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Anion Induced Synthesis and Crystal Structures of Schiff Base Copper(II) and Zinc(II) Complexes with Antibacterial Activity

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Abstract—Two new mononuclear copper(II) complexes, $[Cu(L^a)_2]$ (**I**) and $[Cu(L^aH)_2]Br_2$ (**II**), and two new polynuclear zinc(II) complexes, $[Zn_2(L^b)(CH_3COO)_2(NCS)]$ (**III**) and $[Zn_3(L^b)_2(CH_3COO)_2(N_3)_2]$ (**IV**), where L^a is 5-bromo-2-((3-morpholinopropylimino)methyl)phenolate, L^b is 5-bromo-2-(((2-(pyrrolidin-1-yl)ethyl)imino)methyl)phenolate, were synthesized and characterized by IR and UV–Vis spectra. The molecular structures of the complexes were confirmed by single crystal X-ray determination (CIF files CCDC nos. 2109986 (**I**), 2109987 (**II**), 2109988 (**III**) and 2109989 (**IV**)). The Cu ions in the copper complexes **I** and **II** are coordinated by two phenolate O and two imino N atoms, forming square planar geometry. The Zn atoms in complex **III** are in square planar and tetrahedral geometry, and those in complex **IV** are in trigonal-bipyramidal and octahedral geometry. The bidentate Schiff base ligands in complex **I** are monoanionic, while those in complex **II** are zwitterionic. The tridentate Schiff base ligands in complexes **III** and **IV** are monoanionic. The anions used in the synthesis and crystallization play an important role for the formation of the final structures of the complexes. The complexes were assayed for antibacterial activities by MTT method.

Keywords: Schiff base, copper complex, zinc complex, crystal structure, antibacterial activity

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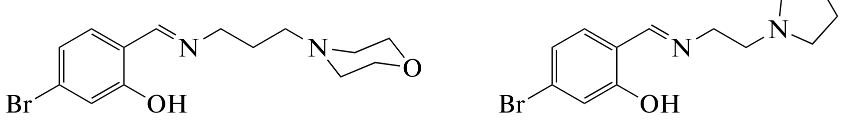
INTRODUCTION

Schiff bases are a kind of biological active compounds, which have received much attention for their antibacterial activities [1–5]. Interestingly, Schiff bases bearing N and O donor ions are well known ligands in coordination chemistry [6]. To date, a large number of Schiff base complexes have been reported. During the search of literature, we found that most of the Schiff base complexes have interesting antibacterial activities [7–11]. When administered by halo-substituent groups, the antibacterial activities can be enhanced [12]. The structures of the complexes are highly related to the physical and biological properties. Thus, how to control synthesis of complexes with aiming structures is full of challenge. However, despite the various methods to modulate the structures of complexes, no general correlation has found so far between anions and structures of the complexes. Studying the influence of anions of metal salts on self-assembly synthesis may help us better understand and control the topologies of complexes. Herein, we report the synthesis, characterization and single crystal structures of two new copper(II) complexes, $[Cu(L^a)_2]$ (**I**) and $[Cu(L^aH)_2]Br_2$ (**II**), and two new zinc(II) complexes, $[Zn_2(L^b)(CH_3COO)_2(NCS)]$ (**III**) and $[Zn_3(L^b)_2(CH_3COO)_2(N_3)_2]$ (**IV**) with the bromo-containing Schiff base ligands 5-bromo-2-[(3-morpholinopropylimino)methyl]phenol (**HL^a**; Scheme 1) and 5-bromo-2-(((2-(pyrrolidin-1-yl)ethyl)imino)methyl)phenol (**HL^b**; Scheme 1). The antibacterial activity of the compounds against Gram-positive bacterial strains (*B. subtilis*, *S. aureus*, and *St. faecalis*) and Gram-negative bacterial strains (*E. coli*, *P. aeruginosa*, and *E. cloacae*) by MTT method was studied.



Scheme 1.

EXPERIMENTAL

Materials and physical methods. 4-Bromosalicylaldehyde, 3-morpholinopropan-1-amine, 2-(pyrrolidin-1-yl)ethanamine, copper acetate, copper bromide, zinc acetate, ammonium thiocyanate and sodium azide were purchased from Aldrich with AR grade. Methanol was commercial obtained and used as received. The Schiff bases HL^a and HL^b were prepared by 4-bromosalicylaldehyde with 3-morpholinopropan-1-amine and 2-(pyrrolidin-1-yl)ethanamine, respectively in methanol [13]. Elemental analyses for C, H and N were performed on a Perkin-Elmer 2400 II analyzer. FT-IR spectra were recorded as KBr pellets on Bruker Tensor-27. UV–Vis spectra were recorded on Lambda 35 spectrophotometer. Single crystal X-ray diffraction was carried out with a Bruker Apex II CCD diffractometer. Molar conductivity was measured in methanol with a DDS-11A molar conductivity meter.

Synthesis of $[Cu(L^a)_2]$ (I). To a stirred methanolic solution (15 mL) of HL^a (0.33 g, 1.0 mmol) was added a methanolic solution (15 mL) of copper acetate (0.20 g, 1.0 mmol). After one hour stirring, the solution was filtered and the filtrate was kept for slow evaporation. The diffraction quality block like blue single crystals that deposited over a period of 3 days were collected by filtration and washed with methanol. The yield was 0.13 g (36%).

For $C_{28}H_{36}N_4O_4Br_2Cu$

Anal. calcd., %	C, 46.97	H, 5.07	N, 7.83
Found, %	C, 47.21	H, 5.18	N, 7.72

IR data (KBr; ν, cm^{-1}): 2964, 2909, 2867, 2825, 2782, 1623, 1581, 1519, 1459, 1430, 1400, 1303, 1269, 1193, 1139, 1115, 1064, 1035, 983, 917, 851, 782, 601, 535, 475, 445. UV–Vis data (methanol; λ, nm (ε, L mol^{-1} cm^{-1})): 230 (21230), 247 (21160), 277 (14510), 357 (5380). Λ_M (10^{-3} mol L^{-1} in methanol): 32 Ω^{-1} cm^2 mol^{-1}.

Synthesis of $[Cu(L^aH)_2]Br_2$ (II). This complex was prepared by the same method as complex **I** with copper acetate replaced by copper bromide (0.22 g, 1.0 mmol). After one hour stirring, the solution was filtered and the filtrate was kept for slow evaporation. The diffraction quality block like blue single crystals that deposited over a period of 5 days were collected by filtration and washed with methanol. The yield was 0.17 g (39%).

For $C_{28}H_{38}N_4O_4Br_4Cu$

Anal. calcd., %	C, 38.31	H, 4.36	N, 6.38
Found, %	C, 38.17	H, 4.45	N, 6.23

IR data (KBr; ν, cm^{-1}): 3100, 2952, 2922, 2867, 2782, 1622, 1581, 1526, 1466, 1431, 1408, 1334, 1301, 1256, 1216, 1199, 1152, 1140, 1113, 1077, 1049, 972, 925, 883, 863, 840, 801, 750, 690, 601, 551, 473, 423. UV–Vis data (methanol; λ, nm (ε, L mol^{-1} cm^{-1})): 219 (19370), 248 (10850), 265 (9790), 320 (3520), 368 (2735). Λ_M (10^{-3} mol L^{-1} in methanol): 211 Ω^{-1} cm^2 mol^{-1}.

Synthesis of $[Zn_2(L^b)(CH_3COO)_2(NCS)]$ (III). To a stirred methanolic solution (15 mL) of HL^a (0.30 g, 1.0 mmol) was added a methanolic solution (15 mL) of zinc acetate dehydrate (0.22 g, 1.0 mmol) and ammonium thiocyanate (0.076 g, 1.0 mmol). After one hour stirring, the solution was filtered and the filtrate was kept for slow evaporation. The diffraction quality block like colorless single crystals that deposited over a period of four days were collected by filtration and washed with methanol. The yield was 0.16 g (53%).

For $C_{18}H_{22}N_3O_5SBrZn_2$

Anal. calcd., %	C, 35.84	H, 3.68	N, 6.97
Found, %	C, 35.71	H, 3.57	N, 7.12

IR data (KBr; ν, cm^{-1}): 3073, 2985, 2906, 2858, 2837, 2076, 1657, 1594, 1539, 1475, 1442, 1391, 1344, 1281, 1200, 1137, 1120, 1073, 1044, 913, 849, 799, 668, 617, 591, 557, 456, 435. UV–Vis data (methanol; λ, nm (ε, L mol^{-1} cm^{-1})): 227 (18520), 240 (20330), 275 (15620), 344 (7460). Λ_M (10^{-3} mol L^{-1} in methanol): 26 Ω^{-1} cm^2 mol^{-1}.

Synthesis of $[Zn_3(L^b)_2(CH_3COO)_2(N_3)_2]$ (IV). This complex was prepared by the same method as complex **III** with ammonium thiocyanate replaced by sodium azide (0.065 g, 1.0 mmol). After one hour stirring, the solution was filtered and the filtrate was kept for slow evaporation. The diffraction quality block like colorless single crystals that deposited over a period of 6 days were collected by filtration and washed with methanol. The yield was 0.14 g (42%).

For $C_{30}H_{38}Br_2N_{10}O_6Zn_3$

Anal. calcd., %	C, 36.37	H, 3.87	N, 14.14
Found, %	C, 36.50	H, 3.96	N, 14.03

IR data (KBr; ν, cm^{-1}): 3078, 2981, 2964, 2926, 2863, 2085, 1645, 1581, 1526, 1459, 1445, 1421, 1399, 1338, 1287, 1240, 1192, 1120, 1068, 1053, 915, 870, 793, 733, 669, 615, 590, 536, 466, 440, 417. UV–Vis data (methanol; λ, nm (ε, L mol^{-1} cm^{-1})): 235 (20780), 275 (10670), 350 (5230). Λ_M (10^{-3} mol L^{-1} in methanol): 23 Ω^{-1} cm^2 mol^{-1}.

X-ray structure determination. Intensity data of the complexes were collected at 298(2) K on a Bruker Apex II CCD diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71073 Å). For data processing and absorption correction the packages SAINT and SADABS were used [14]. Structures of

Table 1. Crystallographic data and refinement details for complexes **I**–**IV**

Parameter	Value			
	I	**II**	**III**	**IV**
Empirical formula	$C_{28}H_{36}N_4O_4Br_2Cu$	$C_{28}H_{38}N_4O_4Br_4Cu$	$C_{18}H_{22}N_3O_5SBrZn_2$	$C_{30}H_{38}Br_2N_{10}O_6Zn_3$
Molecular weight	715.97	877.80	603.09	990.63
Crystal color, habit	Blue, block	Blue, block	Colorless, block	Colorless, block
Crystal size, mm	0.19 × 0.17 × 0.17	0.23 × 0.22 × 0.20	0.19 × 0.18 × 0.18	0.21 × 0.18 × 0.18
Crystal system	Trigonal	Monoclinic	Monoclinic	Monoclinic
Space group	$R\bar{3}$	$P2_1/c$	$P2_1/c$	$P2_1/n$
Unit cell dimensions:				
a, Å	31.0711(12)	6.2896(16)	15.5302(13)	9.5997(13)
b, Å	31.0711(12)	10.9401(16)	8.3459(14)	11.7864(13)
c, Å	8.1347(9)	24.1328(10)	17.7428(12)	16.4449(11)
α, deg	90	90	90	90
β, deg	90	96.131(1)	97.382(1)	95.915(1)
γ, deg	120	90	90	90
V, Å^3	6801.2(9)	1651.1(5)	2280.6(5)	1850.8(3)
Z	9	2	4	2
ρ_{calcd}, g cm^{-3}	1.573	1.766	1.756	1.778
μ, mm^{-1}	3.405	5.540	3.980	4.143
θ Range collected, deg	2.27–25.49	1.70–25.50	2.32–25.50	2.13–25.50
Reflections collected/unique	13566/2803	8611/3085	11790/4247	9305/3440
Observed reflections ($I \geq 2\sigma(I)$)	2181	2250	3009	1981
Data/restraints/parameters	2803/0/178	3085/0/187	4247/0/272	3440/0/232
GOOF on F^2	1.022	1.059	1.029	1.030
R_1, wR_2 ($I \geq 2\sigma(I)$)	0.0311, 0.0657	0.0474, 0.1188	0.0414, 0.0982	0.0446, 0.0971
R_1, wR_2 (all data)	0.0489, 0.0719	0.0723, 0.1303	0.0674, 0.1098	0.1029, 0.1202
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	0.227/–0.357	0.755/–0.495	0.909/–0.517	0.643/–0.466

the complexes were solved by direct and Fourier methods and refined by full-matrix least-squares based on F^2 using SHELXL [15]. The nonhydrogen atoms were refined anisotropically. The hydrogen atoms have been placed at geometrical positions with fixed thermal parameters. Crystallographic data of the complexes are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication (CCDC nos. 2109986 (**I**), 2109987 (**II**), 2109988 (**III**) and 2109989 (**IV**); deposit@ccdc.cam.ac.uk).

Antibacterial activity of the complexes was tested against *B. subtilis*, *S. aureus*, *S. faecalis*, *P. aeruginosa*, *E. coli*, and *E. cloacae* using MTT medium. The minimum inhibitory concentrations (MICs) of the compounds were determined by a colorimetric method using MTT dye [16]. A stock solution of the compounds (50 μg mL^{-1}) in DMSO was prepared and quantities of the compounds were incorporated in specified quantity of sterilized liquid medium. A specified quantity of the medium containing the compounds was poured into micro-titration plates. Suspension of the microorganism was prepared to contain approximately 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 for bacteria. After the MICs were visually determined on each micro-titration plate, 50 μL of phosphate buffered saline (PBS 0.01 mol L^{-1}, pH 7.4: $Na_2HPO_4 \cdot 12H_2O$ 2.9 g, KH_2PO_4 0.2 g, NaCl 8.0 g, KCl 0.2 g, distilled water 1000 mL) containing 2 mg mL^{-1} of MTT was added to each well. Incubation was continued at room temperature for 4–5 h.

Table 2. Selected bond distances (Å) and angles (deg) for complexes **I**–**IV***

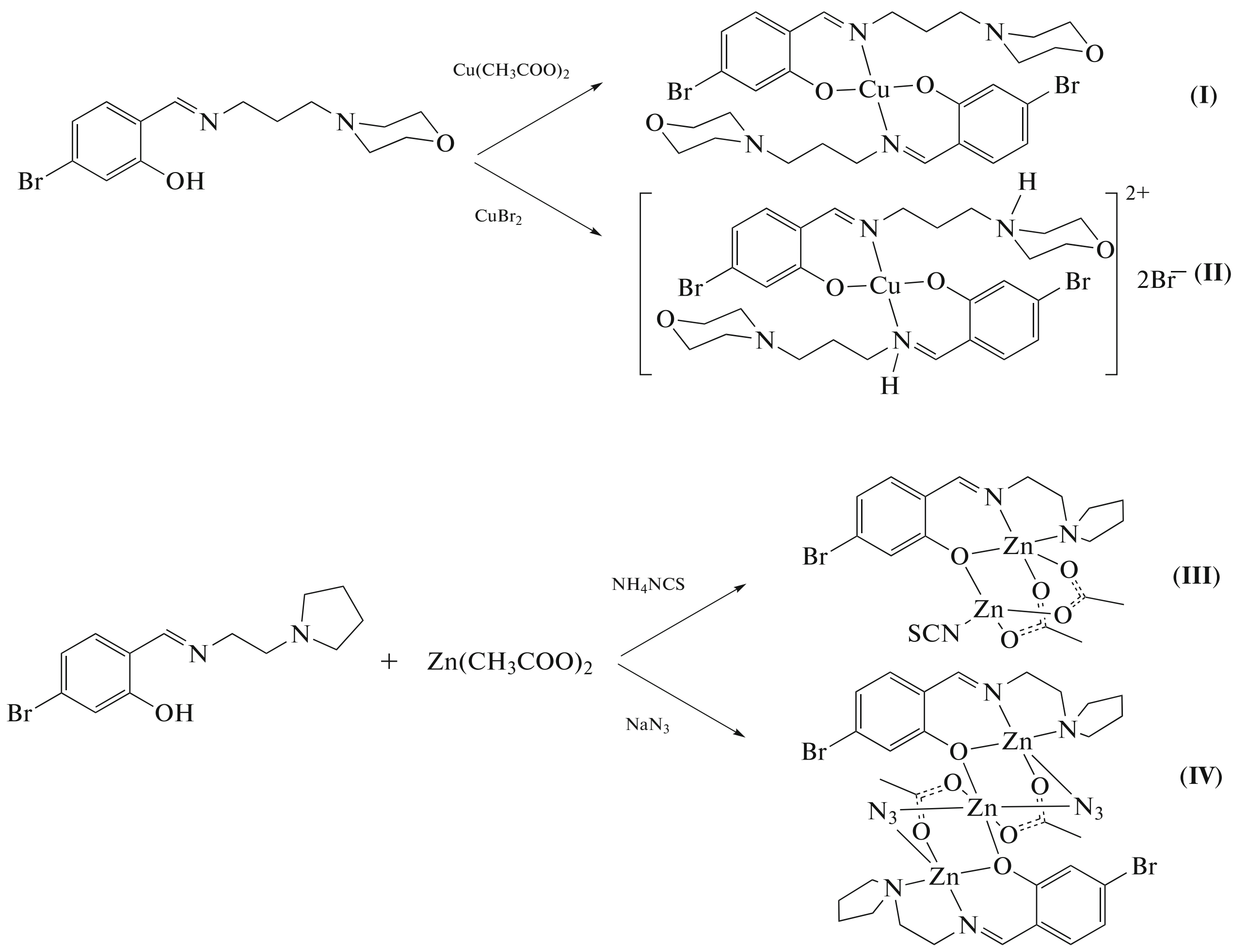
Bond	*d*, Å	Bond	*d*, Å
		I	
Cu(1)–O(1A)	1.9319(16)	Cu(1)–O(1)	1.9320(16)
Cu(1)–N(1A)	2.0015(19)	Cu(1)–N(1)	2.0017(19)
		II	
Cu(1)–O(1)	1.893(4)	Cu(1)–N(1)	1.994(4)
		III	
Zn(1)–O(1)	2.106(3)	Zn(1)–O(2)	2.005(3)
Zn(1)–O(4)	1.974(3)	Zn(1)–N(1)	2.005(4)
Zn(1)–N(2)	2.200(4)	Zn(2)–N(3)	1.913(4)
Zn(2)–O(5)	1.935(3)	Zn(2)–O(3)	1.949(3)
Zn(2)–O(1)	1.950(3)		
		IV	
Zn(1)–O(1)	2.074(4)	Zn(1)–O(2)	2.084(4)
Zn(1)–N(3)	2.219(5)	Zn(2)–O(3)	1.975(4)
Zn(2)–N(3)	2.017(5)	Zn(2)–N(1)	2.025(5)
Zn(2)–O(1)	2.091(4)	Zn(2)–N(2)	2.181(5)
Angle	ω, deg	Angle	ω, deg
		I	
O(1)Cu(1)O(1A)	180	O(1)Cu(1)N(1A)	90.39(8)
O(1)Cu(1)N(1)	89.61(8)	N(1)Cu(1)N(1A)	180
		II	
O(1)Cu(1)O(1A)	180	O(1)Cu(1)N(1A)	87.95(15)
O(1)Cu(1)N(1)	92.05(15)	N(1)Cu(1)N(1A)	180
		III	
O(4)Zn(1)O(2)	105.06(15)	O(4)Zn(1)N(1)	151.32(16)
O(2)Zn(1)N(1)	103.61(16)	O(4)Zn(1)O(1)	90.52(13)
O(2)Zn(1)O(1)	96.39(12)	N(1)Zn(1)O(1)	87.14(15)
O(4)Zn(1)N(2)	94.11(17)	O(2)Zn(1)N(2)	94.45(15)
N(1)Zn(1)N(2)	82.81(19)	O(1)Zn(1)N(2)	166.68(16)
N(3)Zn(2)O(5)	112.48(19)	N(3)Zn(2)O(3)	105.75(17)
O(5)Zn(2)O(3)	111.28(14)	N(3)Zn(2)O(1)	118.59(16)
O(5)Zn(2)O(1)	102.12(14)	O(3)Zn(2)O(1)	106.54(13)
		IV	
O(1)Zn(1)O(1A)	180	O(1)Zn(1)O(2)	91.23(15)
O(1)Zn(1)O(2A)	88.77(16)	O(2)Zn(1)O(2A)	180
O(1)Zn(1)N(3)	77.64(17)	O(1)Zn(1)N(3A)	102.36(17)
O(2)Zn(1)N(3)	89.94(17)	O(2)Zn(1)N(3A)	90.06(17)
N(3)Zn(1)N(3A)	180	O(3)Zn(2)N(3)	106.8(2)
O(3)Zn(2)N(1)	121.29(18)	N(3)Zn(2)N(1)	130.85(19)
O(3)Zn(2)O(1)	91.51(16)	N(3)Zn(2)O(1)	81.94(17)
N(1)Zn(2)O(1)	87.04(17)	O(3)Zn(2)N(2)	92.01(17)
N(3)Zn(2)N(2)	106.74(19)	N(1)Zn(2)N(2)	82.41(19)
O(1)Zn(2)N(2)	169.21(16)		

* Symmetry codes for A: $5/3 - x$, $4/3 - y$, $4/3 - z$ (**I**); $1 - x$, $1 - y$, $1 - z$ (**II**); $1 - x$, $1 - y$, $1 - z$ (**IV**).

The content of each well was removed, and 100 μL of isopropanol containing 5% 1 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 570 nm.

RESULTS AND DISCUSSION

The copper complexes were prepared in a similar method, by the reaction of the Schiff base ligand HL^a with different copper salts, *viz.* copper acetate for **I**, and copper bromide for **II** (Scheme 1). The Schiff base ligands in complex **I** are monoanionic, while those in complex **II** are zwitterionic. The zinc complexes were also prepared in a similar method, by the reaction of the Schiff base ligand HL^b with zinc acetate in the presence of pseudohalide ligands, *viz.* thiocyanate for complex **III** and azide for complex **IV** (Scheme 1). The thiocyanate acts as a terminal ligand in complex **III**, while the azide acts as a end-on bridging ligand in complex **IV**. The poor conductivity of complexes **I**, **III** and **IV** (23–32 Ω^{-1} cm^2 mol^{-1}) indicated that they are nonelectrolytes, while the high conductivity of complex **II** (211 Ω^{-1} cm^2 mol^{-1}) indicated that it is a 1 : 2 electrolyte [17].



Scheme 1.

The characteristic imine stretching is observed at 1622–1623 cm^{-1} for complexes **I** and **II**, and 1645–1657 cm^{-1} for complexes **III** and **IV** [18]. The phenolic C–O stretching bands of the complexes are observed at 1190–1200 cm^{-1} [19]. In general, the infrared spectra of complexes **I** and **II** are similar to each other, except the weak absorption for the N–H bond at 3100 cm^{-1} for complex **II**. Complexes **III** and **IV** revealed strong bands at 1594 and 1581 cm^{-1} for ν_{asym}(OCO) and intense bands at 1391 and 1399 cm^{-1} for ν_{sym}(OCO). The $\Delta\nu$ = 203 cm^{-1} for **III** and 182 cm^{-1} for **IV** can be assigned to *syn-syn* bidentate bridging mode of the acetate ligands [20]. The typical band indicative of the end-on azido ligand for complex **IV** is observed at 2085 cm^{-1} [19]. The ligands coordination to the metal centers are substantiated by weak bands

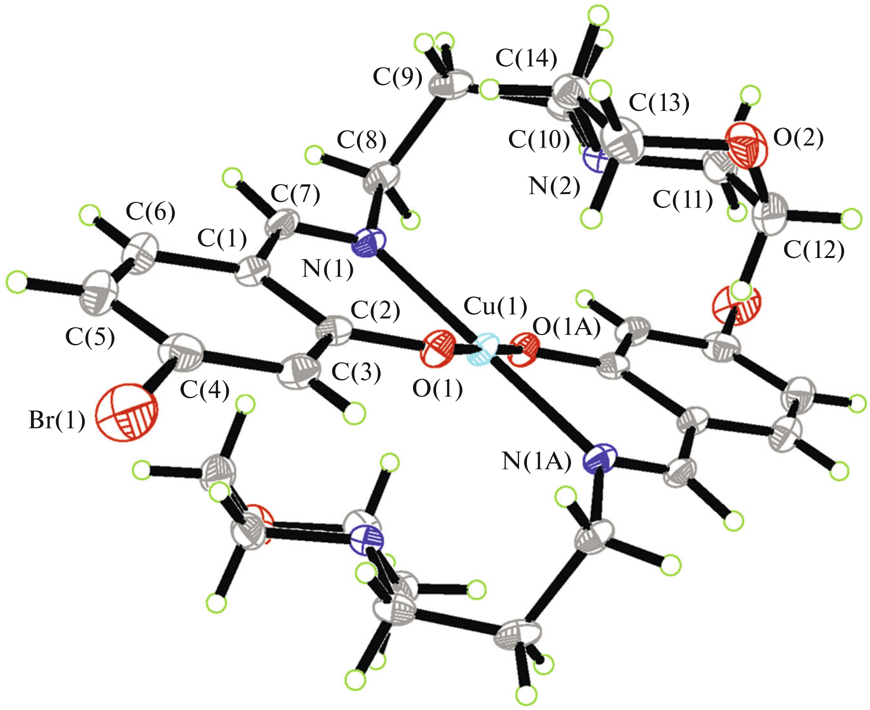


Fig. 1. Molecular structure of complex **I**. Atoms labeled with the suffix A and unlabeled atoms are related to the symmetry operation 5/3 – *x*, 4/3 – *y*, 4/3 – *z*.

appearing for ν_{M-N} and ν_{M-O} at low wavenumbers 400–600 cm^{-1} [19].

The absorption spectral data of the complexes were measured in methanol. In the complexes, peaks between 220–250, 260–280 and 320–370 nm are assigned to $\pi \to \pi^*$, $n \to \pi^*$ and ligand to metal charge transfer transitions, respectively [21].

Molecular structures of complexes **I** and **II** are shown in Figs. 1 and 2, respectively. Both complexes are mononuclear copper species. The Schiff base ligands in complex **I** are monoanionic, which coordinate to the Cu atom through phenolate O and imino N atoms with the morpholine N atom neutralized. The Schiff base ligands in complex **II** are zwitterionic, which also coordinate to the Cu atom through phenolate O and imino N atoms, but with the morpholine N atom protonated. The Cu atom in each complex is coordinated by two N and two O atoms from two Schiff base ligands, forming square planar geometry. The coordination of the Cu atoms is slightly distorted from ideal square planar geometry, as evidenced by the Cu–O and Cu–N bond lengths (1.932(2)–2.002(2) Å for **I**, 1.893(4)–1.994(4) Å for **II**), and the bond angles (89.61(8)°–90.39(8)° for **I**, 87.95(15)°–92.05(15)° for **II**). The Cu–O and Cu–N bonds in complex **I** are longer than those in complex **II**, which might be induced by the weak interaction of the morpholine N atom to the Cu atom in **I** with distance of 2.780(2) Å. Even though, the Cu–O and Cu–N bonds are comparable to those observed in Schiff base copper complexes [22, 23]. As expected, the morpholine rings in both complexes are in chair conformation.

In the crystal structure complex **I**, there is no obvious short contacts among the molecules (Fig. 3). In the crystal structure complex **II**, the Br anions are linked to the complex cations through N–H···Br hydrogen bonds, the complex molecules are stack along the *a* axis *via* π···π interactions (Table 3, Fig. 4).

Molecular structure of complex **III** is shown in Fig. 5. The compound is an acetate bridged dinuclear zinc complex. The separation of the two Zn atoms is 3.128(1) Å. The Zn(1) atom is coordinated in square pyramidal geometry with the basal plane defined by the phenolate O, imino N and pyrrolidine N atoms of the Schiff base ligand, and one acetate O atom (O(4)), and with the apical position occupied by one acetate O atom (O(2)). The average deviation of the four basal donor atoms is 0.798(3) Å, and the displacement of the Zn(1) atom from the least-squares plane defined by the four basal donor atoms is 0.546(2) Å. The coordination of the Zn(1) atom is distorted from ideal square pyramidal geometry, as evidenced by the Zn–O and Zn–N bond lengths from the basal plane (1.974(3)–2.200(4) Å), and the bond angles (82.81(19)°–94.11(17)°), and those among the apical and basal donor atoms (94.45(15)°–105.06(15)°). The Zn(2) atom is coordinated by the phenolate O atom of the Schiff base ligand, two acetate O atoms (O(3) and O(5)), and the thiocyanate N atom, forming tetrahe-

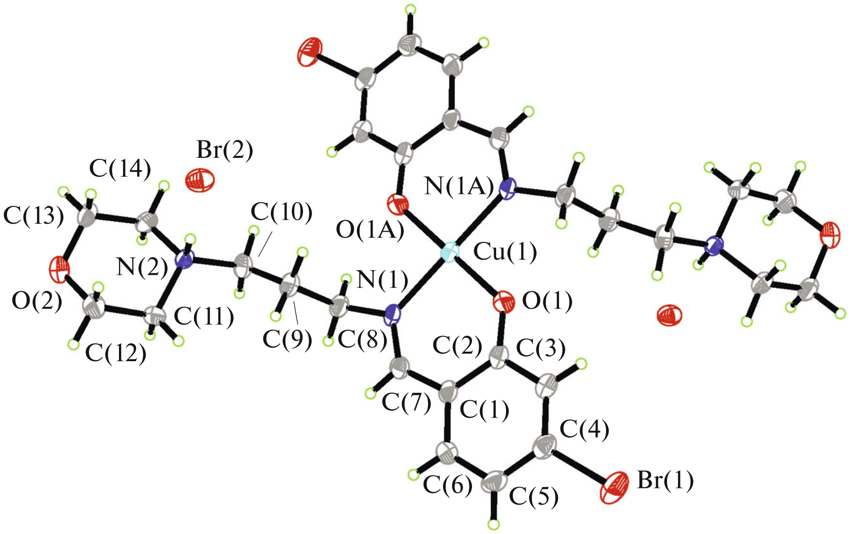


Fig. 2. Molecular structure of complex **II**. Atoms labeled with the suffix A and unlabeled atoms are related to the symmetry operation 1 – *x*, 1 – *y*, 1 – *z*.

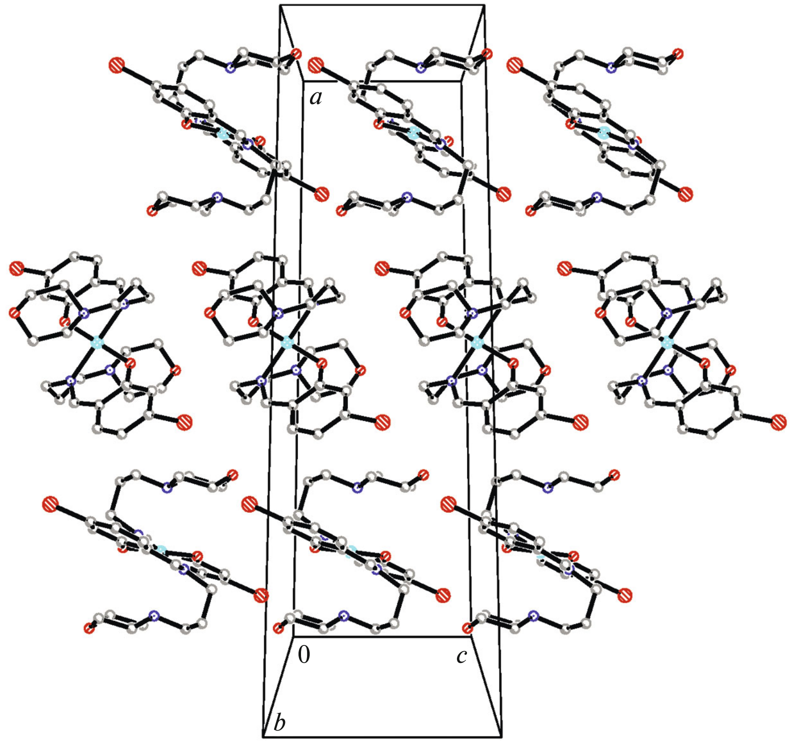


Fig. 3. Molecular packing diagram of complex **I**, viewed along the *b* axis.

dral geometry. The tetrahedral coordination is deviated from ideal geometry, as evidenced by the Zn–O and Zn–N bond lengths (1.913(4)–1.950(3) Å), and bond angles (102.12(14)°–118.59(16)°). Generally, the Zn–O and Zn–N bonds are comparable to those observed in Schiff base zinc complexes [24, 25].

In the crystal structure complex **III**, the molecules are stack along the *a* axis *via* π···π interactions (Table 3, Fig. 6).

Molecular structure of complex **IV** is shown in Fig. 7. The compound is an acetate and end-on azide co-bridged trinuclear zinc complex. The separation of

Table 3. Parameters between the planes for the complexes **II** and **III**

Cg	Distance between ring centroids, Å	Dihedral angle, deg	Perpendicular distance of *Cg*(I) on *Cg*(J), Å	Beta angle, deg	Gamma angle, deg	Slippage	Perpendicular distance of *Cg*(J) on *Cg*(I), Å
			II				
*Cg*1-*Cg*1$^{\#1}$	3.7002(9)	0	3.3511	25.09	25.09	1.569	3.3511
*Cg*1-*Cg*3$^{\#2}$	4.8909	1.141	3.3864	45.69	46.18		–3.4163
*Cg*1-*Cg*3$^{\#1}$	3.7664	1.141	3.3513	26.08	27.15		3.3829
*Cg*2-*Cg*1$^{\#2}$	3.7002(9)	0	3.3511	25.09	25.09	1.569	–3.3511
*Cg*2-*Cg*2$^{\#3}$	3.7002(9)	0	–3.3511	25.09	25.09	1.569	–3.3511
*Cg*2-*Cg*3$^{\#2}$	3.7664	1.141	3.3513	26.08	27.15		–3.3829
*Cg*2-*Cg*3$^{\#1}$	4.8909	1.141	3.3864	45.69	46.18		3.4163

Symmetry codes: $^{\#1}$ $2 - x, -y, -z$; $^{\#2}$ $-1 + x, y, z$; $^{\#3}$ $-x, -y, -z$.
*Cg*1, *Cg*2 and *Cg*3 are the centroids of Cu(1)–O(1)–C(2)–C(1)–C(7)–N(1), Cu(1)–O(1A)–C(2A)–C(1A)–C(7A)–N(1A), and C(1)–C(2)–C(3)–C(4)–C(5)–C(6), respectively in **II**.

			III				
*Cg*4-*Cg*4$^{\#3}$	3.134	0	–2.149	46.70	46.70	2.281	–2.149
*Cg*4-*Cg*5	3.692	59.108	2.121	11.28	54.93		3.621
*Cg*6-*Cg*4	3.134	0.020	–2.149	46.70	46.70	2.281	2.149
*Cg*6-*Cg*6$^{\#3}$	3.134	0	2.149	46.70	46.70	2.281	2.149
*Cg*6-*Cg*5$^{\#3}$	3.692	59.108	2.121	11.28	54.93		–3.621
*Cg*5-*Cg*5$^{\#4}$	3.838	0	–3.771	10.71	10.71	0.713	–3.771

Symmetry codes: $^{\#3}$ $2 - x, -y, -z$; $^{\#4}$ $2 - x, -y, 1 - z$.
*Cg*4, *Cg*5 and *Cg*6 are the centroids of Cu(1)–O(2)–Cu(2A)–O(3), C(8)–C(9)–C(10)–C(11)–C(12)–C(13), and Cu(2)–O(2A)–Cu(1A)–O(3A), respectively in **III**.

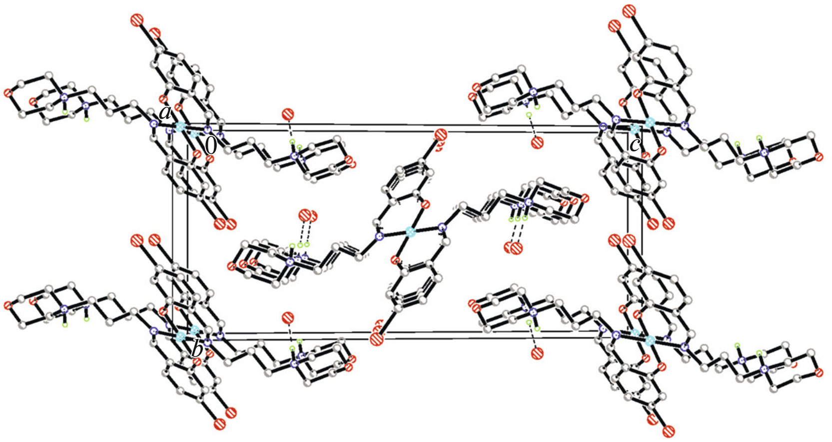


Fig. 4. Molecular packing diagram of complex **II**, viewed along the *a* axis. Hydrogen bonds are drawn as dashed lines.

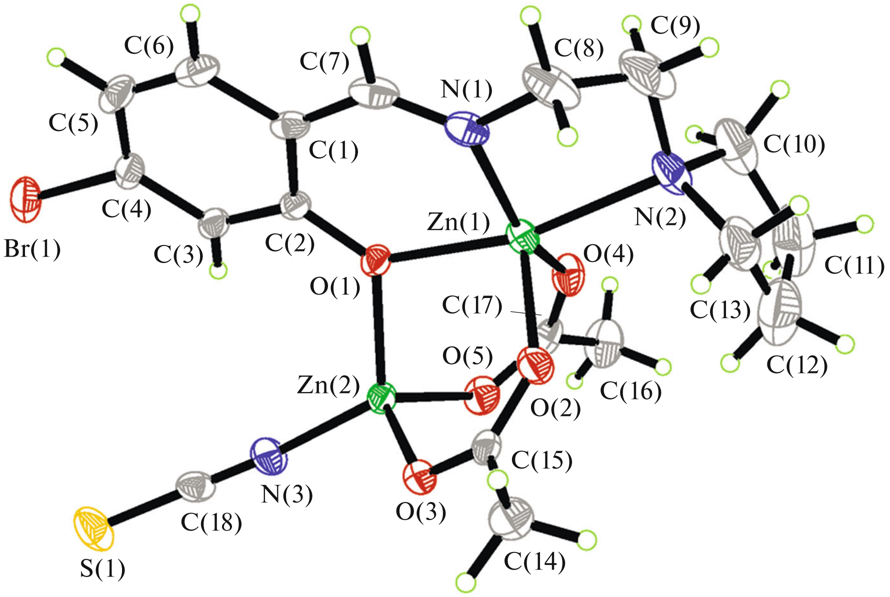


Fig. 5. Molecular structure of complex **III**.

the Zn atoms is 3.055(1) Å. The molecule of the complex possesses a crystallographic inversion center symmetry with the Zn(1) atom lies on the inversion center. The Zn(2) atom is coordinated in trigonal bipyramidal geometry with the basal plane defined by the imino N atom of the Schiff base ligand, one acetate O atom (O(3)), and one azide N atom (N(3)). The displacement of the Zn(2) atom from the least-squares plane defined by the three basal donor atoms is 0.117(2) Å. The coordination of the Zn(2) atom is distorted from ideal trigonal bipyramidal geometry, as evidenced by the Zn–O and Zn–N bond lengths from the basal plane (1.975(4)–2.025(5) Å), and the bond angles (91.51(16)°–130.85(19)°), and those among the axial and basal donor atoms (81.94(17)°–106.74(19)°). The Zn(1) atom is coordinated by two phenolate O atoms from two Schiff base ligands, two azide N atoms, and two acetate O atoms, forming octahedral geometry. The octahedral coordination is deviated from ideal geometry, as evidenced by the Zn–O and Zn–N bond lengths (2.074(4)–2.219(5) Å), and bond angles (77.64(17)°–91.23(15)°). Generally, the Zn–O and Zn–N bonds are comparable to those observed in Schiff base zinc complexes [24, 25].

In the crystal structure complex **IV**, there is no obvious short contacts among the molecules (Fig. 8).

The free Schiff bases and the complexes were screened for antibacterial activities against three Gram-positive bacterial strains (*B. subtilis*, *S. aureus*, and *St. faecalis*) and three Gram-negative bacterial

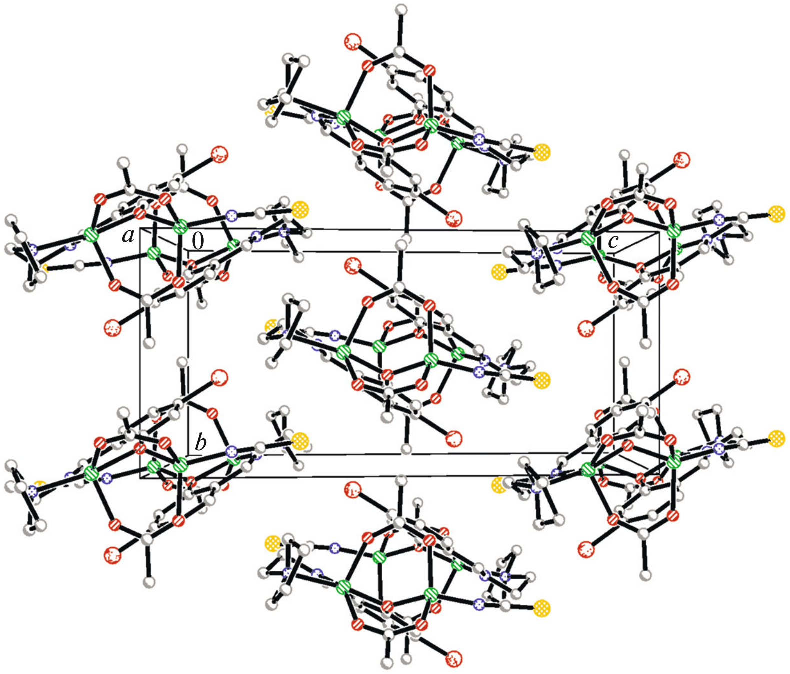


Fig. 6. Molecular packing diagram of complex **III**, viewed along the *a* axis.

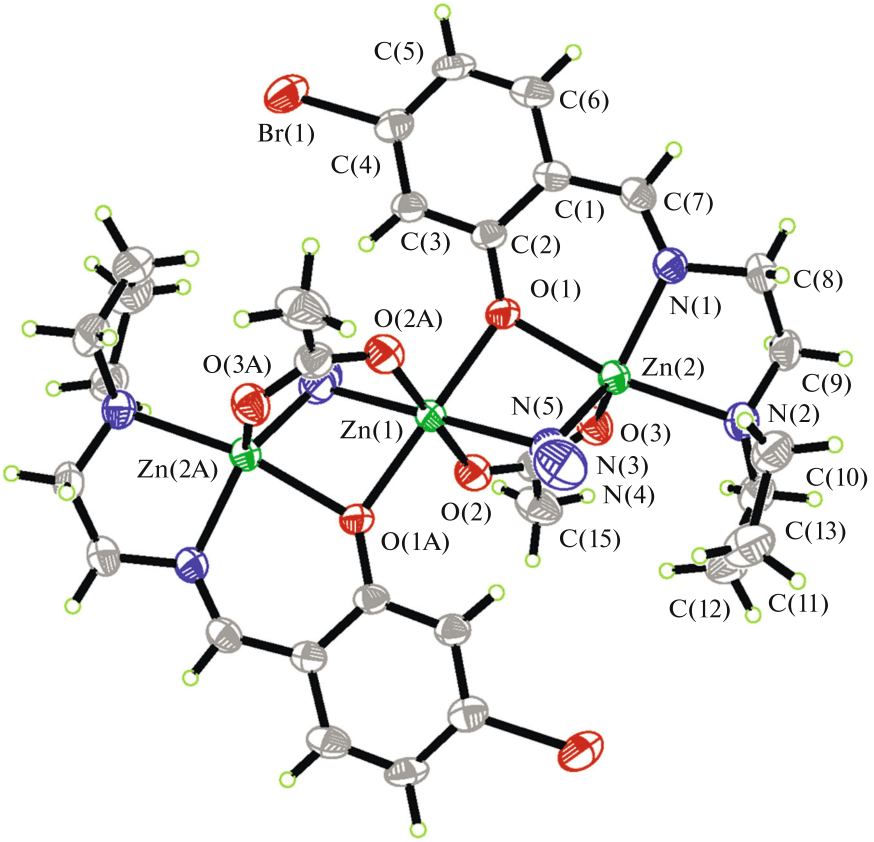


Fig. 7. Molecular structure of complex **IV**. Atoms labeled with the suffix A and unlabeled atoms are related to the symmetry operation 1 – *x*, 1 – *y*, 1 – *z*.

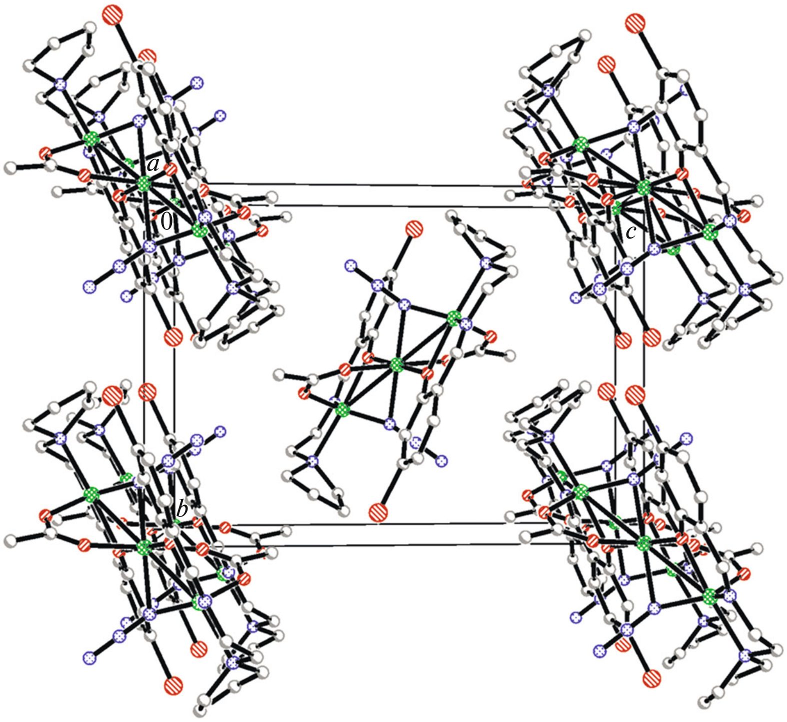


Fig. 8. Molecular packing diagram of complex **IV**, viewed along the *a* axis. Hydrogen bonds are drawn as dashed lines.

strains (*E. coli*, *P. aeruginosa*, and *E. cloacae*) by MTT method. The MICs of the compounds against the bacteria are presented in Table 4. Penicillin and Kanamycin were tested as reference drugs. The free Schiff base HL^a showed good activity against *B. subtilis* and *S. aureus*, and medium activity against *P. aeruginosa*, while no or weak activity against the remaining bacteria strains. The free Schiff base HL^b showed medium activity against *B. subtilis*, and no or weak activity against the remaining bacteria strains. In general, the complexes have stronger activities than the free Schiff bases, and the copper complexes have better activities than the zinc complexes. Complexes **I** and **II** have similar activities against all the bacteria, which have high activity against *B. subtilis* and *S. aureus*, good activity against *St. faecalis* and *P. aeruginosa*, weak activity against *E. coli* and *E. cloacae*. Complex **III** have similar activities against *St. faecalis* and *P. aeruginosa* when compared complex **IV**, but higher activities against the remaining bacteria. Interestingly, the activity of the complexes against *B. subtilis*, *S. aureus*, *St. faecalis*, *P. aeruginosa* and *E. coli* is similar to Penicillin and Kanamycin, which could be apparently reflected by their synergistic effect, and deserves further study.

Thus, two new mononuclear copper(II) complexes and two new polynuclear zinc(II) complexes derived from the Schiff bases 5-bromo-2-((3-morpholinopro-

Table 4. MICs (μg mL^{-1}) of the compounds and related materials

Tested material	Gram positive			Gram negative		
	B. subtilis	*S. aureus*	*St. faecalis*	*P. aeruginosa*	*E. coli*	*E. cloacae*
HL^a	3.12	6.25	>50	12.5	25	>50
HL^b	12.5	25	>50	25	25	>50
I	0.78	1.56	6.25	6.25	12.5	25
II	0.78	1.56	6.25	6.25	12.5	25
III	1.56	6.25	25	6.25	3.12	12.5
IV	3.12	12.5	25	6.25	6.25	25
Penicillin	1.56	1.56	1.56	6.25	6.25	3.12
Kanamycin	0.39	1.56	3.12	3.12	3.12	1.56

pylimino)methyl)phenol and 5-bromo-2-(((2-(pyrrolidin-1-yl)ethyl)imino)methyl)phenol have been synthesized. Their structures were confirmed by single crystal X-ray diffraction. The anions used in the preparation of the complexes have intriguing effects in the formation of versatile structures of the complexes. This paper contributes to the anion induced synthesis of Schiff base copper and zinc complexes. The complexes have effective activity against *B. subtilis*, *S. aureus*, *St. faecalis*, *P. aeruginosa* and *E. coli*, which deserve further study.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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