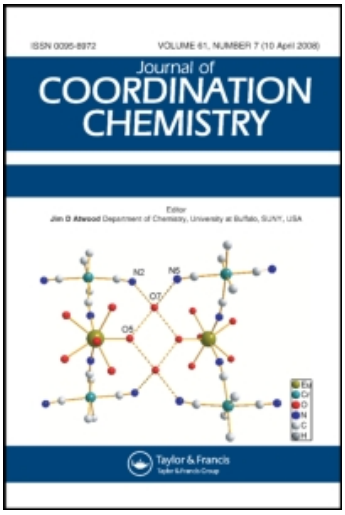

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Xu Tong-Tao[ab]; Xu Xing-You[ab]; Gao Jian[c]; Yang Xu-Jie[a]; Lu Lu-De[a]; Xin Wang[a]
[a] Materials Chemistry Laboratory, Nanjing University of Science & Technology, Nanjing 210094, P.R. China [b] Department of Chemical Engineering, Huaihai Institute of Technology, Lianyungang 222005, P.R. China [c] Department of Chemical Engineering, Lianyungang Technical College, Lianyungang 222006, P.R. China

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Synthesis, structure and antimicrobial study of two new copper(II) complexes derived from *N*-(3-aminopropyl) benzylamine ligand (apba) and *N*-salicylidene-apba

XU TONG-TAO†‡, XU XING-YOU†‡, GAO JIAN§,
YANG XU-JIE†, LU LU-DE*† and XIN WANG†

†Materials Chemistry Laboratory, Nanjing University of Science & Technology, Nanjing 210094, P.R. China
‡Department of Chemical Engineering, Huaihai Institute of Technology, Lianyungang 222005, P.R. China
§Department of Chemical Engineering, Lianyungang Technical College, Lianyungang 222006, P.R. China

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Two new copper(II) complexes were synthesized by reaction of *N*-(3-aminopropyl)benzylamine (L1: apba, for complex **1**) and *N*-salicylidene-apba (L2: for complex **2**) with Cu^{2+}. Crystals of complex **1** were orthorhombic, space group *pccn*, with $a = 15.2149(10)$, $b = 25.0071(16)$, $c = 7.6280(5)$ Å and $\alpha = \beta = \gamma = 90°$. Complex **2** crystals were monoclinic, space group $P2_1/c$, with $a = 8.688(6)$, $b = 12.812(9)$, $c = 16.022(11)$ Å and $\beta = 99.241(10)°$. Structures of the two complexes were centro-symmetric and both Cu(II) atoms were four coordinate with a distorted square-planar geometry. The toxicity of the complexes was evaluated by testing antimicrobial activity against bacterial strands.

Keywords: Copper(II); *N*-(3-Aminopropyl)benzylamine; Crystal structure; Salicylaldehyde; Toxicity

1. Introduction

The family of Schiff bases derived from aliphatic primary amines and salicylaldehyde has proved to be a source of versatile ligands for transition metals including copper(II) [1–4]. There are numerous reports on these transition metal complexes of Schiff bases due to properties such as catalysis [5–6], antimicrobial and antifungal activities [7–10]. However, information on the corresponding derivatives of aromatic diamines with salicylaldehyde is still very scanty. Comparatively little is known about the coordination chemistry of copper with *N*-(3-aminopropyl)benzylamine. The present work is also the first crystallographic study of any derivative of *N*-(3-aminopropyl)benzylamine. In this article, we report the synthesis, structural characterization and toxicity of two new copper(II) complexes derived from *N*-(3-aminopropyl)benzylamine and salicylaldehyde.

*Corresponding author. Tel.: 86-025-84315054. Email: xutongtao_1968@163.com

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2. Experimental

2.1. *Materials and instrumentation*

All starting materials and solvents were of analytical purity. Elemental analyses were determined with a Perkin-Elmer 240C instrument. IR spectra were measured as KBr discs using a Nicolet 5DX FT-IR spectrophotometer. The ES mass spectral measurement of the complex was carried out on a LCQ System (Finngann MAT, USA) using methanol as the mobile phase.

2.2. *Synthesis of N-(3-aminopropyl)benzylamine (apba)*

The ligand apba was synthesized by the procedure as follows: *N*-(2-nitrilethyl)benzylamine (0.625 mol, 100 g), NaOH (0.500 mol, 20 g) and Raney nickel (10 g) were dissolved in 800 mL of ethanol. The mixture was hydrogenated for 2 h under 2.5 Mpa at 60°C. Then the solution was filtered and all solvents were distilled out under vacuum. A colorless oil product was obtained. Yield: 63.4 g, 62%. B.p. 196–197°C (−0.098 MPa). IR (cm^{-1}, KBr)ν: 3350, 3278(s), ν_{as}, $\nu_s(NH_2)$; 2938, 2851(m), ν_{as}, $\nu_s(CH_2)$; 1581(m), $\nu_{(NH)}$; 1454–1488, phenyl; MS m/z (%): 165.3, $M^+ + 1$(91).

2.3. *Synthesis of metal complex 1 $[Cu(L1)_2](ClO_4)_2 \cdot 2H_2O$*

A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.371 g, 1 mmol) in methanol (20 mL) was added in portions to 15 mL of a methanol solution containing apba (0.165 g, 1 mmol). After stirring for 2 h at 45°C, the complex precipitated, was filtered off, washed with methanol and dried *in vacuo*. Blue-purple single crystals suitable for X-ray structure determination were obtained by slow evaporation of the resulting filtrates for about 20 days at ambient temperature. Yield 63%. M.p. 168.4–169.3°C. Anal. Calcd for $C_{20}H_{36}Cl_2CuN_4O_{10}$ (%): C, 38.28; H, 5.74; N, 8.93; Found: C, 38.19; H, 5.79; N, 8.98. IR (cm^{-1}): 3275s ν(NH); 3357, 3459s $\nu(NH_2)$; 1568, 1494m ν(aromatic ring); 1098s $\nu(ClO_4)$.

2.4. *Synthesis of metal complex 2 $[Cu(L2)_2](ClO_4)_2$*

To a stirred solution of salicylaldehyde (0.122 g, 1.0 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ (0.371 g, 1.0 mmol) in 25 mL absolute methanol was added dropwise a solution of apba (0.165 g, 1.0 mmol) in 10 mL absolute methanol at 25°C. After stirring for 3 h at 45°C, the complexes precipitated, were filtered off, washed with methanol and dried *in vacuo*. Deep-green single crystals suitable for X-ray structure determination were obtained by slow evaporation of the resulting filtrates for about 6 days at ambient temperature. Yield 49%, m.p. >195.0°C (dec.). Anal. Calcd for $C_{34}H_{40}Cl_2CuN_4O_{10}$ (%): C, 51.05; H, 5.00; N, 7.01; Found: C, 51.10; H, 4.96; N, 7.09. IR (cm^{-1}): 3252s ν(NH); 1625m ν(C=N); 1551, 1477m ν(aromatic ring); 1095s $\nu(ClO_4)$.

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with caution.

2.5. *X-ray crystallography*

Suitable crystals of **1** and **2** were mounted on a glass fiber. The crystal data were collected at 293(2) K on a Bruker SMART/CCD area-detector diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods using SHELXL-97 and refined by full-matrix least squares calculation on F^2 using SHELXL-97 [11]. All H atoms were placed in calculated positions. Full-matrix least-squares methods were used to refine an overall scale factor, positional and thermal parameters. The details of data collection, refinement and crystallographic data are summarized in table 1.

2.6. *Antimicrobial activity determination*

As a preliminary screening for antimicrobial activity, using agar diffusion method described in the previous paper [12], $[Cu(L1)_2](ClO_4)_2 \cdot 2H_2O$, $[Cu(L2)_2] \cdot (ClO_4)_2$ and

Table 1. Crystal data, data collection and structure refinement parameters for **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{20}H_{36}Cl_2CuN_4O_{10}$	$C_{34}H_{40}Cl_2CuN_4O_{10}$
Formula weight	626.97	799.14
Radiation (Å)	Mo-Kα, 0.71073	Mo-Kα, 0.71073
Crystal system	Orthorhombic	Monoclinic
Space group (Å, °)	*Pccn*	$P2_1/c$
a	15.2149(10)	8.688(6)
b	25.0071(16)	12.812(9)
c	7.6280(5)	16.022(11)
α	90	90
β	90	99.241(10)
γ	90	90
V(Å)	2902.3(3)	1760(2)
Z	4	2
D_{Calcd} (Mg m^{-3})	1.435	1.508
Absorption coefficient (mm^{-1})	0.991	0.836
θ range (°)	1.57–25.00	2.05–25.01
Index ranges	$-16 \le h \le 18$, $-26 \le k \le 29$, $-8 \le l \le 9$	$-10 \le h \le 10$, $-9 \le k \le 15$, $-18 \le l \le 19$
Reflections collected	14098	8851
Independent reflections	2555 [$R_{(int)} = 0.0290$]	3096 [$R_{(int)} = 0.1905$]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max/min transmissions	0.7211 and 0.6919	0.7817 and 0.7364
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2555/0/173	3096/198/233
Goodness-of-fit on F^2	1.050	1.010
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0531$, $wR_2 = 0.1508$	$R_1 = 0.0681$, $wR_2 = 0.1497$
R indices (all data)	$R_1 = 0.0687$, $wR_2 = 0.1733$	$R_1 = 0.1453$, $wR_2 = 0.1841$
Largest diff. peak and hole (e Å^{-3})	1.195 and −0.645	0.721 and −0.709

N-(3-aminopropyl)benzylamine dissolved in DMF were tested against standard strains of *Staphylococcus aureus* CMCC (B) 26 003 and *Escherichia coli* CMCC (B) 44 102, which belong to Gram-positive bacteria and Gram-negative bacteria, respectively. Nutrient agar, thawed by heating in a water bath, was transferred to glass plates and held at 37°C. After test strains were spread on the solid nutrient agar surface, stainless steel tubes ($7.8 \times 6 \times 10\,mm^3$) were placed vertically on the surface. 0.05 mL samples were injected to the steel tubes and allowed to incubate at 37°C for 24 h. The inhibition zone around the disc was calculated as zone diameter in millimeters. Blank tests showed that DMF does not affect the test organisms. All tests were repeated three times and average data were taken as the final result.

3. Results and discussion

3.1. *Crystal structures*

Crystal structure of the centro-symmetrical Cu(II) complex **1** consists of a cationic unit of $[Cu(apba)_2]^{2+}$, H_2O molecule and non-coordinated ClO_4^- anion. The molecular structure of **1** showing the atomic numbering scheme is indicated in figure 1(a). Selected bond lengths and bond angles relevant to the Cu coordination sphere are listed in table 2. The six bond angles formed by Cu(1) and coordinated atoms are 180.00(1), 90.87(13), 89.13(13), 89.13(13), 90.87(13) and 180.00(1)°, respectively. Four bond lengths formed by Cu(1) and coordinated atoms (2.006 Å, 2.006 Å, 2.091 Å, 2.091 Å) are almost equal. So the most noteworthy feature of the molecular structure is the proof that this involves a four-coordinate copper(II) ion, doubly chelated by the four *N* atoms of apba. The environmemt of the copper ion is square planar. The dihedral angle between the plane 1 (composed of atoms Cu(1), N(1), N(2), N(1)A and N(2A)) and the aromatic ring (composed of atoms C(1) to C(6)) is 38.2°. Two aromatic rings are coplanar.

The packing diagram (figure 1b) shows its layer-like crystal structure, which is formed by intermolecular van der Waals forces and hydrogen bonds. The N(2) atoms of apba form three intermolecular hydrogen bonds with O(2), O(3) and O(4) of perchlorate anions, respectively [$N(2)\cdots O(2) = 3.012$ Å and N(2)–$H(2A)\cdots O(2) = 150.54°$; $N(2)\cdots O(4) = 3.127$ Å and N(2)–$H(2B)\cdots O(4) = 138.56°$; $N(2)\cdots O(3) = 2.960$ Å and N(2)–$H(2B)\cdots O(3) = 112.26°$]. Each perchlorate anion forms acceptor hydrogen bonds with amino groups of an adjacent complex cation.

Schiff-base complex **2** also has a four-coordinate CuN_2O_2 environment. In a symmetric unit of 2, copper(II) is doubly chelated by the two N atoms of the Schiff base and two O atoms of salicylaldehyde. The Cu ion in the cationic unit of complex **2** is similar to complex **1**. Of all environments for copper(II) ion in crystals, square planar is the least common [13].

The perspective view of $[Cu(L2)_2]^{2+}$ is shown in figure 2(a) and selected bond lengths and bond angles relevant to the Cu^{2+} coordination sphere are listed in table 3. Most of the bond lengths in the system are in the range of single to double bonds. The bond length of Cu(1)–N(1) and Cu(1)–O(1), being 1.998(5) and 1.905(4) Å, respectively, are

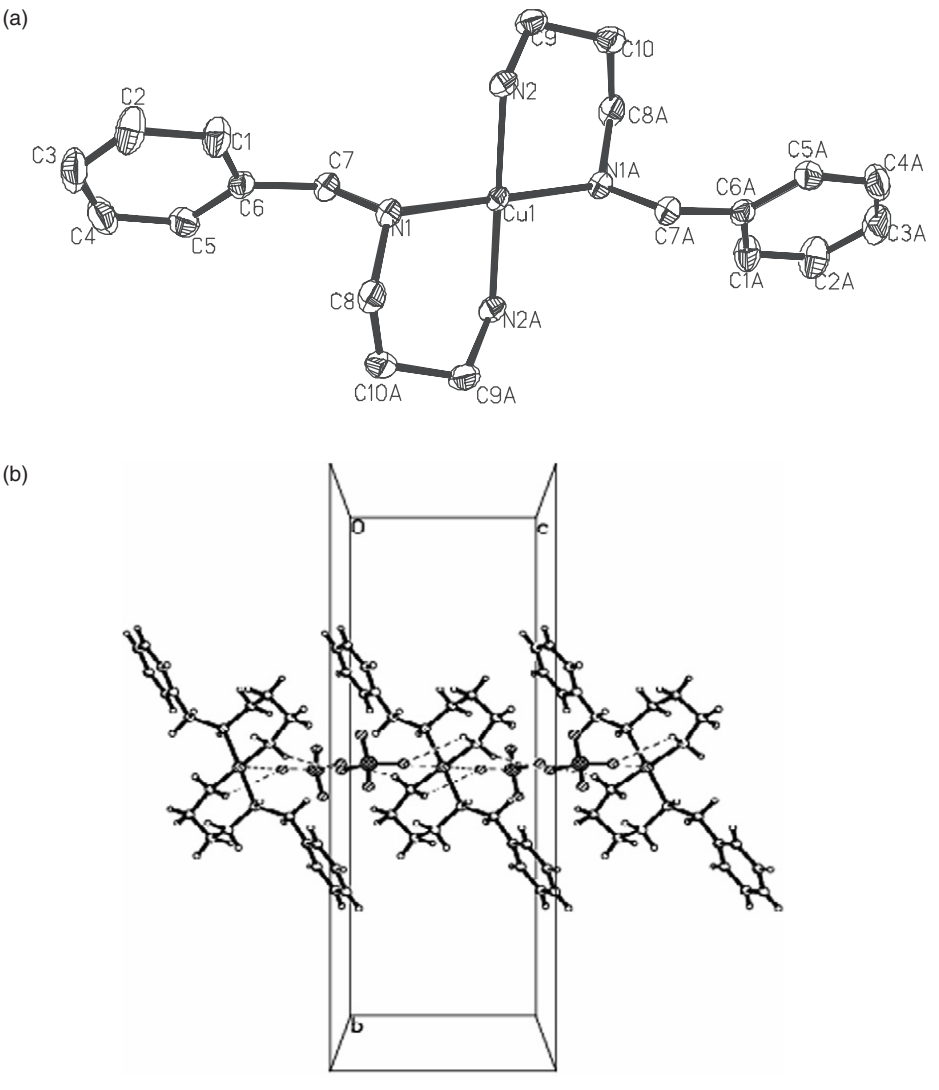

Figure 1. (a) Molecular structure for $[Cu(L1)_2]^{2+}$ (H atoms have been omitted). (b) Molecular crystal packing for **1**.

Table 2. Selected bond distances (Å) and bond angles (°) for $[Cu(L1)_2]^{2+}$.

Cu(1)–N(2)	2.006(3)	Cu(1)–N(1)	2.091(3)
N(2)–C(9)	1.463(5)	C(7)–N(1)	1.486(5)
C(7)–C(6)	1.516(5)	N(1)–C(8)	1.484(5)
N(2)–Cu(1)–N(2)#1	180.00(1)	N(2)–Cu(1)–N(1)	89.13(13)
N(2)#1–Cu(1)–N(1)	90.87(13)	N(2)–C(9)–C(10)	112.3(4)
C(9)–N(2)–Cu(1)	120.7(3)	N(1)–C(7)–C(6)	115.9(3)
C(8)–N(1)–C(7)	113.1(3)	C(8)–N(1)–Cu(1)	116.7(2)
C(7)–N(1)–Cu(1)	109.7(2)	C(5)–C(6)–C(1)	118.7(4)
C(5)–C(6)–C(7)	119.8(4)	C(1)–C(6)–C(7)	121.3(4)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+1, -z+1$.

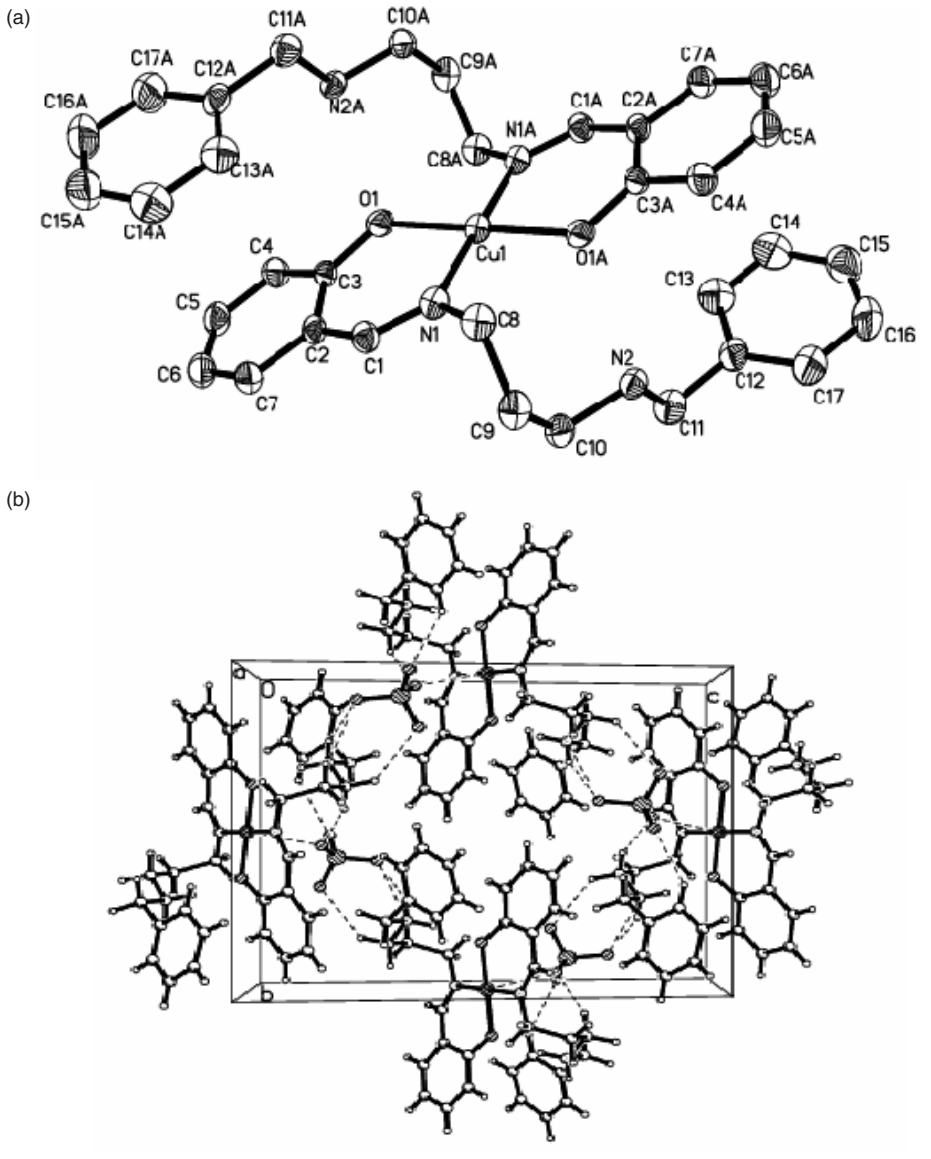

Figure 2. (a) Molecular structure for $[Cu(L2)_2]^{2+}$ (H atoms have been omitted). (b) Molecular crystal packing for **2**.

similar to the previous report [13], but the bond length of Cu(1)–N(1) is somewhat shorter than the corresponding distance in complex **1**. The bond length of C(1)–N(1), C(8)–N(1), C(10)–N(2) and C(11)–N(2) are 1.270, 1.459, 1.487 and 1.457 Å, belonging to the typical C=N Schiff base bond and C–N single bond, respectively [14]. Compared with the normal phenol C–O bond distance of 1.362 Å, the shorter C(3)–O(1) bond distance of 1.305 Å may indicate hyperconjugation. The dihedral angle between plane 1 (composed of Cu(1), N(1), N(1)A, O(1) and O(1)A) and plane 2 (composed of O(1),

Table 3. Selected bond distances (Å) and bond angles (°) for $[Cu(L2)_2]^{2+}$.

Cu(1)–O(1)	1.905(4)	Cu(1)–N(1)	1.998(5)
N(1)–C(1)	1.270(7)	N(1)–C(8)	1.459(7)
N(2)–C(10)	1.457(7)	N(2)–C(11)	1.487(8)
O(1)–C(3)	1.305(7)	C(1)–C(2)	1.422(8)
C(11)–C(12)	1.488(9)	C(12)–C(17)	1.345(10)
C(12)–C(13)	1.373(10)	C(15)–C(16)	1.338(12)
C(14)–C(15)	1.361(10)	C(16)–C(17)	1.391(11)
O(1)#1–Cu(1)–O(1)	180.0	O(1)–Cu(1)–N(1)#1	89.81(19)
O(1)–Cu(1)–N(1)	90.19(19)	N(2)–C(10)–C(9)	114.1(6)
C(1)–N(1)–C(8)	114.7(5)	C(1)–N(1)–Cu(1)	123.8(4)
C(8)–N(1)–Cu(1)	121.4(4)	C(10)–N(2)–C(11)	111.9(5)
C(3)–O(1)–Cu(1)	127.7(4)	N(1)–C(1)–C(2)	127.6(6)
O(1)–C(3)–C(2)	123.3(5)	O(1)–C(3)–C(4)	119.4(5)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+1, -z$.

N(1), C(1) to C(7)) is 17.2°. The dihedral angle between the aromatic ring (composed of atoms C(12) to C(17)) and plane 1 is 11.0°; the aromatic ring and plane 2 is 19.8°. The four aromatic rings in $[CuL2]^{2+}$ are almost coplanar, and therefore a approximately coplanar conjugation system was formed.

Hydrogen bonds occur in the structure extensively. The N(2) atom of *N*-salicylidene-apba atoms form A strong intramolecular hydrogen bond with O(1) of hydroxyl [N(2)–H(2B) = 0.900 Å, H(2B)···O(1) = 1.768 Å, N(2)···O(1) = 2.660 Å and N2–H2B···O1 = 170.94°], and *N*-salicylidene-apba N(2) forms a intermolecular hydrogen bond with O(2) of perchlorate anion [N(2)–H(2B) = 0.900 Å, H(2B)···O(2) = 2.002 Å, N(2)···O(2) = 2.841 Å and N(2)–H(2B)···O(2) = 154.56°]. All the above intramolecular and intermolecular interactions for an infinite three-dimensional framework and stabilize the crystal structure (figure 2b).

3.2. *Spectral characteristics*

The IR spectra of the two complexes resemble each other indicating a similar structural relationship. For **2**, condensation of all primary amine groups and carbonyl groups is confirmed by presence of C=N double stretching bands in the IR region 1625 cm^{-1} and the lack of strong N–H stretching bands at 3200–3340 cm^{-1}. Compared to **2**, the presence of two strong peaks at 3357 and 3459 cm^{-1} is characteristic of the NH_2 group of apba. The strong peaks of both complexes at 1095 and 1098 cm^{-1} without splitting show that ClO_4^- does not coordinate with Cu.

3.3. *Antimicrobial activity*

From the data of table 4, the complexes exhibited antibacterial activity against *S. aureus* and *E. coli*. In the test range, the compounds were more active against the strains with increase of concentration. The two new copper(II) complexes show higher activity against bacteria as compared to apba, especially in the activity against *S. aureus*, indicating that the metal atom is essential.

Table 4. The diameter of inhibition zone (mm).

Compound	Concentration ($mg\,mL^{-1}$)	Diameter of inhibition zone (mm)	
		Staphylococcus aureus	*Escherichia coli*
APBA	20.0	14.9	13.8
	10.0	12.2	11.7
	5.0	11.6	10.9
	2.5	8.4	7.8
1	20.0	23.6	22.7
	10.0	21.8	20.7
	5.0	19.7	19.2
	2.5	12.3	13.4
2	20.0	25.8	21.9
	10.0	23.4	20.6
	5.0	20.1	19.3
	2.5	11.9	11.2

Comparing $[Cu(L2)_2]\cdot(ClO_4)_2$ with $[Cu(L1)_2](ClO_4)_2\cdot 2H_2O$ the activities were basically similar to *E. coli* but different with respect to the activities against *S. aureus* in the concentration of 20.0–2.5 $mg\,mL^{-1}$. This may indicate that the ligand is a factor to the antibacterial activity also, consistent with previous study [15, 16].

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