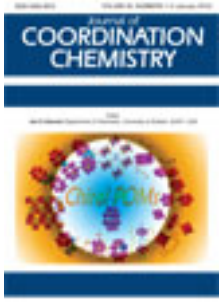

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Synthesis, crystal structures, and urease inhibition studies of two new Schiff-base copper complexes derived from n-butylamine

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Synthesis, crystal structures, and urease inhibition studies of two new Schiff-base copper complexes derived from *n*-butylamine

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Two Schiff-base copper(II) complexes, bis(N-*n*-butyl-5-chlorosalicylaldiminato) copper(II) (**1**) and bis(N-*n*-butyl-4-methoxysalicylaldiminato) copper(II) (**2**), were synthesized and their solid-state structures were determined by X-ray crystallography. Complex **1** displays a distorted square-planar geometry, while **2** possesses square-planar geometry. Copper(II) complexes **1** and **2** showed strong inhibitory activity against jack bean urease ($IC_{50} = 2.7,\ 3.5\,\mu mol\,L^{-1}$), compared with acetohydroxamic acid ($IC_{50} = 63.00\,\mu mol\,L^{-1}$). A molecular modeling study was carried out *via* the DOCK program to gain understanding of the potent inhibitory activity of these copper species against jack bean urease.

Keywords: Schiff-base copper(II) complexes; Crystal structures; 5-Chlorosalicylaldehyde; 4-Methoxysalicylaldehyde; Urease inhibitors

1. Introduction

Transition metal complexes of Schiff bases derived from salicylaldehyde and its derivatives have potential applications [1–9], acting as single-molecule magnets (SMMs) [2], as luminescent probes [3], as catalysts for specific DNA [4, 5], and RNA [6] cleavage reactions. Salen-type Schiff bases may be bidentate N,O- [7] or tridentate N,O,O-donors [8] to yield a variety of complexes with other ligands, such as azide, thiocyanate, and carboxylate. Schiff-base copper(II) complexes attract considerable interest because they display a range of stereochemistries from square planar to pseudo-tetrahedral in the solid state [10–13]. It has been proposed that the extent of distortion from square-planar geometry in those molecules results from the size of the substituent at the coordinating nitrogen [11], electronic effects [12], and crystal-packing forces [13, 14]. For example, pseudo-tetrahedral distortion in the solid-state structures of some

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copper(II) complexes with tetradentate thiolate Schiff bases (N_2S_2) depends on the backbone flexibility and as the backbone becomes more flexible, distortion grows [15].

Urease (urea amidohydrolase; E.C.3.5.1.5) catalyzes the rapid hydrolysis of urea in algae, bacteria, fungi, and plants, which causes negative side effects in health such as kidney stones, pyelonephritis, peptic ulcers [16], and in agriculture such as the efficiency of soil nitrogen fertilization, root damage and ammonia volatilization [17]. It is important to find excellent urease inhibitors [18]. Some transition metal complexes (M = Cu, Co, Ni, etc.) with potent inhibitory activities against urease have been reported by our group [19]. Mononuclear copper(II) complexes show better inhibitory activities. In this article, we report two new Schiff-base copper(II) complexes, bis(N-*n*-butyl-5-chlorosalicylaldiminato) copper(II) (**1**) and bis(N-*n*-butyl-4-methoxysalicylaldiminato) copper(II) (**2**). A preliminary docking study using the DOCK program was performed to model the inhibitory activity of these Schiff-base copper complexes against jack bean urease.

2. Results and discussion

2.1. *Synthesis*

The Schiff bases in this article were prepared by the reaction of *n*-butylamine with 5-chlorosalicylaldehyde and 4-methoxysalicylaldehyde in 75–89% yield in methanol. These ligands are yellow crystallite, stable compounds in air at room temperature, soluble in common polar organic solvents, such as MeCN, MeOH, and EtOH. Complexes **1** and **2** were obtained from the reaction of the Schiff bases with $Cu(NO_3)_2 \cdot 3H_2O$ in methanol. The elemental analyses are in agreement with the chemical formulae for **1** and **2**.

2.2. *Crystal structure description*

The Schiff bases of **1** and **2** were obtained from condensation of *n*-butylamine with 5-chlorosalicylaldehyde and 4-methoxysalicylaldehyde, respectively. Single-crystal X-ray diffraction reveals that bis(N-*n*-butyl-5-chlorosalicylaldiminato) copper(II) (**1**) crystallizes in the triclinic space group *P*-1. The solid-state structure of **1** is shown in figure 1. The [CuO_2N_2] unit of **1** is slightly distorted from square planar toward tetrahedral geometry. The dihedral angle between two planes O1–Cu1–N1 and O2–Cu1–N2 of **1** is 10.0(2)°. Dihedral angles of 0° and 90° would be expected for planar and tetrahedral geometries, respectively [20, 21]. The deviation may result from weak Cu1 $\cdots$ O2# interactions [2.693(4) Å] between adjacent molecules (symmetry code: # $1-x$, $1-y$, $2-z$), constructing a dinuclear copper unit. These units further form a 3-D network *via* intermolecular Cl2 $\cdots$ Cu1# interactions [3.573(7) Å] as shown in figure 2 (symmetry code: # $1-x$, $-y$, $2-z$). Analogous square-planar copper(II) species were previously reported [22].

In contrast to **1**, bis(N-*n*-butyl-5-methoxysalicylaldiminato) copper(II) (**2**) crystallizes in the monoclinic system, with space group $P2_1/c$. The crystal structure of **2** is shown in figure 3. In **2**, the copper(II) is four-coordinate by two imino nitrogen atoms and two phenolic oxygen atoms from two bidentate Schiff-base ligands in the usual *trans*

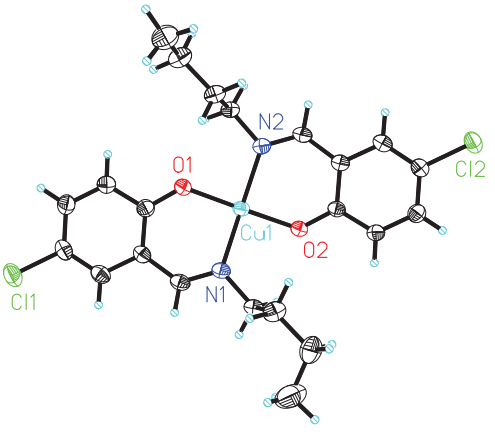

Figure 1. An ORTEP diagram showing molecular structure of **1**. Thermal ellipsoids are shown at 30% probability level.

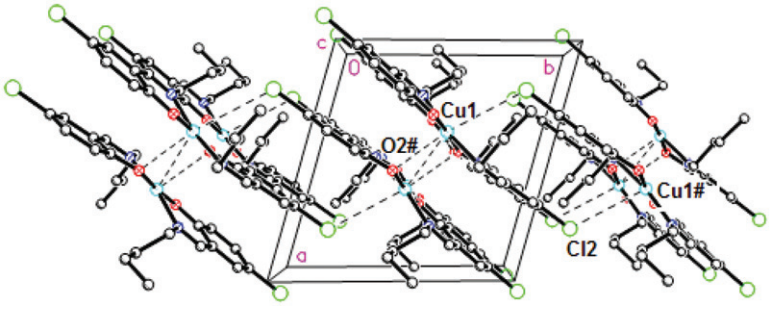

Figure 2. Molecular packing of **1** viewed along the *c*-axis of the unit cell.

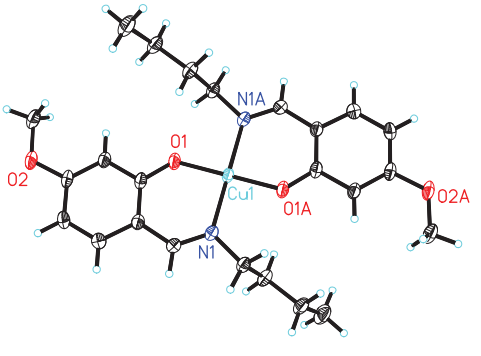

Figure 3. An ORTEP diagram showing molecular structure of **2** (symmetry code: A $1-x, -y, -z$). Thermal ellipsoids are shown at 30% probability level.

arrangement. The copper(II) of **2** lies on a center-of-inversion to offer a square-planar geometry (symmetry code: $1-x, -y, -z$) and axial positions are vacant. Analogous square-planar copper(II) species were previously reported [23, 24]. Adjacent molecules

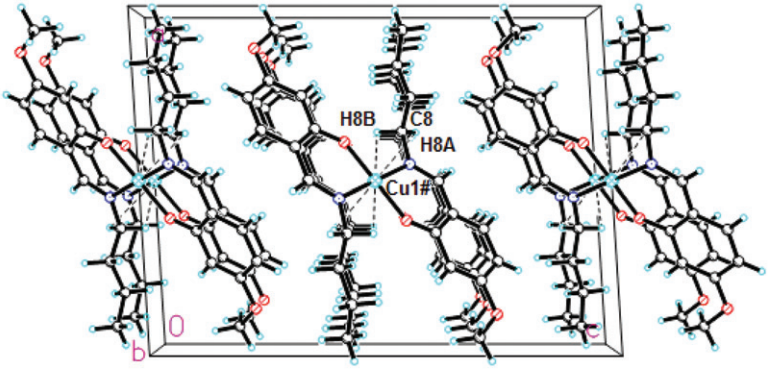

Figure 4. Molecular packing of **2** viewed along the *b*-axis of the unit cell.

Table 1. Crystal data for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{22}H_{26}Cl_2CuN_2O_2$	$C_{24}H_{32}CuN_2O_4$
Molecular weight	484.89	476.06
Temperature (K)	291(2)	291(2)
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	$P2_1/c$
Unit cell dimensions (Å, °)		
a	10.0896(13)	13.251(3)
b	10.1001(14)	4.8850(13)
c	11.5270(15)	17.858(5)
α	96.858(2)	90.00
β	91.112(2)	93.558(4)
γ	105.658(2)	90.00
Volume (Å^3), *Z*	1121.3(3), 2	1153.7(5), 2
Calculated density (g cm^{-3})	1.436	1.370
F(000)	502	502
μ(Mo-Kα) (mm^{-1})	1.232	0.979
Data/restraint/parameters	4347/0/264	2856/0/144
Goodness-of-fit on F^2	1.006	1.004
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0487, 0.1064	0.0533, 0.1385

of **2** were connected through intermolecular C8–H8A $\cdots$ Cu1# [3.046(2) Å] and C8–H8B $\cdots$ Cu1# bonds [3.040(2) Å] as shown in figure 4 (symmetry code: # x, $1+y$, z).

Table 1 summarizes the unit-cell parameters and details of data collection for the crystallographic studies of **1** and **2**. Selected bond lengths and angles from **1** are presented in comparison with those for **2** in table 2. The differences in bond length of E–Cu (E = O, N) and the angles subtended at copper(II) in **1** and **2** are small, suggesting that steric and electronic effects between the 5-chloro group and 4-methoxy group are slightly different. These results indicate that crystal-packing forces play a key role in determining conformational detail of such copper(II) species [25].

2.3. *Inhibitory activity against Jack bean urease*

Two Schiff bases derived from 5-chlorosalicylaldehyde and 4-methoxysalicylaldehyde and the corresponding copper(II) complexes **1** and **2** were screened for inhibitory

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1			
Cu1–O1	1.892(3)	O1–Cu1–N1	91.55(11)
Cu1–O2	1.910(2)	O1–Cu1–N2	87.77(11)
Cu1–N1	2.005(3)	O1–Cu1–O2	175.77(11)
Cu1–N2	2.016(3)	O2–Cu1–N1	90.26(10)
N1–C7	1.286(4)	O2–Cu1–N2	91.05(10)
N2–C18	1.285(4)	N1–Cu1–N2	170.66(10)
2			
Cu1–O1	1.8793(16)	O1–Cu1–N1	91.75(8)
Cu1–O1#a	1.8793(16)	O1#a–Cu1–N1#a	91.75(8)
Cu1–N1	2.0063(19)	O1#a–Cu1–O1	180.00(16)
Cu1–N1#a	2.0063(19)	O1–Cu1–N1#a	88.25(8)
N1–C7	1.290(3)	O1#a–Cu1–N1	88.25(8)
N1#a–C7#a	1.290(3)	N1–Cu1–N1	180.00(11)

Symmetry code: #a: $1-x, -y, -z$.

activity against jack bean urease. The Schiff bases exhibit no ability to inhibit the urease ($IC_{50} = 100\,\mu mol\,L^{-1}$). Compared with the standard inhibitor acetohydroxamic acid (AHA, $IC_{50} = 63.00\,\mu mol\,L^{-1}$), **1** and **2** display potent inhibitory activity against jack bean urease ($IC_{50} = 2.7$ and $3.5\,\mu mol\,L^{-1}$). Generally, heavy metal ions are believed to inhibit urease by binding to the sulfhydryl groups of cysteines, and possibly nitrogen- (histidine) and oxygen- (aspartic and glutamic acids) in the urease active site [26]. Thus it can be seen that coordination to copper(II) ion improved inhibitory activity [27]. Complex **1** derived from 5-chlorosalicylaldehyde is slightly more potent than **2**. This defines the minimal substitution patterns in the aromatic ring for obtaining inhibitory activity against jack bean urease.

2.4. *Molecular docking study*

As shown in figure 5(a) and (b), the binding models of **1** and **2** with jack bean urease were simulated using the Dock program to validate their structure–activity relationships [28–31]. The complex molecules were well-filled in the active pocket of the urease. Additional interactions have been established in a variety of conformations because of the flexibilities of the chelating phenolic oxygen atom and the amino acid residues of the urease. The small cluster (20 occurrences) was ranked by energy level in the best position of the complex-urease modeled molecules where the binding energy of the amino acid residues and **1** and **2** are $-5.15\,kcalmol^{-1}$ and $-4.97\,kcalmol^{-1}$, respectively. The phenol of **1** forms weak O···O interactions with the carboxylate of Asp494 (Asp494 $O\cdots O1_{complex\text{-}\mathbf{1}} = 2.997(2)$ Å) in the complex-urease modeled **1** (figure 5a). In contrast, weak O···O interactions exist between the methoxyl of **2** and the carboxylate of Asp494 (Asp494 $O\cdots O2\#_{complex\text{-}\mathbf{2}} = 2.856(2)$ Å) (symmetry code: # $1-x, -y, -z$). One hydrogen-bonding interaction forms between NH of MET637 and OMe of the complex (figure 5b). The hydrogen-bonding distance and angle of MET637 N–$H\cdots O2_{complex\text{-}\mathbf{2}}$ are 3.063(2) Å and 161.9(2)°, respectively. The results of molecular docking provide an understanding of the present inhibitory activity of the two Schiff-base copper complexes against jack bean urease.

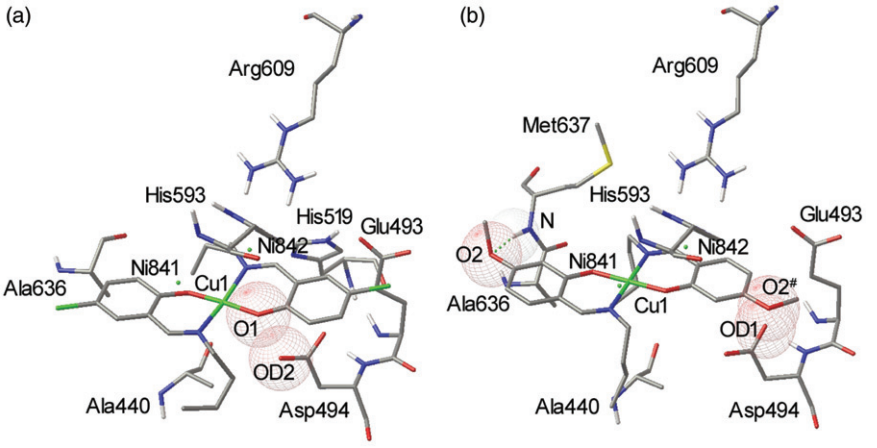

Figure 5. Molecular-binding model of **1** (a) and **2** (b) with the active site of jack bean urease. Hydrogen bonds are presented as green dotted lines. Available in color online.

3. Experimental

3.1. *Materials and measurements*

Urease (from jack beans, type III, activity 22 units/mg solid), HEPES (Ultra) buffer, and urea (Molecular Biology Reagent) were from Sigma. 5-Chlorosalicylaldehyde and 4-methoxysalicylaldehyde were purchased from Aldrich and used without purification. Elemental analyses for C, H, and N were carried out on a Perkin-Elmer 2400 analyzer. IR spectra of solid samples were recorded using KBr pellets on a Nexus 870 FT-IR spectrophotometer between 4000 and 400 cm^{-1}.

3.2. *Complexes synthesis*

3.2.1. Synthesis of bis(N-*n*-butyl-5-chlorosalicylaldiminato) copper(II) (1). 5-Chlorosalicylaldehyde (313 mg, 2 mmol) and *n*-butylamine (146 mg, 2 mmol) were dissolved in methanol (25 mL). The mixture was stirred for 30 min to give an orange solution, which was added to a methanol solution (10 mL) of $Cu(NO_3)_2 \cdot 3H_2O$ (241 mg, 1 mmol). The mixture was stirred for another 15 min at room temperature to give a yellow-green solution and then filtered. The filtrate was kept in air for 7 days, black block crystals were formed. The crystals were isolated, washed three times with distilled water, and dried in a vacuum desiccator containing anhydrous $CaCl_2$. Yield: 75%. Anal. Calcd for $C_{22}H_{26}Cl_2CuN_2O_2$: C, 54.49; H, 5.40; N, 5.78. Found (%): C, 54.40; H, 5.52; N, 5.71. IR data (KBr, cm^{-1}): 3447, 2960, 2920, 2855, 1626, 1532, 1465, 1387, 1314, 1180, 1109, 818, 720, 658, 466, 427.

3.2.2. Synthesis of bis(N-*n*-butyl-4-methoxysalicylaldiminato) copper(II) (2). 4-Methoxysalicylaldehyde (304 mg, 2 mmol) and *n*-butylamine (146 mg, 2 mmol) were dissolved in methanol (25 mL). The mixture was stirred for 30 min to give an orange solution, which was added to a methanol solution (2 mL) of $Cu(NO_3)_2 \cdot 3H_2O$ (241 mg, 1 mmol).

The mixture was stirred for another 15 min at room temperature to give a yellow-green solution and then filtered. The filtrate was kept in air for 7 days, black block crystals were formed. The crystals were isolated, washed three times with distilled water, and dried in a vacuum desiccator containing anhydrous $CaCl_2$. Yield: 77%. Anal. Calcd for $C_{24}H_{32}CuN_2O_4$: C, 60.55; H, 6.77; N, 5.88. Found (%): C, 60.39; H, 6.88; N, 5.89. IR data (KBr, cm^{-1}): 3464, 2958, 2933, 2856, 1625, 1537, 1450, 1402, 1026, 833, 788, 507, 455.

3.3. *Crystal structure determinations*

X-ray crystallographic data [32] were collected on a Bruker SMART Apex II CCD diffractometer using graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation. The collected data were reduced using SAINT and empirical absorption corrections were performed using SADABS. The structures were solved by direct methods and refined against F^2 by full-matrix least squares using SHELXTL version 5.1. All of the non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed geometrically in ideal positions and constrained to ride on their parent atoms. The crystallographic data for **1** and **2** are summarized in table 1. Selected bond lengths and angles are given in table 2.

3.4. *Measurement of jack bean urease inhibitory activity*

The measurement of urease was carried out according to the procedure reported by Tanaka [33]. Generally, the assay mixture, containing 25 µL of jack bean urease (12 kU L^{-1}) and 25 µL of the tested complexes of different concentrations (dissolved in DMSO : H_2O = 1 : 1 (v/v)), was preincubated for 1 h at 37°C in a 96-well assay plate. After preincubation, 200 µL of 100 mmolL^{-1} HEPES (N-[2-hydroxy-ethyl] piperazine-N′-[2-ethanesulfonic acid]) buffer [34] pH = 6.8 containing 500 mmolL^{-1} urea and 0.002% phenol red were added and incubated at 37°C. The reaction time was measured by microplate reader (570 nm), which was required to produce enough ammonium carbonate to raise the pH of HEPES buffer from 6.8 to 7.7, the end-point being determined by the color of phenol red indicator [35].

3.5. *Docking simulations*

Molecular docking of the inhibitor with the three-dimensional structure of jack bean urease (entry 3LA4 in the Protein Data Bank) was carried out using the DOCK 4.2 program suite [28–31]. The graphical user interface AutoDockTools (ADT 1.4.5) was performed to setup every inhibitor–enzyme interaction, where all hydrogen atoms were added, Gasteiger charges were calculated and non-polar hydrogen atoms were merged to carbon atoms. The Ni initial parameters are set as $r = 1.170$ Å, $q = +2.0$, and van der Waals well depth of 0.100 kcal mol^{-1}. As performed by the graphical user interface AutoDockTools, the catalytic center and the peripheral anionic site of the target protein were scanned to evaluate the modeled binding mode of the inhibitor–urease complex. The flexible docking of the ligand structures was done by the Lamarckian genetic

algorithm (LGA), searching for favorable bonding conformations of the ligands at the sites of the target protein.

4. Conclusion

This report describes the synthesis, crystal structures, and urease inhibitory activity of two Schiff-base copper complexes, bis(N-*n*-butyl-5-chlorosalicylaldiminato) copper(II) (**1**) and bis(N-*n*-butyl-4-methoxysalicylaldiminato) copper(II) (**2**). The geometry and extent of distortion in the solid state of these complexes have been interpreted from steric considerations and complemented with the help of electronic effects. On the basis of the experimentally tested activity of **1** and **2** against jack bean urease, the preliminary results of a molecular docking study provide hints on the structure–activity relationship of such Schiff-base copper species.

Supplementary material

CCDC Nos 761919 and 761920 contain the supplementary crystallographic data for **1** and **2**. 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.

Acknowledgments

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