)	163(6)
O3–H3C···O2	0.82	1.95	2.751(7)	164(7)
O2–H2B···O1	0.85	1.86	2.661(6)	158(7)

Symmetry codes: #1: $x, y, 1 + z$; #2: $3/2 + x, ½ – y, ½ + z$; #3: $3/2 + x, ½ – y, –½ + z$; #4: $x, ½ – y, –½ + z$; #5: $x, ½ – y, ½ + z$; #6: $2 – x, –½ + y, ½ – z$; #7: $x, 3/2 – y, –½ + z$; #8: $x, y, –1 + z$.

3. 4. Antimicrobial Activity

The compounds and related starting materials were assayed for antibacterial activities against Gram positive bacterial strains *Bacillus subtilis* and *Staphylococcus aureus*, and Gram negative bacterial strains *Escherichia coli* and *Pseudomonas fluorescence* by MTT method. The MIC (minimum inhibitory concentration, μg mL^{-1}) values against the bacteria are summarized in Table 4. Penicillin G was used as a reference. The three zinc complexes have better activities against all the bacteria strains than the free Schiff base and zinc chloride. Complexes **1** and **2** show strong activity against *B. subtilis*, *S. aureus* and *E. coli*, while medium activity against *P. fluorescence*. Complex **3** shows similar activities against *S. aureus* and *E. coli* as complex **2**, but lower activity against *B. subtilis and P. fluorescence*. Complexes **1** and **2** have stronger or similar activity against all the bacteria than Penicillin G. Complex **3** has stronger activity against *E. coli* and *P. fluorescence*, while weaker or similar activity against *B. subtilis* and *S. aureus* than Penicillin G. However, the three complexes have no activity on the fungal strains *Candida albicans* and *Aspergillus niger*. The complexes have similar antimicrobial activities with the zinc complexes derived from 5-bromo-2-((cychlopentylimino)methyl)phenol,[6d] and higher activities than the nickel complexes with Schiff base ligands.[18]

Table 4. Antibacterial activities of the assayed compounds (MIC, μg mL^{-1})

Tested material	*B. subtilis*	*S. aureus*	*E. coli*	*P. fluorescence*
1	1.2	2.3	9.4	18.8
2	2.3	4.7	9.4	18.8
3	4.7	4.7	9.4	37.5
L	9.4	18.8	37.5	> 150
$ZnCl_2$	18.8	18.8	75	> 150
Penicillin G	2.3	4.7	>150	> 150

4. Conclusion

In this paper, three new zinc complexes were synthesized from Schiff base 5-bromo-2-(((2-piperazin-1-yl)ethyl)imino)methyl)phenol with zinc chloride in the absence or presence of ammonium thiocyanate. The complexes were characterized by physico-chemical methods. X-ray single crystal structure determination indicates that the zinc atoms in the complexes are in square pyramidal coordination. The chloride ligand can be replaced by thiocyanate ligand. The complexes have strong activities against bacteria *B. subtilis*, *S. aureus* and *E. coli*, which deserve further study.

Acknowlegments

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Supplementary Data

CCDC 2314879 (**1**), 2314880 (**2**) and 2314881 (**3**) contain the supplementary crystallographic data for the compounds. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Povzetek

Sintetizirali smo tri nove cinkove(II) komplekse $[ZnCl_2L]\cdot CH_3OH$ (**1**), $[ZnClL(NCS)]\cdot 2CH_3OH\cdot 0.5H_2O$ (**2**) in $[ZnL(NCS)_2]\cdot CH_3OH\cdot H_2O$ (**3**), kjer je L zwitterionska oblika 5-bromo-2-(((2-piperazin-1-il)etil)imino)metil)fenola, NCS pa je tiocianatni anion, v različnih molskih razmerij L, cinkovega klorida in amonijevega tiocianata v metanolu. Kompleksi so bili okarakterizirani z IR in UV-Vis spektroskopijo. Strukture treh kompleksov so bile določene z mononokristalno rentgensko analizo. V kompleksih so atomi Zn v tetraedrični koordinaciji. Ligand Schiffove baze se koordinira na atom Zn prek fenolatnega kisikovega atoma ter amino in imino dušikovega atoma. Preostali dve mesti zasedata dva Cl za **1**, en Cl in en NCS za **2** ter dva NCS za **3**. Spojine imajo protimikrobno aktivnost.