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Synthesis, Crystal Structure, and Antibacterial Evaluation of a Copper(II) Compound Derived From 1,2-Diaminobenzene-*N,N′*-bis(3-methoxysalicylideneimine)

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A copper(II) compound, $[CuL][CuL(OH_2)]\cdot ClO_4\cdot 0.5CH_3OH$, where L = 1,2-diaminobenzene-*N,N′*-bis(3-methoxysalicylidenei mine), has been synthesized and characterized by means of spectroscopic methods and single-crystal X-ray structure determination. The compound crystallizes in the orthorhombic space group $Cmc2_1$ with unit cell dimensions $a = 17.981(3)$ Å, $b = 17.776(3)$ Å, $c = 14.047(3)$ Å, $V = 4489.8(14)$ Å^3, $Z = 4$, $R_1 = 0.0511$, and $wR_2 = 0.1267$. The asymmetric unit of the compound contains one mononuclear [CuL] unit, in which the Cu atom adopts a square-planar geometry, one mononuclear $[CuL(OH_2)]$ unit, in which the Cu atom adopts a square-pyramidal geometry, one perchlorate anion, and one half methanol solvate. The compound was tested for its antibacterial activities to assess its inhibiting potential.

Keywords antibacterial activity, copper compound, crystal structure, Schiff base, X-ray diffraction

INTRODUCTION

Schiff bases have often been used as versatile chelating ligands in coordination chemistry. Schiff bases with donors such as O, N, and S have structure similarities with neutral biological systems and due to presence of imine groups are utilized in elucidating the mechanism of transformation of rasemination reaction in biological system.[1–3] The Schiff bases prepared from salicylaldehyde and its derivatives are interesting and have received considerable attention not only for their application in coordination chemistry[4–6] but also for their importance in medicinal and pharmaceutical fields. Most Schiff bases and their complexes show biological activities including antibacterial,[7–9] antifungal,[9,10] antitumor,[11] anticancer,[10] anticorrosion, and anti-inflammatory activities. As a continuation of the biological activities of Schiff base complexes, in the present article, I report a new Schiff base copper compound with the ligand 1,2-diaminobenzene-*N,N′*-bis(3-methoxysalicylideneimine).

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EXPERIMENTAL

General Considerations

All materials were obtained from commercial sources and used as received. Copper perchlorate was prepared by the reaction of basic cupric carbonate with perchloric acid in distilled water. The Schiff base ligand was prepared according to the literature procedure.[12] Infrared spectra were collected on a Nicolet 5SXC FT-IR spectrometer (Linyi University, China) as KBr pellets. Electronic absorption (UV-Vis) spectra were collected on a Cary 500 UV-Vis-NIR spectrophotometer (Linyi University, China). Microanalyses for C, H, and N were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer (Linyi University, China).

Preparation of the Copper Compound

To a methanolic solution (20 mL) of the Schiff base ligand (0.38 g, 1 mmol) was added a methanolic solution (10 mL) of copper perchlorate (0.37 g, 1 mmol). The reaction mixture was gently heated at 50°C for 30 min while stirring and the complex precipitated was recrystallized from methanol, yielding well-shaped single crystals suitable for X-ray diffraction. Yield: 45%. Elemental Anal. Calcd. for $C_{46}H_{44}ClCu_2N_4O_{14}$: C, 53.15; H, 4.27; N, 5.39. Found: C, 52.93; H, 4.40; N, 5.51%. IR (KBr, cm^{-1}): 1605 (C=N). UV-Vis (toluene, λ, nm, (ε, M^{-1} cm^{-1})): 325 (21200), 339 (17900), 357 (14500), 403 (11300), 458 (14500), 693 (2730).

Crystal Structure Determination and Refinement

Crystal data, data collection and refinement parameters for the compound are listed in Table 1. Data were obtained on a Bruker Apex II diffractometer (Shandong University, China) equipped with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. The structure of the compound was solved by direct methods and refined on F^2 by full-matrix least-squares using

TABLE 1
Crystal data and structure refinement for the compound

Empirical formula	$C_{46}H_{44}ClCu_2N_4O_{14}$
M/g mol^{-1}	1039.4
Crystal size/mm	0.30 × 0.27 × 0.27
2θ range/deg	1.61–27.00
Completeness to 2θ (%)	100
h; k; l range	–22, 22; –14, 22; –17, 17
Temperature/K	298(2)
Crystal system	Orthorhombic
Space group	$Cmc2_1$
a/Å	17.981(3)
b/Å	17.776(3)
c/Å	14.047(3)
V/Å^3	4489.8(14)
Z	4
D_{calc}/g cm^{-3}	1.538
F(000)	2140
μ/mm^{-1}	1.080
Max/min transmission	0.759/0.738
Reflections collected (R_{int})	12853 (0.0438)
Independent reflections	4776
Observed reflections	3718
Parameters refined	320
Restraints	43
Max/min $\Delta\rho$/e Å^{-3}	0.813/–0.384
R_1, wR_2 [$I > 2\sigma(I)$]	0.0511, 0.1267
R_1, wR_2 (all data)	0.0703, 0.1382
Goodness-of-fit on F^2	1.018

TABLE 2
Selected bond lengths (Å) and angles (°) for the compound

Bond lengths			
Cu1-O3	1.896(4)	Cu1-N2	1.926(4)
Cu2-O1	1.905(3)	Cu2-N1	1.930(4)
Cu2-O9	2.431(6)		
Bond angles			
O3-Cu1-O3A	89.2(2)	O3-Cu1-N2A	177.2(2)
O3-Cu1-N2	93.6(2)	N2-Cu1-N2A	83.7(3)
O1-Cu2-O1A	87.8(2)	O1-Cu2-N1A	172.7(2)
O1-Cu2-N1	93.6(2)	N1-Cu2-N1A	84.2(3)
O1-Cu2-O9	96.2(2)	N1-Cu2-O9	90.8(2)

Symmetry operation for A: 1 – x, y, z.

SHELX-97.[13] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions, assigned fixed isotropic thermal parameters at 1.2 or 1.5 times the equivalent isotropic U of the atoms to which they are attached and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in the structure factor calculations. Selected bond lengths and angles are listed in Table 2.

Antibacterial Activities

Antibacterial activities of the compound were investigated using agar well diffusion method.[14] The activities of the free Schiff base ligand and standard drug imipenem were studied against the *Staphylococcus aureus* and *Bacillus subtilis* (as gram-positive bacteria) and *Pseudomonas aeruginosa*, *Escherichia coli*, and *Salmonella typhi* (as gram-negative

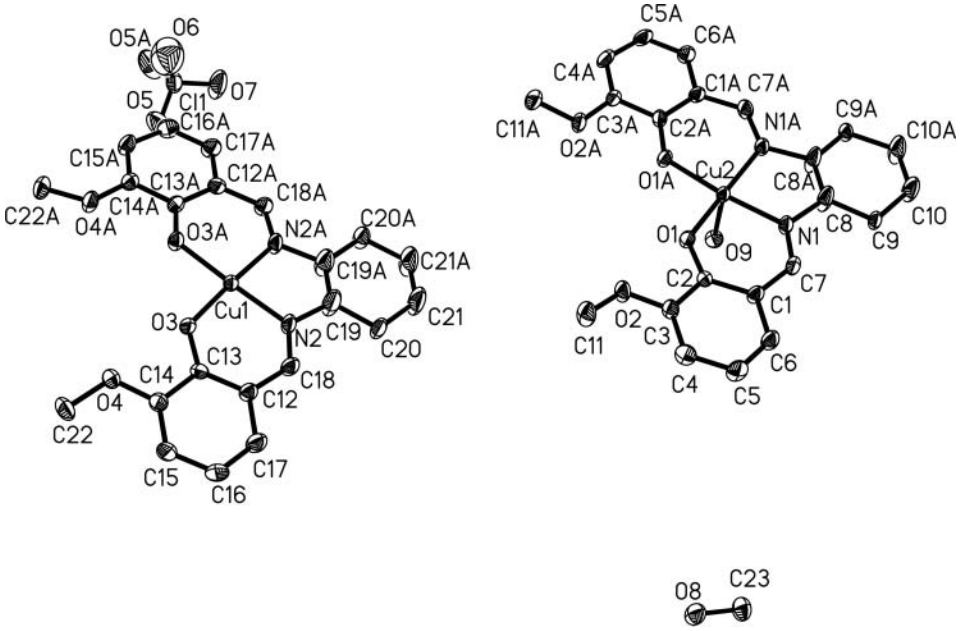

FIG. 1. Molecular structure of the complex. Hydrogen atoms have been omitted for clarity. Symmetry operation for A: 1 – x, y, z.

bacteria). Strains were obtained from Dalian Medical University. The solution of 2 μg/mL of each compound (free Schiff base ligand and Imipenem) in DMSO was prepared for testing against bacteria. Centrifuged pellets of bacteria from a 24 h old culture containing approximately 10^4–10^6 CFU (colony forming unit) per milliliter were spread on the surface of Muller Hinton Agar plates. Wells were created in medium with the help of a sterile metallic bores and nutrients agar media (agar 20 g + beef extract 3 g + peptones 5 g) in 1000 mL of distilled water (pH 7.0), autoclaved and cooled down to 45°C. Then it was seeded with 10 mL of prepared inocula to have 10^6 CFU/mL. Petri plates were prepared by pouring 75 mL of seeded nutrient agar. The activities were determined by measuring the diameters of the inhibition zones (in mm). The growth inhibition was calculated according to Rahman et al.[14]

RESULTS AND DISCUSSION

The Schiff base ligand was prepared by a 1:2 condensation of benzene-1,2-diamine with 3-methoxysalicylaldehyde in methanol. Reaction of the ligand with copper perchlorate in methanol gave the copper compound.

Structure Description of the Compound

The crystal structure analysis of the compound reveals that it contains a [CuL] unit, a [CuL(OH_2)] unit, a perchlorate anion, and one half methanol solvate in the asymmetric unit (Figure 1). In [CuL], the Cu atom is in a square-planar geometry, coordinated by two imine N and two phenolate O atoms of L. In [CuL(OH_2)], the Cu atom is in a square-pyramidal geometry, coordinated by two imine N and two phenolate O atoms of L in the basal plane, and weakly coordinated by one water O atom at the apical position. In [CuL(OH_2)], the C8-C9-C10-C10A-C9A-C8A (symmetry code for A: 1 – *x*, *y*, *z*) benzene ring forms a dihedral angle of 1.5(3)° with the C1-C6 benzene ring. In [CuL], the C19-C20-C21-C21A-C20A-C19A benzene ring forms a dihedral angle of 7.7(3)° with the C12-C17 benzene ring. The Cu-O and Cu-N bonds in the basal plane of [CuL(OH_2)] are slightly longer than those in [CuL], and all of them are in the range of similar Schiff base copper(II) complexes with square-planar and square-pyramidal geometries.[15–18] In the three-dimensional crystal structure of the compound, the [CuL] and [CuL(OH_2)] molecules are linked together by four intermolecular O−H···O hydrogen bonds (Table 3, Figure 2).

TABLE 3
Hydrogen-bond geometry for the compound (Å, °)

D−H···*A*	*D*−H	H···*A*	*D*···*A*	*D*−H···*A*
O9−H9W···O3	0.94(1)	2.30(2)	3.01(3)	132(3)
O9−H9W···O4	0.94(1)	2.02(2)	2.86(3)	147(3)

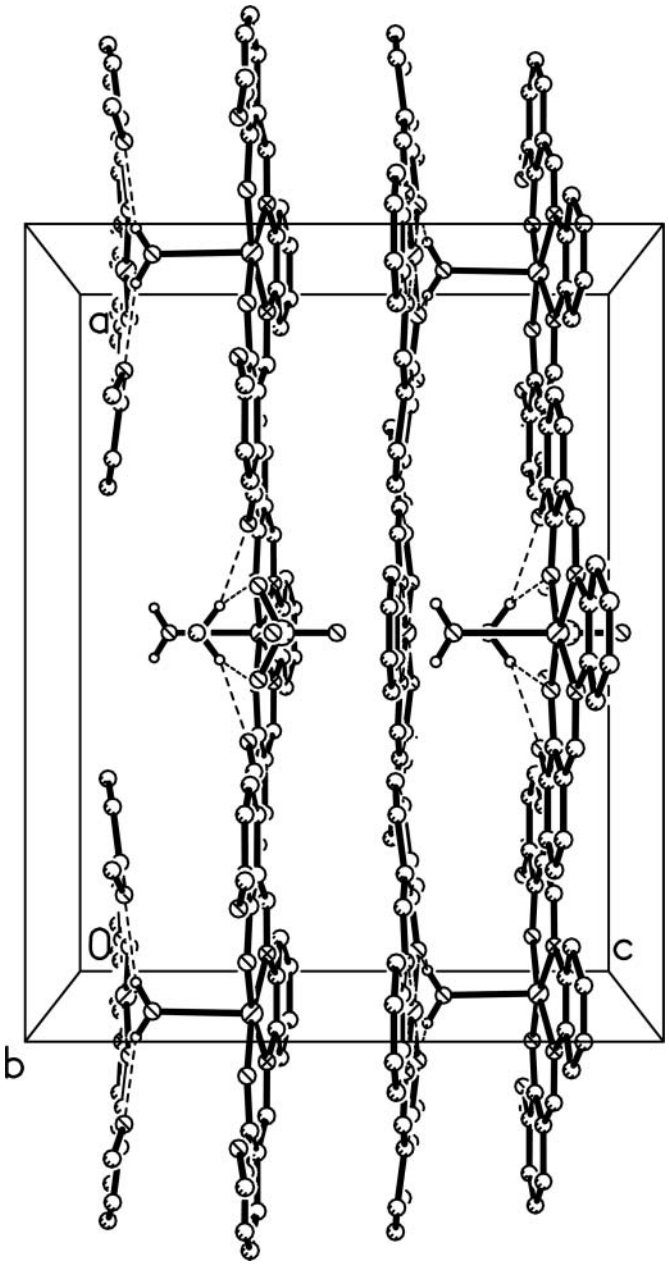

FIG. 2. The molecular packing structure of the complex, viewed along the *y* axis. Hydrogen bonds are drawn as dashed lines.

Antibacterial Activity

The copper compound, the free Schiff base ligand, and the standard drug imipenem were screened separately for their antibacterial activities against the bacteria *Staphylococcus aureus*, *Bacillus subtilis*, *Pseudomonas aeruginosa*, *Escherichia coli*, and *Salmonella typhi*. The diffusion agar technique was used to evaluate the antibacterial activities of the compounds.[19] The results are summarized in Table 4. From the results, it is obvious that the copper compound is more active toward gram-positive

TABLE 4
Bactericidal screening data of the tested materials (inhibition zone in mm)

Microorganism	Copper compound	Free Schiff base ligand	Imipenem
Staphylococcus aureus	++++	++	++++
Bacillus subtilis	+++	++	++++
Pseudomonas aeruginoca	+	–	++++
Escherichia coli	++	–	++++
Salmonella typhi	+	–	++++

++++ = excellent activity (>90% inhibition); +++ = significant activity (70–90% inhibition); ++ = moderate activity (40–70% inhibition); + = weak activity (<40% inhibition), – = no activity.

strains than gram-negative strains. This may be caused by the difference in the structures of the cell walls. The walls of gram-negative cells are more complex than those of gram-positive cells. The copper compound showed excellent activity against *Staphylococcus aureus* and significant activity against *Bacillus subtilis*, but weak or moderate activities against the gram-negative strains. The free Schiff base ligand has moderate activities against *Staphylococcus aureus* and *Bacillus subtilis* but no activity against *Pseudomonas aeruginoca*, *Escherichia coli*, and *Salmonella typhi*. In general, the copper compound showed stronger antibacterial activities than the free Schiff base ligand.

CONCLUSION

A copper(II) compound with the Schiff base ligand 1,2-diaminobenzene-*N,N′*-bis(3-methoxysalicylideneimine) were prepared and characterized. The antibacterial evaluation indicates that the compound may be used as an efficient antibacterial material. This is in accordance with those reported previously that metal complexes showed stronger antibacterial activities than the free Schiff base ligands.[20–22]

SUPPLEMENTARY MATERIALS

Crystallographic data for the structural analyses has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 866129. Copy of this information maybe obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 366 033, e-mail: deposit@ccdc.cam.ac.uk or on the web www: http://www.ccdc.cam.ac.uk.

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