HYDROGEN-BOND INDUCED SYNTHESIS, CHARACTERIZATION, AND CRYSTAL STRUCTURES OF END-TO-END AZIDO-BRIDGED POLYMERIC COPPER(II) COMPLEXES DERIVED FROM TRIDENTATE SCHIFF BASES

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(Received: January 8, 2013 - Accepted: March 27, 2013)

ABSTRACT

Two new end-to-end azido-bridged polymeric copper(II) complexes, $[CuL^1(\mu_{1,3}-N_3)]_n$ (1) and $[CuL^2(\mu_{1,3}-N_3)]_n$ (2), where L^1 and L^2 are the monoanionic form of 5-methoxy-2-[(2-methylaminoethylimino)methyl]phenol and 4-chloro-2-[(3-dimethylaminopropylimino)methyl]phenol, have been prepared and structurally characterized by elemental analysis, IR spectra, and single crystal X-ray determination. Complex (1) crystallizes in the orthorhombic space group $P2_12_12_1$, with unit cell dimensions a = 7.6651(9) Å, b = 8.3213(9) Å, c = 20.149(2) Å, V = 1285.2(2) Å^3, Z = 4, R_1 = 0.0296, and wR_2 = 0.0697. Complex (2) crystallizes in the orthorhombic space group *Pbca*, with unit cell dimensions a = 10.353(1) Å, b = 13.069(2) Å, c = 22.265(2) Å, V = 3012.6(7) Å^3, Z = 8, R_1 = 0.0400, and wR_2 = 0.1014. Each Cu atom in the complexes is in a square pyramidal coordination, with three donor atoms of the Schiff base ligand and one azido N atom defining the basal plane, and with another azido N atom occupying the apical position. The Cu···Cu distances are 5.173(2) Å in (1) and 5.277(2) Å in (2). Hydrogen bonds can influence the bridging mode of the azide ligand.

Keywords: Schiff base; Copper; Polymeric complex; Crystal structure; Azide

INTRODUCTION

Polymeric structures of complexes with bridging groups are currently attracting much attention for their interesting structures and wide applications[1-3]. Schiff bases derived from salicylaldehyde and its derivatives are a kind of versatile ligands in coordination chemistry. The rational design and construction of polymeric structures of complexes with Schiff bases are of particular interest in coordination and structural chemistry. The preferred way to construct polynuclear complexes is the use of suitable bridging groups, such as N_3^-, NCS^-, $N(CN)_2^-$, dicarboxylate, 4,4'-bipy, and so on[4-7]. Among the bridging groups, azide ligand has been received particular interest because it is very useful to design extended polynuclear complexes. It can bind up to three metal atoms when acting as a monatomic bridge (end-on, EO) and up to six using the two terminal nitrogen atoms to bridge (end-to-end, EE) (Scheme 1)[8-10]. A major obstacle to a more comprehensive study of such azide-based polymeric coordination complexes is the lack of rational synthetic procedures, since with the present state of knowledge it is hardly possible to determine which coordination mode will be adopted by the azide ligand and whether the sought-after alternating chain structure will finally be formed. Hydrogen bonds are known as an important factor for the self-assembly of complexes[11-13]. Our recent research indicated that hydrogen bonds can influence the bridging modes of azide ligands[14]. As a continuation of the work on self-assembly preparation of azido-bridged polymeric complexes, in this paper, two new end-to-end azido-bridged polymeric copper(II) complexes, $[CuL^1(\mu_{1,3}-N_3)]_n$ (1) and $[CuL^2(\mu_{1,3}-N_3)]_n$ (2), where L^1 and L^2 are the monoanionic form of 5-methoxy-2-[(2-methylaminoethylimino)methyl]phenol (HL^1; Scheme 1) and 4-chloro-2-[(3-dimethylaminopropylimino)methyl]phenol, (HL^2; Scheme 2), were prepared and structurally characterized.
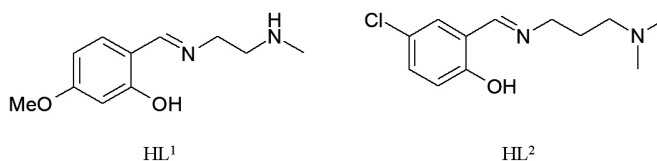
Scheme 2. The Schiff base ligands.

## EXPERIMENTAL

Materials and Methods: Starting materials, reagents and solvents with AR grade were purchased from commercial suppliers and were used without further purification. The Schiff bases were prepared according to the literature method[15]. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded on a Jasco FT/IR-4000 spectrometer as KBr pellets in the 4000-200 cm^{-1} region. Single crystal structural X-ray diffraction was carried out on a Bruker SMART 1000 CCD area-detector diffractometer. Molar conductance of the complexes at concentration of 10^{-3} M in absolute methanol was measured with a Shanghai DDS–11A conductometer. Thermal stability analysis was performed on a Perkin-Elmer Pyris Diamond TG-DTA thermal analyses system.

Synthesis of Complex (1): To the methanolic solution (10 mL) of HL^1 (0.021 g, 0.1 mmol) was added a methanolic solution (10 mL) of copper nitrate (0.024 g, 0.1 mmol) and an aqueous solution of sodium azide (0.007 g, 0.1 mmol) with stirring. The mixture was stirred for 30 min at room temperature to give a blue solution. After keeping the solution in air for a few days, blue block-shaped crystals of the complex, suitable for X-ray crystal structural determination, were formed on slow evaporation of the solvent. The crystals were isolated, washed three times with methanol and dried in air. Yield 53%. Characteristic IR data (KBr, cm^{-1}): 3207 (N–H), 2036 (N$_3$), 1601 (C=N). *Anal.* Calc. for $C_{11}H_{15}CuN_5O_2$: C 42.2, H 4.8, N 22.4%. Found: C 42.3, H 4.9, N 22.3%.

Synthesis of Complex (2): Complex (2) was prepared by the same method as described for complex (1), but with HL^1 replaced with HL^2 (0.024 g, 0.1 mmol). Yield 71%. Characteristic IR data (KBr, cm^{-1}): 2045 (N$_3$), 1603 (C=N). *Anal.* Calc. for $C_{12}H_{16}ClCuN_5O$: C 41.7, H 4.7, N 20.3%. Found: C 41.5, H 4.9, N 20.3%.

Data collection, structural determination and refinement: Diffraction intensities for the complexes were collected at 298(2) K using a Bruker SMART 1000 CCD area-detector diffractometer with MoKα radiation (λ = 0.71073 Å). The collected data were reduced with the SAINT program[16], and multi-scan absorption correction was performed using the SADABS
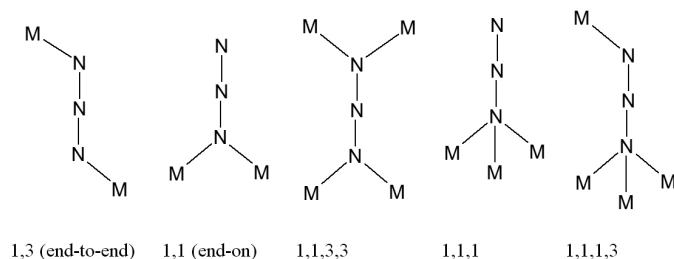
Scheme 1. Bridging modes of the azide ligand.

program[17]. The structures of the complexes were solved by direct method, and were refined against F^2 by full-matrix least-squares method using SHELXTL[18]. All of the non-hydrogen atoms were refined anisotropically. The amino hydrogen atom of complex (1) was located from a difference Fourier map and refined istropically, with N–H distance restrained to 0.90(1) Å. The remaining hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. The crystallographic data for the complex are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

Table 1 Crystallographic data for the complexes

Compounds	**1**	**2**
Empirical formula	$C_{11}H_{15}CuN_5O_2$	$C_{12}H_{16}ClCuN_5O$
Formula weight	312.8	345.3
Temperature/K	298(2)	298(2)
Wavelength/Å	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$Pbca$
a/Å	7.6651(9)	10.353(1)
b/Å	8.3213(9)	13.069(2)
c/Å	20.149(2)	22.265(2)
V/Å³	1285.2(2)	3012.6(7)
Z	4	8
μ/mm⁻¹	1.705	1.630
D_c/g cm⁻³	1.617	1.523
Reflections collected	7653	16226
Unique reflections	2780	3283
Observed reflections [$I \geq 2\sigma(I)$]	2507	2538
Parameters	177	183
Restraints	1	0
$F(000)$	644	1416
R_{int}	0.0296	0.0383
Goodness of fit on F^2	1.033	1.088
R_1 [$I \geq 2\sigma(I)$]	0.0296	0.0400
wR_2 [$I \geq 2\sigma(I)$]	0.0697	0.1014
R_1 (all data)	0.0348	0.0554
wR_2 (all data)	0.0716	0.1136
Largest diff. Peak and hole (e Å⁻³)	0.435, –0.277	0.600, –0.561

Table 2 Selected bond lengths/Å and angles/° for the complexes.

(1)			
Cu1-O1	1.913(2)	Cu1-N1	1.940(2)
Cu1-N2	2.049(2)	Cu1-N3	1.976(2)
Cu1-N5A	2.545(2)		
O1-Cu1-N1	93.3(1)	O1-Cu1-N3	90.9(1)
N1-Cu1-N3	161.2(1)	O1-Cu1-N2	176.8(1)
N1-Cu1-N2	84.4(1)	N3-Cu1-N2	92.1(1)
O1-Cu1-N5A	87.8(1)	N1-Cu1-N5A	94.1(1)
N2-Cu1-N5A	90.2(1)	N3-Cu1-N5A	104.4(1)
Symmetry code for A: $1 - x$, $1/2 + y$, $1/2 - z$.			
(2)			
Cu1-O1	1.935(2)	Cu1-N1	1.994(2)
Cu1-N2	2.106(2)	Cu1-N3	2.011(3)
Cu1-N5A	2.380(3)		
O1-Cu1-N1	89.4(1)	O1-Cu1-N3	87.2(1)
N1-Cu1-N3	162.8(1)	O1-Cu1-N2	172.2(1)
N1-Cu1-N2	93.0(1)	N3-Cu1-N2	88.3(1)
O1-Cu1-N5A	96.9(1)	N1-Cu1-N5A	94.7(1)
N3-Cu1-N5A	102.5(1)	N2-Cu1-N5A	90.3(1)
Symmetry code for A: $1/2 + x$, y, $1/2 - z$.			

RESULTS AND DISCUSSION

The Schiff bases HL¹ and HL² were readily prepared by the condensation reaction of 4-methoxysalicylaldehyde with *N*-methylethane-1,2-diamine, and 5-chlorosalicylaldehyde with *N,N*-dimethylpropane-1,3-diamine, respectively, in methanol. The copper complexes were prepared by the reaction of the Schiff bases, copper nitrate, and sodium azide in methanol under room temperature. The oily product of the Schiff bases and crystalline product of the complexes are stable in air, and soluble in common polar organic solvents such as DMSO, DMF, methanol, ethanol, and acetonitrile, but insoluble in water. The molar conductance values for complexes **1** and **2** measured in methanol at a concentration of 10⁻³ M are 21 and 25 Ω⁻¹ cm² mol⁻¹, respectively, suggesting they are non-electrolytes[19].

Structural Description of the Complexes: The molecular structures of complexes (1) and (2) are shown in Figs. 1 and 2, respectively. X-ray crystallography reveals that both complexes are end-to-end azido-bridged polymeric copper(II) species. The Cu···Cu distances are 5.173(2) Å in (1) and 5.277(2) Å in (2). Both Schiff bases serve as tridentate ligands to form five- and six-membered chelate rings with Cu atom in the complexes. The coordination geometry around each metal center can be best described as a slight distorted square pyramid, with the three donor atoms of the Schiff base ligand and one azido N atom defining the basal plane, and with another azido N atom occupying the apical position. The Cu atoms in the complexes lie 0.142(2) Å for (1) and 0.210(2) Å for (2) from the least-squares planes defined by the basal donor atoms, in the direction of the apical ligands. The coordinate bond distances and bond angles in (1) are shorter than those in (2), which might caused by the existence of five-membered chelate ring Cu1-N1-C8-C9-N2 in (1), while six-membered chelate ring Cu1-N1-C8-C9-C10-N2 in (2). When compared to other similar complexes[15,20-23], it can be seen that the bond differences are not unusual.

In the crystal structure of complex (1), [CuL¹] units are linked through end-to-end azido bridges, as well as intermolecular N–H···O and C–H···N hydrogen bonds (Table 3), to form chains running along *b* axis (Fig. 3). In the crystal structure of complex (2), [CuL²] units are linked through end-to-end azido bridges, as well as intermolecular C–H···N hydrogen bonds (Table 3), to form chains running along *a* axis (Fig. 4).

Table 3 Hydrogen-bond geometry (Å, °) of the complexes.

| D–H···A	$d(D$–H) (Å)	d(H···A) (Å)	$d(D$···A) (Å)	Angle(D–H···A) (°)
(1)				
N2–H2···O1ⁱ	0.90(1)	2.29(1)	3.192(3)	178(4)
C9–H9A···N3ⁱ	0.97	2.59(1)	3.445(3)	146(4)
C10–H10B···N3	0.96	2.56(1)	3.081(3)	114(4)
(2)				
C8–H8B···N3ⁱⁱ	0.97	2.59(1)	3.557(3)	176(4)
C12–H12B···N3	0.96	2.37(1)	2.919(3)	116(4)

Symmetry codes: (i) $1 - x$, $1/2 + y$, $1/2 - z$; (ii) $1/2 - x$, $-1/2 + y$, z.
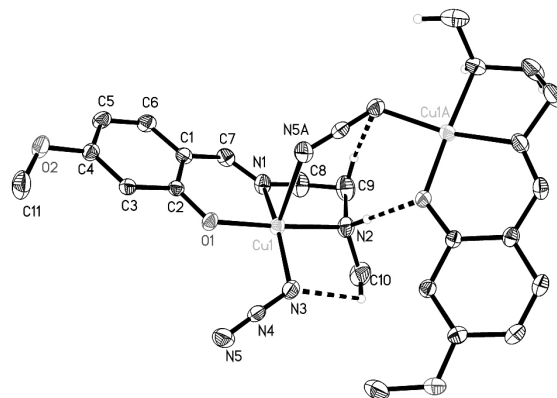
Fig. 1 A perspective view of the asymmetric unit of complex (1). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen bonds are shown as dashed lines.
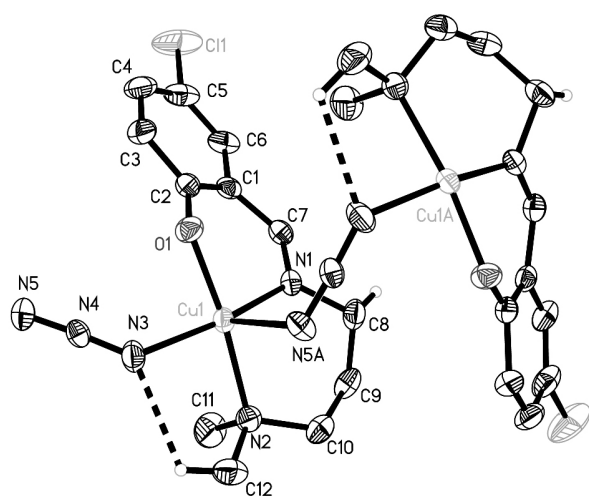
Fig. 2 A perspective view of the asymmetric unit of complex (2). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen bonds are shown as dashed lines.
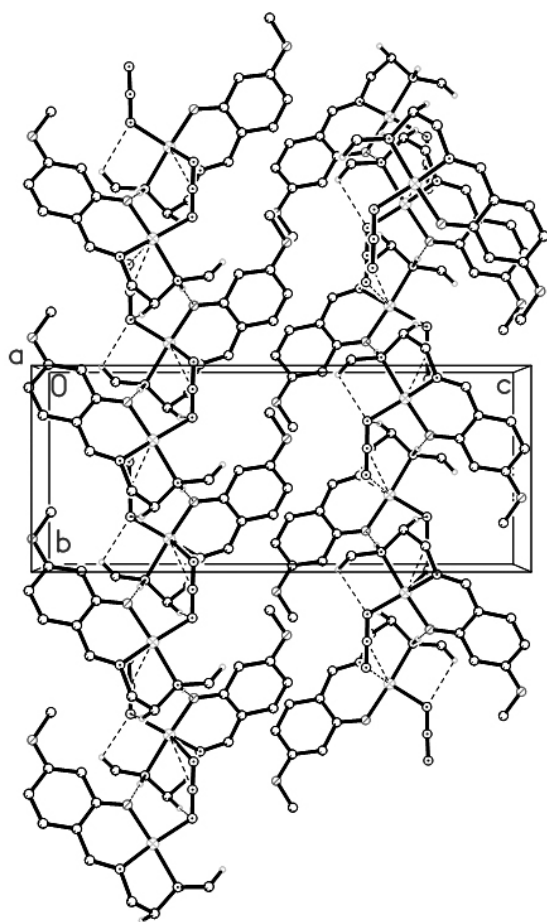
Fig. 3 Molecular packing of complex (1), viewed along the *a* axis. Hydrogen bonds are shown as thin dashed lines.
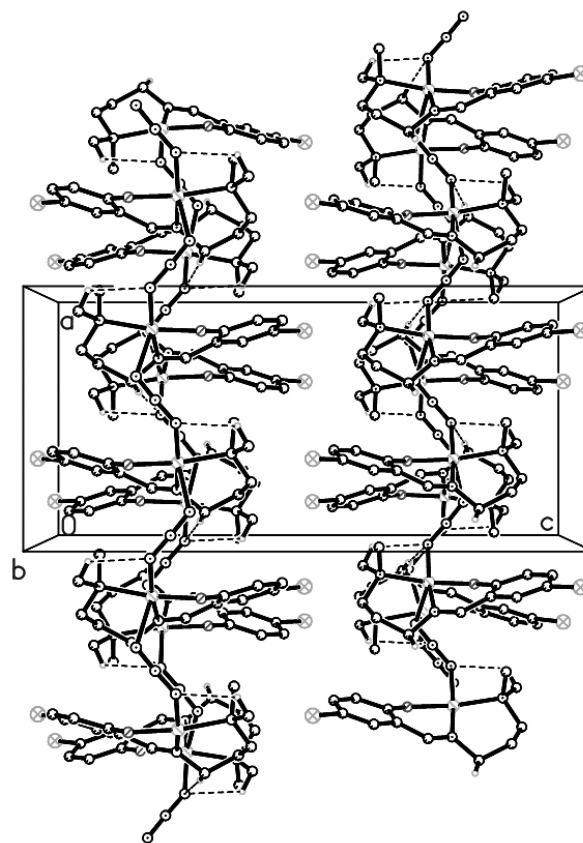
Fig. 4 Molecular packing of complex (2), viewed along the *b* axis. Hydrogen bonds are shown as thin dashed lines.

IR spectra: The IR spectra of the Schiff bases and their complexes provide information about the metal-ligand bonding. The weak and broad absorptions in the region 3250–3400 cm^{-1} are assigned to the O–H groups of the free Schiff bases. In the spectrum of complex (2), the weak and sharp band at 3207 cm^{-1} is assigned to the vibration of N–H group. The strong absorption bands at 1615 cm^{-1} for HL[1] and 1618 cm^{-1} for HL[2] are assigned to the azomethine groups, v(C=N)[24]. These bands are shifted to lower wave numbers in the spectra of the complexes (1601 cm^{-1} for (1) and 1603 cm^{-1} for (2)), attributed to coordination of the azomethine nitrogen atoms to the metal atoms. The strong absorption bands of the Ar–O bonds for the free Schiff bases are located at about 1239 cm^{-1}, which are observed at lower wave numbers for the complexes (1219 cm^{-1} for (1) and 1216 cm^{-1} for (2)). The intense bands indicative of the azide ligands are located at 2036 cm^{-1} for (1) and 2045 cm^{-1} for (2)[25]. Weak absorption bands indicative of the Cu–O and Cu–N bonds are observed in the region 300–650 cm^{-1}.

CONCLUSION

In summary, we have reported the self-assembly preparation, crystal structures, and characterization of two new end-to-end azido-bridged polymeric copper(II) complexes derived from the tridentate Schiff bases 5-methoxy-2-[(2-methylaminoethylimino)methyl]phenol and 4-chloro-2-[(3-dimethylaminopropylimino)methyl]phenol. The results revealed that the hydrogen bonds may influence the bridging modes of the azido ligands. More work needs to be carried out to investigate the influence factors, such as solvent and temperature used for the crystallization, steric effects of the ligands, as well as the molar ratio of the starting materials.

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