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Hydrogen Bonding Influenced Coordination Mode of Azide Ligand in Schiff Base Copper(II) Complexes: Synthesis, Crystal Structures, and Antibacterial Activity

D. L. Peng[a, b, *]

[a] *Key Laboratory of Surface and Interface Science of Henan Province, School of Material and Chemical Engineering, Zhengzhou University of Light Industry, Zhengzhou, 450001 P.R. China*

[b] *Henan Collaborative Innovation Center of Environmental Pollution Control and Ecological Restoration, Zhengzhou University of Light Industry, Zhengzhou, 450001 P.R. China*

**e-mail: pengdonglai2015@sina.com*

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Abstract—Two copper(II) complexes, [CuL^{1}N$_3$] (**I**) and [CuL^2($\mu_{1,1}$-N$_3$)] (**II**), where L^1 = 2-[(2-diethylaminoethylimino)methyl]-4,6-difluorophenolate, L^2 = 2,4-difluoro-6-[(2-isopropylaminoethylimino)-methyl]phenolate, have been prepared and structurally characterized by elemental analyses, IR and UV-Vis spectra, as well as single crystal X-ray determination (CIF files CCDC nos. 1848289 (**I**) and 1848290 (**II**)). In complex **I**, the Cu atom is in square planar coordination, with the azide ligand in terminal coordination mode. In complex **II**, the Cu atom is in square pyramidal coordination, with the azide ligand in end-on bridging mode. The crystals are stabilized by hydrogen bonds, which influence the coordination mode of the azide ligand. The complexes have strong antibacterial activity against *B. subtilis* and *S. aureus*.

Keywords: Schiff base, copper complex, hydrogen bonds, crystal structure, antibacterial activity

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INTRODUCTION

The rational design and preparation of polymeric structures have attracted remarkable attention in coordination chemistry to develop new and functional molecular-based materials [1–3]. Among the complexes, copper-azido system is one of the most popular among synthetic chemists. A variety of copper-azido complexes with discrete or one-, two-, and three-dimensional polymeric structures have been reported, in which the azido ligand exhibits diverse bridging modes ranging from $\mu_{1,1}$ (end-on, EO) and $\mu_{1,3}$ (end-to-end, EE) to $\mu_{1,1,1}$, $\mu_{1,1,3}$, $\mu_{1,1,1,1}$, $\mu_{1,1,3,3}$, and $\mu_{1,1,1,3,3,3}$, depending upon the steric and electronic demands of the co-ligands [4–8]. Schiff bases derived from salicylaldehyde and its derivatives usually possess two or more donor atoms, which can chelate to transition metal atoms to form a variety of complexes [9–12]. Metal complexes with Schiff base ligands have attracted much attention in the fields of magnetic, catalytic, as well as biological materials [13–19]. Herein, we report the synthesis, characterization, and self-assembly of two new copper(II) complexes, [CuL^{1}N$_3$] (**I**) and [CuL^2($\mu_{1,1}$-N$_3$)] (**II**), where L^1 = 2-[(2-diethylaminoethylimino)methyl]-4,6-difluorophenolate, L^2 = 2,4-difluoro-6-[(2-isopropylaminoethylimino)methyl]phenolate.

EXPERIMENTAL

Materials and methods. All the reagents and solvents used in the synthesis were procured commercially and used without subsequent purification. Microanalyses (C, H, N) were performed using a Perkin-Elmer 2400 elemental analyzer. Infrared spectra were measured on KBr disks with a Hitachi I-5040 FT-IR spectrophotometer. Electronic spectra were measured with a Lambda 35 spectrophotometer. Single crystal X-ray data were collected on a Bruker SMART APEX II diffractometer.

Synthesis of complex I. A methanol solution (10 mL) of copper(II) acetate monohydrate (0.1 mmol, 19.9 mg) was added to the methanol solution (10 mL) of HL^1 (0.1 mmol, 25.6 mg) and NaN$_3$ (0.1 mmol, 6.5 mg). The reaction mixture was magnetic stirred for 1 h at ambient temperature to give brown solution. Single crystals suitable for X-ray diffraction were obtained from the filtrate by slow evaporation in a refrigerator. The yield was 210 mg (56%).

IR data (KBr; ν, cm^{-1}): 2051 (N$_3$), 1639 (CH=N), 1450, 1358, 1260, 1159, 1077, 949, 859, 540, 525. Electronic spectra (methanol; λ_{max}, nm (ε_{max}, L mol^{-1} cm^{-1})): 270 (19,150), 375 (8,532).

For $C_{13}H_{17}F_2N_5OCu$

Anal. calcd., %	C, 43.27	H, 4.75	N, 19.41
Found, %	C, 43.10	H, 4.83	N, 19.26

Synthesis of complex II. A methanol solution (10 mL) of copper(II) acetate monohydrate (0.1 mmol, 19.9 mg) was added to the methanol solution (10 mL) of HL^2 (0.1 mmol, 24.2 mg) and NaN_3 (0.1 mmol, 6.5 mg). The reaction mixture was magnetic stirred for 1 h at ambient temperature to give brown solution. Single crystals suitable for X-ray diffraction were obtained from the filtrate by slow evaporation in a refrigerator. The yield was 183 mg (52%).

IR data (KBr; ν, cm^{-1}): 3289 (NH), 2048 (N_3), 1641 (CH=N), 1447, 1259, 1155, 1083, 948, 854, 537. Electronic spectra (methanol; λ_{max}, nm ($\varepsilon_{max,}$ L mol^{-1} cm^{-1})): 270 (20,270), 375 (8,785).

For $C_{12}H_{15}F_2N_5OCu$

Anal. calcd., %	C, 41.56	H, 4.36	N, 20.19
Found, %	C, 41.71	H, 4.45	N, 20.02

X-ray crystallography. Data collection for the complexes was performed with a Bruker Apex II CCD diffractometer at 298 K. The structures were solved by direct methods with SHELXS-97 and refined by full-matrix least squares (SHELXL-97) on F^2 [20]. All non-hydrogen atoms were refined anisotropically. The amino H atom of complex **II** was located from electronic density map and refined isotropically with N–H distance restrained to 0.90 Å. The remaining hydrogen atoms were placed geometrically and refined with a riding model, with isotropic displacement coefficients $U(\mathrm{H}) = 1.2\ U(\mathrm{C})$ or $1.5\ U(\mathrm{C_{methyl}})$. Crystallographic data for complexes **I** and **II** are summarized in Table 1. Selected bond lengths and angles are listed in Table 2, hydrogen bond distances and bond angles are given in Table 3.

Supplementary material for structures has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1848289 (**I**) and 1848290 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Antibacterial activity. The antibacterial activities were tested against *B. subtilis* ATCC 6633, *E. coli* ATCC 35218, *P. putida* TS 1138 and *S. aureus* ATCC 25923 using MH medium (Mueller–Hinton medium: casein hydrolysate 17.5 g, soluble starch 1.5 g, beef extract 1000 mL). The MICs (minimum inhibitory concentrations) of the test compounds were determined by a colorimetric method using the dye MTT [3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide]. A stock solution of the synthesized compound (50 µg mL^{-1}) in DMSO was prepared and quantities of the test compounds were incorporated in specified quantity of sterilized liquid MH medium. A specified quantity of the medium containing the compound was poured into microtitration plates. A suspension of the microorganism was prepared to contain approximately 10^5 cfu mL^{-1} and applied to microtitration plates with serially diluted compounds in DMSO to be tested and incubated at 37°C for 24 h. After the MICs were visually determined on each of the micro-titration plates, 50 µL of PBS (phosphate buffered saline 0.01 mol L^{-1}, pH 7.4: Na_2HPO_4 2.9 g, KH_2PO_4 0.2 g, NaCl 8.0 g, KCl 0.2 g, distilled water 1000 mL) containing 2 mg of MTT per mL^{-1} was added to each well. Incubation was continued at room temperature for 4–5 h. 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 550 nm.

RESULTS AND DISCUSSION

The complexes were prepared by reaction of equimolar quantities of the Schiff base ligands with copper acetate and sodium azide in methanol. Crystals of the complexes are stable in air, and soluble in methanol, ethanol, DMF and DMSO, insoluble in water. The molar conductance of the complexes is 23 Ω^{-1} cm^2 mol^{-1} for **I** and 15 Ω^{-1} cm^2 mol^{-1} for II, indicating that the complexes are non-electrolytes.

Complex **I** is a mononuclear copper(II) compound, with the azide ligand in a terminal coordination mode (Fig. 1a). The Cu atom is coordinated by the phenolate oxygen, imino nitrogen and amino nitrogen of the Schiff base ligand L^1, and azido nitrogen, forming square planar geometry. The Cu–O and Cu–N bond lengths in the complex are comparable to those reported for Schiff base copper(II) complexes [21–23].

Complex **II** is an end-on azido-bridged polynuclear copper(II) compound with the azide ligand in $\mu_{1,1}$-bridging coordination mode (Fig. 1b). The Cu atom is coordinated by the phenolate oxygen, imino nitrogen and amino nitrogen of the Schiff base ligand L^2, and two azido nitrogen, forming square pyramidal geometry. The Cu– and Cu–N bond lengths in the complex are similar to those of complex **I**, and also comparable to those reported for Schiff base copper(II) complexes [21–23]. There is a N–H···N hydrogen bond in the molecule, which might contribute to the formation of polynuclear complex with bridging azide groups.

The crystal packing structures of complexes **I** and **II** are shown as Fig. 2. In the packing structure of **I**, molecules are running along the *y* axis with C–H···F

Table 1. Crystallographic data and structure refinement for complex **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	360.86	346.83
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/c$
a, Å	6.9264(7)	20.887(3)
b, Å	13.873(1)	9.504(1)
c, Å	31.215(2)	7.253(1)
β, deg		93.96(1)
V, Å^3	2999.5(4)	1436.4(3)
Z	8	4
ρ_{calcd}, g cm^{-3}	1.598	1.604
Crystal size, mm	0.27 × 0.23 × 0.23	0.17 × 0.13 × 0.13
$\mu(MoK_\alpha)$, mm^{-1}	1.487	1.549
Minimum and maximum transmission	0.6897 and 0.7261	0.7787 and 0.8240
$F(000)$	1480	708
$\lambda(MoK_\alpha)$	0.71073	0.71073
Scan mode	ω	
Number of reflections	11171	7740
Unique reflections	2799	2684
R_{int}	0.0694	0.0553
Observed reflections ($I > 2\sigma(I)$)	2287	1544
Parameters	201	192
Restraints	0	1
Goodness of fit on F^2	1.280	1.034
R_1, wR_2 ($I > 2\sigma(I)$)	0.0750, 0.1961	0.0611, 0.1306
R_1, wR_2 (all data)	0.0875, 0.2023	0.1165, 0.1647

Table 2. Selected bond lengths (Å) and angles (deg) for complexes **I** and **II***

Bond	*d*, Å	Bond	*d*, Å
		I	
Cu(1)–O(1)	1.898(5)	Cu(1)–N(1)	1.941(5)
Cu(1)–N(2)	2.076(6)	Cu(1)–N(3)	1.947(7)
		II	
Cu(1)–O(1)	1.921(4)	Cu(1)–N(1)	1.942(5)
Cu(1)–N(2)	2.054(4)	Cu(1)–N(3)	1.981(5)
Cu(1)–N(3*A*)	2.751(5)		
Angle	**ω, deg**	**Angle**	**ω, deg**
		I	
O(1)Cu(1)N(1)	93.6(2)	O(1)Cu(1)N(3)	93.7(2)
N(1)Cu(1)N(3)	169.1(3)	O(1)Cu(1)N(2)	170.8(2)
N(1)Cu(1)N(2)	84.4(2)	N(3)Cu(1)N(2)	89.7(3)
		II	
O(1)Cu(1)N(1)	93.07(19)	O(1)Cu(1)N(3)	90.2(2)
N(1)Cu(1)N(3)	165.4(2)	O(1)Cu(1)N(2)	177.74(18)
N(1)Cu(1)N(2)	84.9(2)	N(3)Cu(1)N(2)	92.0(2)
N(1)Cu(1)N(3*A*)	87.2(2)	N(2)Cu(1)N(3*A*)	96.6(2)
N(4)Cu(1)N(3*A*)	91.0(2)	O(1)Cu(1)N(3*A*)	82.4(2)

* Symmetry code for *A*: *x*, 3/2 – *y*, –1/2 + *z*.

Table 3. Hydrogen bond distances (Å) and bond angles (deg) for complexes **I** and **II***

D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
		I		
C(7)–H(7)···F(1)$^{\#1}$	0.93	2.48	3.3207(3)	150
C(8)–H(8*B*)···N(5)$^{\#2}$	0.97	2.61	3.5462(4)	163
C(10)–H(10*A*)···N(5)$^{\#2}$	0.97	2.55	3.4564(3)	155
		II		
N(2)–H(2)···N(5)$^{\#3}$	0.91	2.36	3.194(7)	153

* Symmetry codes: $^{\#1}$ 1/2 – *x*, 1/2 + *y*, *z*; $^{\#2}$ –1/2 – *x*, 1/2 + *y*, *z* ; $^{\#3}$ *x*, 3/2 – *y*, 1/2 + *z*.

and C–H···N hydrogen bonds. In the packing structure of **II**, molecules are running along the *z* axis with N–H···N hydrogen bonds.

In the infrared spectra of the complexes, the bands corresponding to the azomethine (CH=N) groups are observed at 1639 cm^{-1} for **I** and 1641 cm^{-1} for **II** [24]. The typical absorptions for the azide ligands are located at 2051 cm^{-1} for **I** and 2048 cm^{-1} for **II**. The electronic spectra of the complexes were recorded

Table 4. MIC (μg mL^{-1}) values of the antibacterial activity of the complexes

Compound	*B. subtilis*	*E. coli*	*P. putida*	*S. aureus*
I	1.56	6.25	25.0	0.39
II	1.56	6.25	25.0	0.39
Penicillin	0.78	>100	12.5	3.13

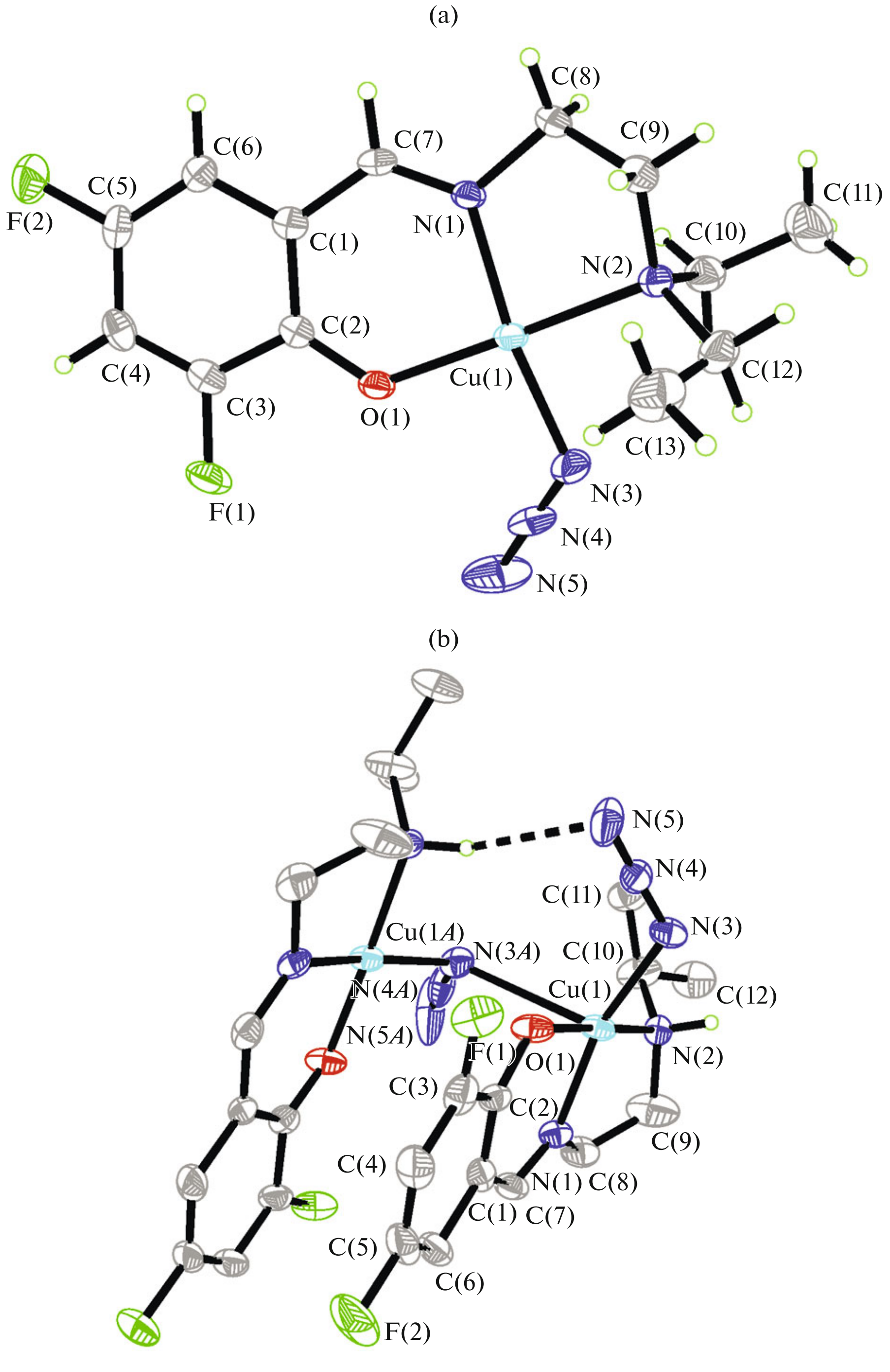

Fig. 1. Molecular structures of complexes **I** (a) and **II** (b). Atoms labeled with the suffix *A* are at the symmetry position: *x*, 3/2 – *y*, –1/2 + *z*.

using the methanol as solvent. The absorptions appear in the range 270–380 nm are most likely due to the $\pi \rightarrow \pi^*$ transitions and ligand-to-metal charge transfer.

The complexes were screened for antibacterial activity against *B. subtilis* ATCC 6633, *E. coli* ATCC 35218, *P. putida* TS 1138 and *S. aureus* ATCC 25923 by the MTT method. The MIC values of the complexes against these bacteria are presented in Table 4. The antibiotic Penicillin was included as a reference. In general, the two copper complexes have the same activities against the bacteria. It is interesting that for *S. aureus*, the complexes are most active with MIC value of 0.39 μg mL^{-1}. As for *B. subtilis*, the complexes also have strong activity. So, the complexes showed a wide range of bactericidal activities against the bacte-

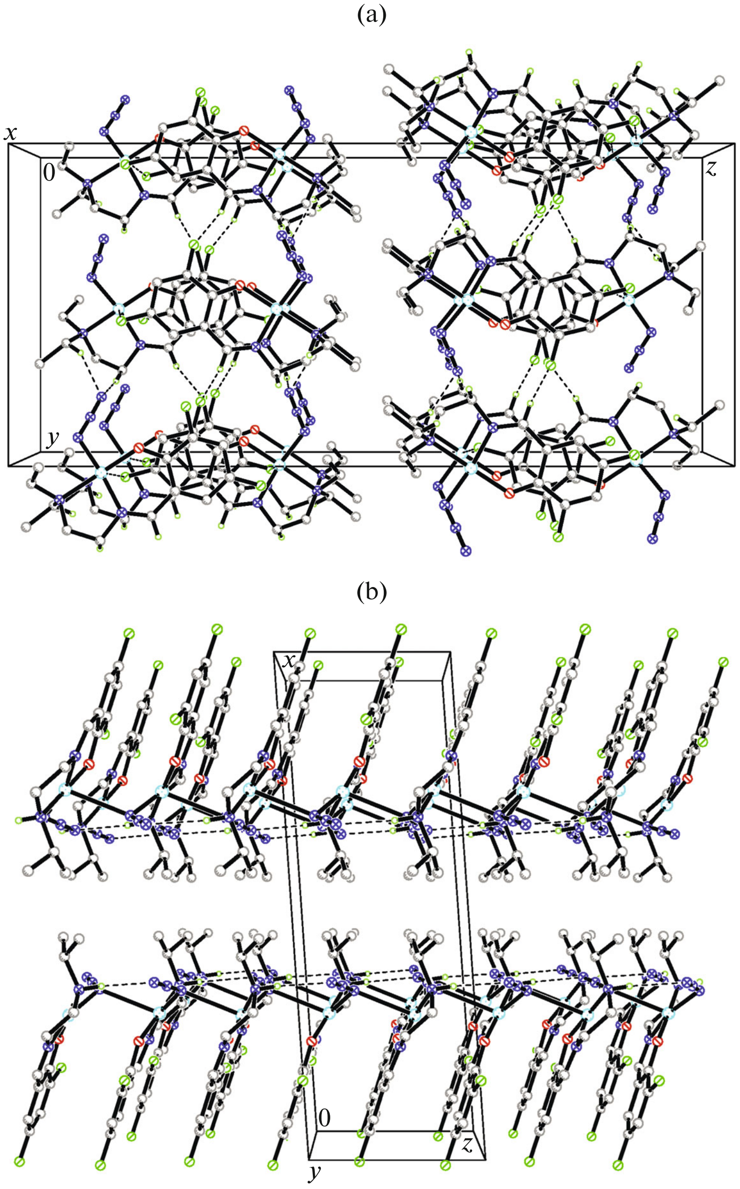

Fig. 2. Molecular packing structures of complexes **I** (a) and **II** (b). Hydrogen bonds are shown as dashed lines.

ria, more potent than, or similar with commercial antibiotic Penicillin.

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