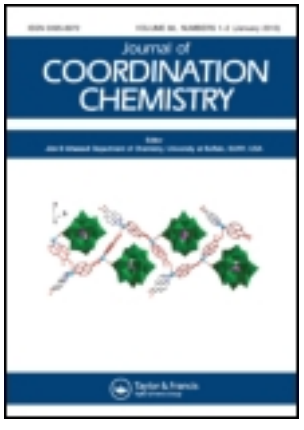

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Synthesis, characterization, and antibacterial activities of two new copper(II) glycinate complexes incorporating 2-(4′-thiazolyl)benzimidazole/2-(2-pyridyl)benzimidazole

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Synthesis, characterization, and antibacterial activities of two new copper(II) glycinate complexes incorporating 2-(4′-thiazolyl)benzimidazole/2-(2-pyridyl)benzimidazole

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Two new complexes, [Cu(TBZ)(Gly)(H_2O)]Cl (**1**) and [Cu(HPB)(Gly)Cl] · $2H_2O$ (**2**) (TBZ = 2-(4′-thiazolyl)benzimidazole, HPB = 2-(2-pyridyl)benzimidazole, and Gly = glycinate), have been synthesized and characterized by elemental analysis, molar conductivity, UV-Vis, and IR methods. The complexes, structurally characterized by single-crystal X-ray crystallography, show a slightly distorted square-pyramidal coordination geometry in which two nitrogen atoms of TBZ or HPB and the carboxylate oxygen and amino nitrogen of glycinate bind in the plane and a water or chloride coordinated at the axial site. The complexes, free ligands, and copper(II) chloride were tested for their ability to inhibit growth of *Bacillus subtilis*, *Staphylococcus aureus*, and *Salmonella*. The results show that the complexes have good antibacterial activities against the microorganisms compared with their ligands and copper(II) chloride.

Keywords: Copper(II) complexes; 2-(4′-Thiazolyl)benzimidazole; 2-(2-Pyridyl)benzimidazole; Glycinate; Antibacterial activity

1. Introduction

N-heterocyclic ligands and their metal chelates received interest for gaining insight into models for protein–nucleic acid interactions and probes of DNA structure and for obtaining information about drug design [1–6]. Among these ligands are benzimidazole and its derivatives whose complexes play a wide range of biological activities including antibacterial, antifungal, antiamoebic, antimicrobial, antiparasitic, and antitumor [7–12]. For example, 2-benzimidazole derivatives such as 2-(4′-thiazolyl)benzimidazole (TBZ) and 2-(2-pyridyl)benzimidazole (HPB) exhibit antibacterial, antitumor, and mycobacterial activities [13, 14]. Combinations of pharmaceutical agents with metal

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ions can improve their biological activities and decrease their toxicities. Hence, metal complexes of 2-benzimidazole derivatives are of importance [15–17].

Various side groups of *L*-α-amino acids as the basic structural units of proteins have potential to recognize the specific base sequence through hydrogen-bond formation with nucleic bases in DNA [18, 19], and incorporation of *L*-α-amino acids in drug molecule-metal ion systems may increase their biocompatibilities and antibacterial activities [20]. Hence, metal complexes containing *L*-α-amino acid ligands can serve as a new type of antibacterial agent. We have synthesized and characterized two new complexes: [Cu(TBZ)(Gly)(H_2O)]Cl (**1**) and [Cu(HPB)(Gly)Cl] · $2H_2O$ (**2**) (TBZ = 2-(4′-thiazolyl)benzimidazole, HPB = 2-(2-pyridyl)benzimidazole, and Gly = glycinate). The complexes were tested for their abilities to inhibit the growth of *Bacillus subtilis*, *Staphylococcus aureus*, and *Salmonella*.

2. Experimental

2.1. *Reagents and apparatus*

All reagents were commercially available and of reagent grade. Microorganisms such as *B. subtilis*, *S. aureus*, and *Salmonella* were supplied by Guangdong Key Laboratory of Plant Molecular Breeding, South China Agricultural University.

The carbon, hydrogen, and nitrogen elemental analyses were performed with a Vario EL elemental analyzer. Molar conductances were measured in 1×10^{-3} mol L^{-1} methanol using a DSS-12A digital molar conductometer at room temperature. Infrared (IR) spectra were recorded with KBr pellets in a Nicolet ACATAR 360 FT-IR spectrometer from 4000 cm^{-1} to 400 cm^{-1}. Electronic absorption spectra were recorded on an Amersham Pharmacia Biotech UV-Vis 4000 spectrophotometer.

2.2. *Synthesis of the complexes*

The complexes were prepared by dissolving $CuCl_2 \cdot 2H_2O$ (1.0 mmol), glycine (1.0 mmol), and NaOH (1.0 mmol) in 10 mL of water with stirring. To this solution, 40 mL of ethanol solution of 2-(4′-thiazolyl)benzimidazole (1.0 mmol) or 2-(2-pyridyl)benzimidazole (1.0 mmol) was added dropwise with stirring for about 30 min. The resulting solution was left to evaporate at room temperature. After several weeks, light green crystals were obtained.

Complex **1**: Yield: 76%. Anal. Calcd for $C_{12}H_{15}CuN_4O_4SCl$ ($M_r = 410.33$) (%): C, 35.12; H, 3.68; N, 13.65. Found (%): C, 35.56; H, 3.59; N, 13.65. IR data (KBr pellets, ν/cm^{-1}): 3452(s,br), 3326(s), 3269(s), 3109(m), 3090(m), 2973(w), 1635(vs), 1439(m), 1406(m). UV-Vis [methanol, λ/nm (ε/L $mol^{-1} cm^{-1}$)]: 239 (13,768), 302(23,350), 645(55). Λ_m (in methanol, S cm^2 mol^{-1}): 74.1.

Complex **2**: Yield: 81%. Anal. Calcd for $C_{14}H_{17}ClCuN_4O_4$ ($M_r = 404.31$) (%): C, 41.59; H, 4.24; N, 13.86. Found (%): C, 42.03; H, 4.28; N, 13.91. IR data (KBr discs, ν/cm^{-1}): 3398(s,br), 3315(s), 3260(s), 3116(m), 3090(m), 2971(w), 1628(vs), 1483(m), 1392(m). UV-Vis [methanol, λ/nm (ε/L $mol^{-1} cm^{-1}$)]: 240 (17,330), 324(18,490), 633(50). Λ_m (in methanol, S cm^2 mol^{-1}): 70.4.

Solubility and stability: The complexes were highly soluble in MeOH, EtOH, DMF, and DMSO, less soluble in H_2O, and insoluble in hydrocarbon solvents. The complexes were stable in the solid and solution phases.

2.3. *X-ray structural determination of the complexes*

Single-crystal X-ray diffraction experiments for the two copper(II) complexes were made on a Bruker APEX II CCD system diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298 K. The crystal structures were solved by direct methods followed by Fourier syntheses. Structure refinements were performed by full-matrix least-squares procedures using SHELXL-97 on F^2 [21]. Atomic scattering factors were taken from the International Tables for X-ray crystallography [22]. Crystal data, some experimental details of data collection, and refinement for the complexes are listed in table 1.

2.4. *Test of antibacterial activity*

The antibacterial activities of the two complexes were investigated using twofold serial tube dilution technique against *B. subtilis*, *S. aureus*, and *Salmonella*. The inhibition of

Table 1. Crystal data, experimental details of data collection, and refinement for **1** and **2**.

Complexes	**1**	**2**
Empirical formula	$C_{12}H_{15}CuN_4O_4SCl$	$C_{14}H_{17}ClCuN_4O_4$
Formula weight	410.33	404.31
Temperature (K)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pbca*
Unit cell dimensions (Å, °)		
a	21.959(12)	9.2936(18)
b	19.686(10)	17.626(3)
c	7.398(4)	20.274(4)
α	90	90
β	90	90
γ	90	90
Volume (Å^3), *Z*	3198(3), 8	3321(11), 8
Calculated density (g cm^{-3})	1.704	1.617
Absorption coefficient (mm^{-1})	1.687	1.503
F(000)	1627	1656
Crystal size (mm^3)	$0.10 \times 0.16 \times 0.18$	$0.15 \times 0.18 \times 0.20$
θ range for data collection (°)	1.9–27.8	2.0–27.8
Limiting indices	$-27 \le h \le 28$; $-25 \le k \le 19$; $-8 \le l \le 9$	$-9 \le h \le 12$; $-22 \le k \le 21$; $-26 \le l \le 26$
Reflections collected	18,427	18,928
Independent reflections	3747 [R(int) = 0.132]	3900 [R(int) = 0.069]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	18,427/3747/220	18,928/3900/0.069
Goodness-of-fit on F^2	0.975	1.012
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0602$, $wR_2 = 0.1344$	$R_1 = 0.0457$, $wR_2 = 0.0887$
R indices (all data)	$R_1 = 0.1110$, $wR_2 = 0.1585$	$R_1 = 0.0967$, $wR_2 = 0.1047$
Largest difference peak and hole (e Å^{-3})	1.31 and −0.83	0.47 and −0.55

growth of these organism produced by various concentrations of the complexes was compared under same conditions with inhibition of growth of the same organism in the presence of metal salt or the parent ligands.

A standard volume (10 mL) of LB (Luria broth medium, containing 1% w/v peptone, 0.5% w/v NaCl, and 0.5% w/v beef, $pH = 7.4 \pm 0.2$) that would support the growth of the test organism was added to several labeled identical assay tubes. Minimal inhibitory concentrations (MICs) were determined using a series of twofold dilutions in liquid media containing 512–32 $\mu g\,mL^{-1}$ of the compounds being tested. Dilution for metal salts and the parent ligands were also prepared and a control tube containing no test compound was also included. Assay tubes were incubated at $37 \pm 1^{\circ}C$ for 24 h. If a particular concentration of a tested compound inhibits the bacterial growth, half the concentration of the compound was tried. This procedure was continued to a concentration at which the bacteria grow normally. The lowest concentration that inhibits the bacterial visible growth was defined as the MIC value. The experiments were undertaken in duplicate and all the operations were carefully performed under aseptic conditions.

3. Results and discussion

3.1. *General aspects*

Elemental analyses of **1** and **2** are in good agreement with the following formulae, [Cu(TBZ)(Gly)(H_2O)]Cl (**1**) and [Cu(HPB)(Gly)Cl] · $2H_2O$ (**2**). The molar conductivities for the complexes in methanol are, respectively, 74.1 and 70.4 $S\,cm^2\,mol^{-1}$, indicating 1 : 1 electrolytes in methanol [23]; the chloride was not or is weakly coordinated to Cu(II), in agreement with the results obtained by single-crystal X-ray crystallography.

IR spectra of the two complexes show ν(O–H) absorption bands of H_2O at 3260–3452 cm^{-1}. Bands at 2927–3120 cm^{-1} for the complexes can be attributed to $\nu_{as}(-NH_2)$ and $\nu_s(-NH_2)$ of coordinated NH_2 groups. The absence of any band at 1750–1700 cm^{-1} in IR spectra of the isolated complexes suggests the coordination of COO^- of Gly to Cu(II) ion. Bands at 1635 cm^{-1} and 1406 cm^{-1} for **1** and 1628 cm^{-1} and 1392 cm^{-1} for **2** can be attributed, respectively, to antisymmetric and symmetric stretches of coordinated carboxylate. The $\Delta\nu(-COO^-)$ ($\nu_{as}(-COO^-) - \nu_s(-COO^-) > 200\,cm^{-1}$) values are consistent with monodentate carboxylate [24]. Thus, the monovalent anion of Gly is coordinated to copper as a N,O-bidentate ligand, in agreement with single-crystal X-ray diffraction. Bands at 1439 cm^{-1} for **1** and 1483 cm^{-1} for **2** are assigned to stretch of C=N of TBZ and HPB, respectively, and confirm their coordination to copper [25]; alternatively, this band could be ascribed to deformation of NH of the N–H group belonging to the amino acid [26].

3.2. *Crystal structure*

3.2.1. Description of the structure of [Cu(TBZ)(Gly)(H_2O)]Cl (1). The local coordination structure and the crystal packing view of **1** are shown in figures 1 and 2, respectively. Selected bond lengths and angles are collected in table 2.

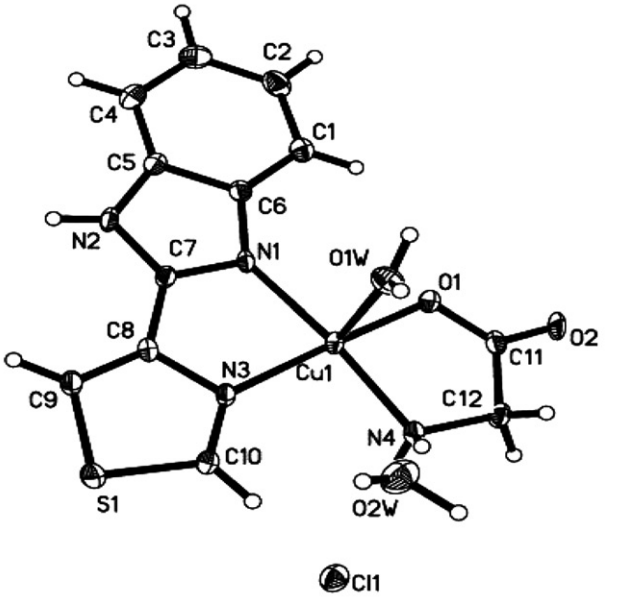

Figure 1. ORTEP drawing of [Cu(TBZ)(Gly)(H_2O)]Cl (**1**).

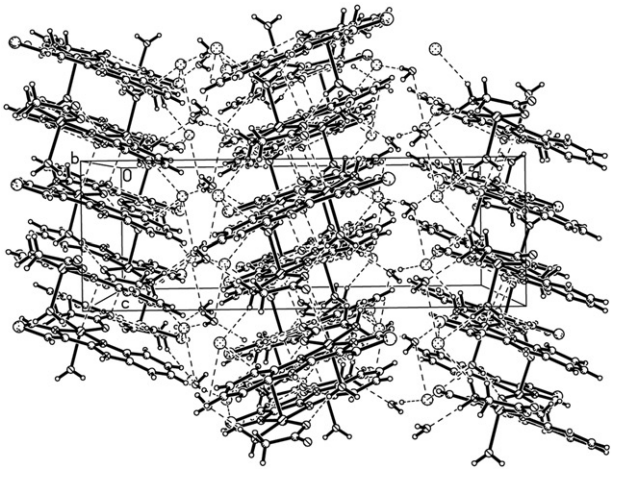

Figure 2. The packing diagram in **1**.

The complex consists of $[Cu(TBZ)(Gly)(H_2O)]^+$ and chloride. The Cu(II) is coordinated to two nitrogen atoms of TBZ and the carboxylate oxygen and amino nitrogen of Gly in the plane with water axial. The resulting coordination geometry can be described as a slightly distorted square pyramid ($\tau_1 = (\beta - \alpha)/60 = (172.83 - 172.15)/60 = 0.01$) [27]. N1, N3, N4, O1, and Cu1 for $[Cu(TBZ)(Gly)(H_2O)]^+$ deviate by 0.0123, 0.0363, 0.0123, 0.0382, and 0.0991 Å, respectively, from the least-squares plane

Table 2. Selected bond lengths (Å) and angles (°) for **1** with e.s.d.s in parentheses.

Cu1–O1	1.965(3)	Cu1–N3	2.027(4)
Cu1–O(1W)	2.260(4)	Cu1–N4	1.981(4)
Cu1–N1	2.010(4)		
O1W···Cl1[a]	3.111(4)	N2···O2[b]	2.731(5)
O1W···O1[c]	2.970(5)	N4···O2W	2.941(6)
N4···Cl1	3.327(5)	O2W···Cl1[d]	3.141(6)
C9···O2[b]	3.295(6)	C10···O2W	3.191(7)
O1–Cu1–O(1W)	91.08(13)	O(1W)–Cu1–N3	96.77(15)
O1–Cu1–N1	98.04(13)	O(1W)–Cu1–N4	92.97(16)
O1–Cu1–N3	172.15(14)	N1–Cu1–N3	81.60(14)
O1–Cu1–N4	84.71(13)	N1–Cu1–N4	172.83(16)
O(1W)–Cu1–N1	93.59(15)	N3–Cu1–N4	94.77(14)

Symmetry transformations used to generate equivalent atoms: [a] $x, y, -1+z$; [b] $-x, 1/2+y, 1/2-z$; [c] $-x, -y, -z$; [d] $1/2-x, -y, -1/2+z$.

($6.628x - 3.165y - 6.952z = -1.9464$) defined by N1, N3, N4, O1, and Cu1, indicating that the five equatorial atoms (O1, N1, N2, N5, and Cu1) in the cation are nearly coplanar.

The main bond lengths and bond angles of **1** are similar to bond lengths [Cu1–O1 = 1.943(7) Å, Cu1–O7W = 2.390(10) Å, Cu1–N1 = 1.962(8) Å, Cu1–N2 = 2.002(8) Å, and Cu(1)–N(3) = 1.979(8) Å] and bond angles [O1–Cu1–O7W = 96.8(3)°, O1–Cu1–N1 = 93.5(3)°, O1–Cu1–N2 = 170.3(4)°, O1–Cu1–N3 = 85.9(3)°, N1–Cu1–7W = 87.9(3)°, N2–Cu1–O7W = 91.4(3)°, N3–Cu1–O7W = 94.6(4)°, N1–Cu1–N2 = 81.6(3)°, N1–Cu1–N3 = 177.5(4)°, and N3–Cu1–N2 = 98.7(4)°] of a corresponding complex in the literature [28].

Many intermolecular hydrogen bonds exist in the crystal of the complex, such as O1W···Cl = 3.111(4) Å $(x, y, -1+z)$, N2···O2 = 2.731(5) Å $(-x, 1/2+y, 1/2-z)$, O1W···O1 = 2.970(5) Å $(-x, -y, -z)$, N4···O2W = 2.941(6) Å, N4···Cl1 = 3.327(5) Å, and O2W···Cl1 = 3.141(6) Å $(1/2-x, -y, -1/2+z)$. There is also significant π–π stacking interaction between adjacent $[Cu(TBZ)(Gly)(H_2O)]^+$ cations with an interplanar distance *ca* 3.497 Å. As a result, a 2-D supramolecular architecture is generated.

3.2.2. Description of the structure of [Cu(HPB)(Gly)Cl]·2H$_2$O (2). The coordination structure and crystal packing view of **2** are shown in figures 3 and 4, respectively; selected bond lengths and angles are collected in table 3.

The complex consists of neutral [Cu(HPB)(Gly)Cl] and two uncoordinated water molecules. The Cu(II) is coordinated to two nitrogen atoms of HPB and the carboxylate oxygen and the amino nitrogen of Gly in the molecular plane; a chloride is coordinated at the axial site. The resulting coordination geometry can be described as a slightly distorted square pyramid ($\tau_2 = (\beta - \alpha)/60 = (172.83 - 172.15)/60 = 0.08$) [27], which is similar to that of **1**. N1, N3, N4, O1, and Cu1 deviate by −0.0074, 0.1039, 0.1072, 0.0029, and 0.2155 Å, respectively, from the least-squares plane ($5.624x - 13.344y - 4.994z = -1.1724$) defined by N1, N3, N4, O1, and Cu1, indicating that the five equatorial atoms (O1, N1, N2, N5, and Cu1) in the molecule are not coplanar.

The main bond lengths and bond angles of **2** are similar to the corresponding bond lengths [Cu1–Cl1 = 2.510(2) Å, Cu1–O1 = 1.918(6) Å, Cu1–N1 = 2.020(7) Å,

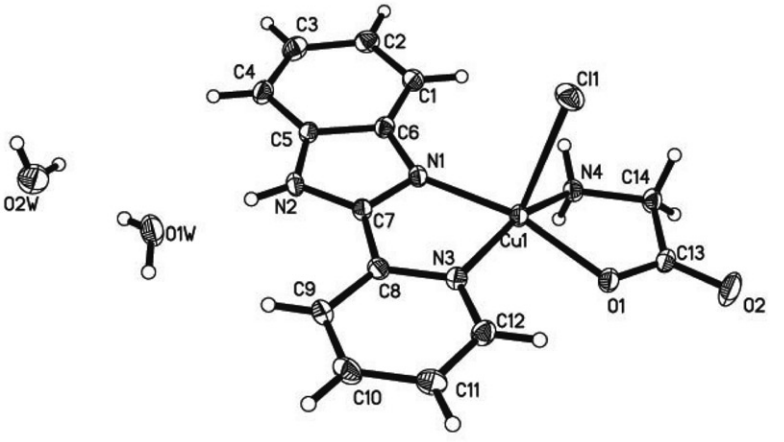

Figure 3. ORTEP drawing of $[Cu(HPB)(Gly)Cl] \cdot 2H_2O$ (**2**).

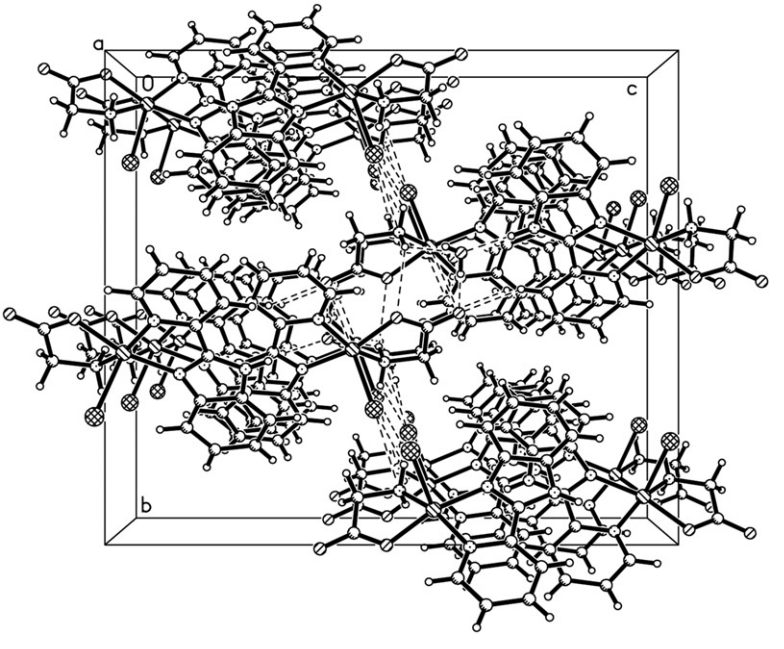

Figure 4. The packing diagram in **2**.

Cu1–N2 = 2.021(6) Å, Cu1–N3 = 1.994(7) Å] and bond angles [O1–Cu1–Cl1 = 99.36(19)°, N1–Cu1–Cl1 = 93.8(2)°, N2–Cu1–Cl1 = 99.63(19)°, N3–Cu1–Cl1 = 98.1(2)°, O1–Cu1–N1 = 165.5(2)°, O1–Cu1–N2 = 90.6(2)°, O1–Cu1–N3 = 84.6(3)°, N3–Cu1–N1 = 99.5(3)°, N3–Cu1–N(2) = 162.1(3)°, and N1–Cu1–N(2) = 81.2(3)°] of complexes in the literatures [29, 30].

Table 3. Selected bond lengths (Å) and angles (°) for **2** with e.s.d.s in parentheses.

Cu1–Cl1	2.5474(12)	Cu1–N3	2.031(3)
Cu1–O1	1.952(2)	Cu1–N4	1.998(3)
Cu1–N1	1.990(3)		
O1W···O2W	2.750(5)	N2···O1W	2.724(4)
O1W···O2[a]	2.729(5)	O2W···Cl1[b]	3.140(4)
N4···O1[c]	3.179(4)	N4···O1W[b]	3.301(4)
N4···Cl1[d]	3.275(3)	O2W···Cl1[e]	3.215(4)
C9···O2 [a]	3.168(5)	C12···O1	2.995(4)
Cl1–Cu1–O1	96.08(8)	O1–Cu1–N3	89.88(10)
Cl1–Cu1–N1	97.20(8)	O1–Cu1–N4	82.77(11)
Cl1–Cu1–N3	104.88(8)	N1–Cu1–N3	81.66(11)
Cl1–Cu1–N4	93.47(8)	N1–Cu1–N4	101.61(11)
O1–Cu1–N1	165.72(10)	N3–Cu1–N4	160.87(11)

Symmetry transformations used to generate equivalent atoms: [a] $-x+1/2, -y, z-1/2$; [b] $x+1/2, y, -z+1/2$; [c] $-x+1, -y, -z+1$; [d] $x+1/2, -y+1/2, -z+1$; [e] $x, -y+1/2, z-1/2$.

Table 4. MIC ($\mu g\,mL^{-1}$) of the complexes, $CuCl_2$, 2-(4′-thiazolyl)benzimidazole, and 2-(2-pyridyl)benzimidazole for the assayed bacteria.

Compound	*B. subtilis* (*G*+)	*S. aureus* (*G*+)	*Salmonella* (*G*−)
$CuCl_2$	256	256	256
TBZ	512	512	512
HPB	128	128	256
[Cu(TBZ)(Gly)(H_2O)]Cl (**1**)	128	128	128
[Cu(HPB)(Gly)Cl]·$2H_2O$ (**2**)	32	32	32

Many intermolecular hydrogen bonds (table 3) exist in the crystal of **2**, such as O1W···O2W = 2.750(5) Å, N2···O1W = 2.724(4) Å, O1W···O2 = 2.729(5) Å $(-x+1/2, -y, z-1/2)$, O2W···Cl1 = 3.140(4) Å $(x+1/2, y, -z+1/2)$, N4···O1 = 3.179(4) Å $(-x+1, -y, -z+1)$, N4···O1W = 3.301(4) Å $(x+1/2, y, -z+1/2)$, N4···Cl1 = 3.275(3) Å $(x+1/2, -y+1/2, -z+1)$, O2W···Cl1 = 3.215(4) Å $(x, -y+1/2, z-1/2)$, C9···O2 = 3.168(5) Å $(-x+1/2, -y, z-1/2)$, and C12···O1 = 2.995(4) Å. Moreover, there is p–π stacking interaction between N(2) and phenzene ring from adjacent [Cu(HPB)(Gly)Cl] molecules with a distance *ca* 3.387 Å.

3.3. *Antibacterial activity*

The efficiencies of copper(II) chloride, 2-(4′-thiazolyl)benzimidazole, 2-(2-pyridyl)benzimidazole and the complexes have been tested against three microorganisms: one Gram(−) (*Salmonella*) and two Gram(+) (*B. subtilis*, *S. aureus*). The results of the MIC [31] expressed in $\mu g\,mL^{-1}$ are listed in table 4.

Copper(II) chloride, 2-(4′-thiazolyl)benzimidazole, and 2-(2-pyridyl)benzimidazole exhibit weak antimicrobial activities against the strains; the activities of 2-(4′-thiazolyl)benzimidazole and 2-(2-pyridyl)benzimidazole as free ligands were similar to 2,2′-bipyridine and much weaker than 1,10-phenanthroline [32]. The antibacterial activities of [Cu(TBZ)(Gly)(H_2O)]Cl (**1**) and [Cu(HPB)(Gly)Cl]·$2H_2O$ (**2**) were better

than free ligands or copper chloride. Thus antibacterial activities of the complexes should be attributed to undissociated complexes. The antimicrobial activities of metal complexes is generally concerned with the five main factors [33]: (i) the nature of the parent ligands; (ii) the chelate effect of the ligands, i.e., bidentate ligands such as TBZ and HPB, show higher antimicrobial efficiency than complexes with monodentate ligands; (iii) the total charge of the complex in solution; (iv) the nature of the counter ion in the case of the ionic complex; (v) the nuclearity of the metal center in the complex; dinuclear centers are more active than mononuclear ones. Only the first two factors are present in the two complexes, i.e., the chelate effect provided by the bidentate ligands and their nature. The better antibacterial activity of the complexes compared with the free ligands TBZ and HPB or copper(II) chloride salt may be mainly attributed to the existence of coordination of Cu(II) [34–36]. The larger antibacterial activity of **2** compared with **1** can be attributed to the parent ligands, in which HPB exhibits higher antibacterial efficiency than TBZ. Similarly, the poor antibacterial activity of the complexes compared with the complexes of quinolones can be principally attributed to the difference of the nature of the ligands, in which quinolones with higher lipophilicity are good enzyme inhibitors, with stronger antibacterial activity than HPB and TBZ [32].

4. Conclusions

Two new complexes: [Cu(TBZ)(Gly)(H_2O)]Cl (**1**) and [Cu(HPB)(Gly)Cl] · $2H_2O$ (**2**), have been synthesized and characterized. In the resultant complexes, each central Cu(II) ion is five-coordinate with a distorted square-pyramidal coordination geometry. The complexes show increased antimicrobial activity in comparison to their parent ligands and copper(II) chloride salt against the three microorganisms tested: *B. subtilis*, *S. aureus*, and *Salmonella*. The results may be valuable in further exploiting and developing novel antibacterial drugs.

Supplementary material

Tables of atomic coordinates, isotropic thermal parameters, and complete bond distances and angles for **1** (CCDC-784544) and **2** (CCDC-784545) have been deposited with the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk; Website: http://www.ccdc.cam.ac.uk).

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