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Synthesis and Crystal Structures of Two Azido-Bridged Copper(II) Complexes with Schiff Bases[1]

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Abstract—Two new end-on azido-bridged dinuclear copper(II) complexes with the formula $[Cu(\mu_{1,1}\text{-}N_3)_2(IEP)_2]$ (**I**) and $[Cu(\mu_{1,1}\text{-}N_3)_2(EMP)_2]$ (**II**), where IEP and EMP are the deprotonated forms of 2-[1-(2-isopropylaminoethylimino)ethyl]phenol and 2-ethoxy-6-[(2-methylaminoethylimino)methyl]phenol, respectively, were synthesized. Both complexes were characterized by elemental analyses and IR spectra. The crystal structures were determined by the X-ray diffraction. The crystal of **I** is monoclinic: space group $P2_1/c$, $a = 9.662(2)$, $b = 15.282(3)$, $c = 10.639(2)$ Å, $\beta = 115.418(10)°$, $V = 1418.9(5)$ Å^3, $Z = 2$. The crystal of **II** is monoclinic: space group $P2_1/n$, $a = 12.588(2)$, $b = 7.705(1)$, $c = 14.481(2)$, $\beta = 91.736(5)°$, $V = 1403.9(2)$ Å^3, $Z = 2$. The two Cu atoms in each complex are bridged by two end-on azide groups. Each Cu atom is in a square pyramidal coordination. The Cu···Cu distances are 3.230(2) Å in **I** and 3.150(2) Å in **II**.

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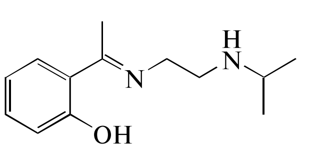
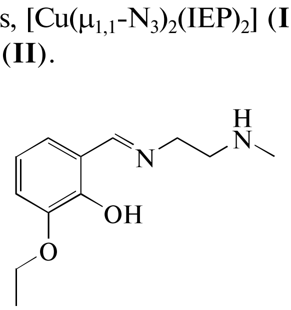
INTRODUCTION

Polynuclear complexes are of great interest in many fields [1–3]. The main strategy for designing the polynuclear complexes is to use suitable bridging groups. Azide is a versatile bridging group, which can bind two and more metal atoms in the $\mu_{1,1}$ (end-on), $\mu_{1,3}$ (end-to-end), $\mu_{1,1,1}$, $\mu_{1,1,3}$, and many other modes, yielding various polynuclear complexes [4–7]. Multidentate Schiff bases have been widely used in the preparation of metal complexes [7–9]. In the present work, two new Schiff bases, 2-[1-(2-isopropylaminoethylimino)ethyl]phenol (**HIEP**) and 2-ethoxy-6-[(2-methylaminoethylimino)methyl]phenol (**HEMP**), were synthesized. To our knowledge, no metal complexes derived from HIEP and HEMP have been reported so far. We synthesized and characterized two end-on azido-bridged dinuclear copper(II) complexes, $[Cu(\mu_{1,1}\text{-}N_3)_2(IEP)_2]$ (**I**) and $[Cu(\mu_{1,1}\text{-}N_3)_2(EMP)_2]$ (**II**).



HIEP



HEMP

EXPERIMENTAL

Materials and methods. Commercially available 2'-hydroxyacetophenone, 3-ethoxysalicylaldehyde, N-isopropylethylenediamine, and N-methylethylenediamine of AR grade were available from Alfa Aesar. Other solvents and reagents were made in China and used as obtained. C, H, and N elemental analyses were performed with a PerkinElmer 240C elemental analyzer. The IR spectra (KBr pellets) were measured with a FT-IR 170-SX (Nicolet) spectrophotometer.

Synthesis of HIEP. 2'-Hydroxyacetophenone (1.0 mmol, 0.136 g) and N-isopropylethylenediamine (1.0 mmol, 0.102 g) were mixed in a methanol solution (30 ml). The mixture was stirred for 30 min at reflux, and the solvent was evaporated to give a yellow oil of HIEP.

For $C_{13}H_{20}N_2O$

anal. calcd., %:	C, 70.9;	H, 9.2;	N, 12.7.
Found, %:	C, 70.5;	H, 9.3;	N, 12.5.

Synthesis of HEMP. 3-Ethoxysalicylaldehyde (1.0 mmol, 0.166 g) and N-methylethylenediamine (1.0 mmol, 0.074 g) were mixed in a methanol solution (30 ml). The mixture was stirred for 30 min at reflux, and the solvent was evaporated to give yellow oil of HEMP.

For $C_{12}H_{18}N_2O_2$

anal. calcd., %:	C, 64.8;	H, 8.2;	N, 12.6.
Found, %:	C, 64.5;	H, 8.2;	N, 12.8.

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[1] The article is published in the original.

Table 1. Crystallographic and experiment data for the complexes **I** and **II***

Parameter	Value	
	I	**II**
M	649.7	653.7
Crystal size, mm	0.20 × 0.18 × 0.18	0.20 × 0.20 × 0.18
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a, Å	9.662(2)	12.588(1)
b, Å	15.282(3)	7.705(1)
c, Å	10.639(2)	14.481(2)
β, deg	115.418(10)	91.736(5)
V, Å^3	1418.9(5)	1403.9(2)
Z	2	2
μ_{Mo}, mm^{-1}	1.543	1.565
T_{min}	0.748	0.745
T_{max}	0.769	0.766
Reflections/parameters	7454/187	6642/186
Independent reflections	2809	2363
F(000)	676	676
Goodness-of-fit on F^2	0.977	0.967
R_1, wR_2 ($I \geq 2\sigma(I)$)*	0.0588, 0.1267	0.0471, 0.1036
R_1, wR_2 (all data)*	0.0986, 0.1513	0.0765, 0.1157

* $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \left[\Sigma w\left(F_o^2 - F_c^2\right)^2 \Big/ \Sigma w\left(F_o^2\right)^2\right]^{1/2}$.

Table 2. Coordinate bond lengths and bond angles for the complexes*

Bond	d, Å	Bond	d, Å
	I		
Cu(1)–O(1)	1.867(4)	Cu(1)–N(1)	1.955(4)
Cu(1)–N(3)	2.003(4)	Cu(1)–N(2)	2.022(5)
Cu(1)–N(3)^{i}	2.417(4)		
	II		
Cu(1)–O(1)	1.907(3)	Cu(1)–N(1)	1.931(4)
Cu(1)–N(3)	1.989(3)	Cu(1)–N(2)	2.051(4)
Cu(1)–N(3)^{ii}	2.510(4)		
Angle	ω, deg	Angle	ω, deg
	I		
O(1)Cu(1)N(1)	93.9(2)	O(1)Cu(1)N(3)	89.3(2)
N(1)Cu(1)N(3)	169.9(2)	O(1)Cu(1)N(2)	177.5(2)
N(1)Cu(1)N(2)	86.1(2)	N(3)Cu(1)N(2)	90.3(2)
O(1)Cu(1)N(3)^{i}	94.4(2)	N(1)Cu(1)N(3)^{i}	102.7(2)
N(3)Cu(1)N(3)^{i}	86.6(2)	N(2)Cu(1)N(3)^{i}	88.1(2)
	II		
O(1)Cu(1)N(1)	93.5(2)	O(1)Cu(1)N(3)	91.4(2)
N(1)Cu(1)N(3)	166.7(2)	O(1)Cu(1)N(2)	174.5(2)
N(1)Cu(1)N(2)	84.8(2)	N(3)Cu(1)N(2)	91.3(2)
O(1)Cu(1)N(3)^{ii}	88.9(2)	N(1)Cu(1)N(3)^{ii}	100.5(2)
N(3)Cu(1)N(3)^{ii}	91.9(2)	N(2)Cu(1)N(3)^{ii}	86.3(2)

* Symmetry codes: ^{i} 2 – x, – y, 2 – z; ^{ii} 1 – x, – y, – z.

Synthesis of [Cu($\mu_{1,1}$-N_3)$_2$(IEP)$_2$] (I). To a stirred methanolic solution (20 ml) of HIEP (0.5 mmol, 0.110 g) and sodium azide (0.5 mmol, 0.033 g) was added a methanolic solution (5 ml) of $Cu(ClO_4)_2 \cdot 7H_2O$ (0.5 mmol, 0.194 g). The mixture was stirred for 30 min at room temperature to give a deep blue solution. Blue block-shaped crystals of **I**, suitable for X-ray single-crystal analysis, were formed on the slow evaporation of the solvents for a week. The isolated crystals were washed three times with cold methanol and dried in a vacuum over anhydrous $CaCl_2$.

For $C_{26}H_{38}N_{10}O_2Cu_2$

anal. calcd., %:	C, 48.1;	H, 5.9;	N, 21.6.
Found, %:	C, 48.6;	H, 6.1;	N, 21.3.

Synthesis of [Cu($\mu_{1,1}$-N_3)$_2$(EMP)$_2$] (II). To a stirred methanolic solution (20 ml) of HEMP (0.5 mmol, 0.111 g) and sodium azide (0.5 mmol, 0.033 g) was added a methanolic solution (5 ml) of $Cu(ClO_4)_2 \cdot 7H_2O$ (0.5 mmol, 0.194 g). The mixture was stirred for 30 min at room temperature to give a deep blue solution. Blue block-shaped crystals of **II**, suitable for X-ray single-crystal analysis, were formed on the slow evaporation of the solvents for a week. The isolated crystals were washed three times with cold methanol and dried in a vacuum over anhydrous $CaCl_2$.

For $C_{24}H_{34}N_{10}O_4Cu_2$

anal. calcd., %:	C, 44.1;	H, 5.2;	N, 21.4.
Found, %:	C, 43.8;	H, 5.5;	N, 21.0.

X-ray structure determination. Diffraction intensities for the complexes were collected at 298(2) K using a Bruker SMART APEX II CCD area-detector with MoK_α radiation (λ = 0.71073 Å). The collected data were reduced using the SAINT program [10], and multiscan absorption corrections were performed using the SADABS program [11]. The structures were solved by direct methods and refined against F^2 by full-matrix least-squares methods using the SHELXTL package [12]. All of the non-hydrogen atoms were refined anisotropically. The amino H atoms in both complexes were located from difference Fourier maps and refined isotropically, with N–H distances restrained to 0.90 Å. Other H atoms in the complexes

Table 3. Geometric parameters of hydrogen bonds for complexes **I** and **II***

Contact D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
I				
N(2)–H(2)···O(1)^{i}	0.90	2.40(2)	3.282(5)	167(6)
II				
N(2)–H(2)···O(1)^{ii}	0.90	2.25(2)	3.084(4)	155(4)
N(2)–H(2)···O(2)^{ii}	0.90	2.58(4)	3.291(5)	137(4)

* Symmetry codes: ^{i} $2 - x, -y, 2 - z$; ^{ii} $1 - x, -y, -z$.

were placed in calculated positions and constrained to ride on their parent atoms. The crystallographic data for the complexes are summarized in Table 1. Selected bond lengths and angles are given in Table 2. Hydrogen bonds are listed in Table 3.

Crystallographic data for the two complexes have been deposited with the Cambridge Crystallographic Data Centre (nos. 768497 (I) and 768498 (II); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

To design and synthesize polynuclear structures of metal complexes, the selection of ligands and the bridging groups is important. We herein designed and synthesized two new Schiff base ligands, HIEP and HEMP. Both Schiff bases were readily synthesized with high yields and purity, which can chelate to the metal atoms through the phenolate O, imine N, and/or amine N atoms. The azide is used as a bridging group in the synthesis. Both complexes were readily synthesized under the similar synthetic procedure.

The Schiff bases are yellow oils. They can be diluted with methanol, ethanol, acetonitrile, and chloroform. The blue block-shaped crystals of the two complexes are stable in air at room temperature, soluble in methanol, ethanol, and acetonitrile and insoluble in water.

In the IR spectra of the Schiff bases, the weak absorption bands at about 3450 cm^{-1} are assigned to the stretching vibration of the hydroxy groups, which is absent in the complexes. The weak and sharp bands at about 3260 cm^{-1} are assigned to the N–H stretching

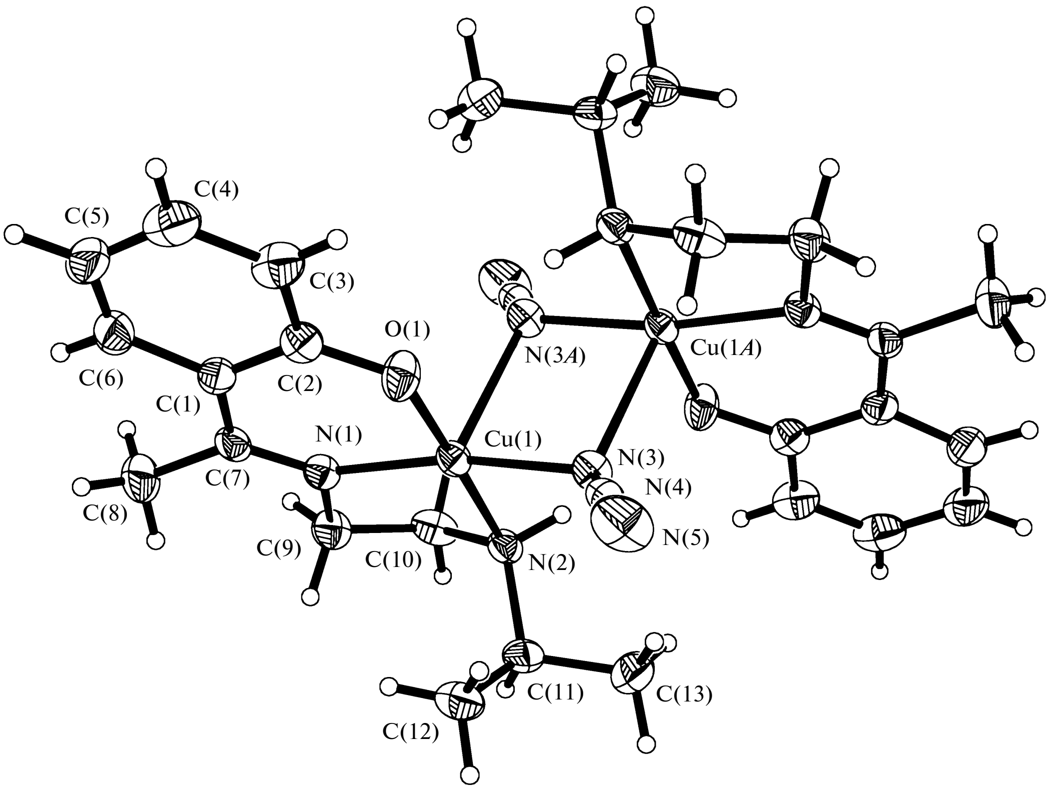

Fig. 1. Molecular structure of **I** at 30% ellipsoid.

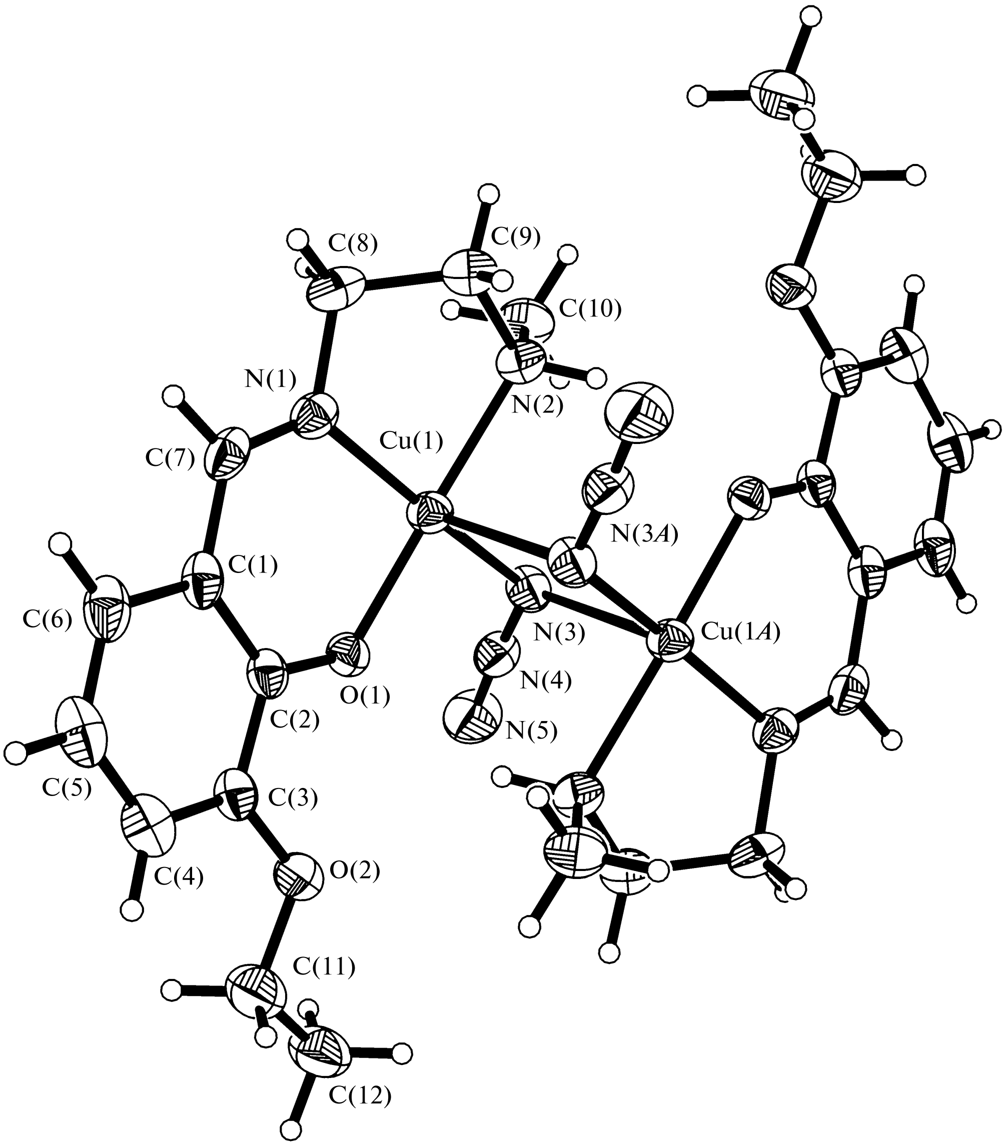

Fig. 2. Molecular structure of **II** at 30% ellipsoid.

vibration. The strong absorption bands at 1621 cm^{-1} for HIEP and 1627 cm^{-1} for HEMP are assigned to the azomethine groups, which are shifted to lower frequencies in the complexes (1615 cm^{-1} for **I** and 1618 cm^{-1} for **II**). The intense absorption bands of the azide groups in both complexes are at 2040 cm^{-1}.

The molecular structures of **I** and **II** are shown as Figs. 1 and 2, respectively. Both complexes are two end-on azido-bridged centrosymmetric dinuclear copper(II) compounds, with the inversion centers lying at the midpoint of the two Cu atoms. The Cu···Cu distances are 3.230(2) Å in **I** and 3.150(2) Å in **II**.

Each Cu atom in the complexes is in a square pyramidal coordination with one phenolate O, one imine N, and one amine N atoms of one Schiff base ligand and with one N atom of an azide group, defining the basal plane. The apical position of the square pyramid is occupied by one N atom of another azide group. The τ values [13] are 0.127 for **I** and 0.130 for **II**. The coordinate bond lengths and angles in both complexes are comparable to each other and also comparable to those observed in other similar copper(II) complexes [7, 14–16].

The two [CuL] units (L is IEP for **I** and EMP for **II**) in each complex are linked not only by the two end-on azide bridges, but also intermolecular N–H···O hydrogen bonds. There were two N–H···O hydrogen bonds in **I** and four in **II**, which might lead to the longer Cu···Cu distance in **I** than that in **II**.

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