DOI: 10.1002/zaac.200600198

Anion-controlled Syntheses and Crystal Structures of a Pair of Novel Azide-bridged Copper(II) Complexes Constructed from 4-Chloro-2-[(2-dimethylaminoethylimino)methyl]phenol

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Received July 11th, 2006.

Abstract. A pair of novel azide-bridged polynuclear copper(II) complexes, $[CuL(\mu_{1,1}\text{-}N_3)]_n$ (**1**) and $[Cu_4L_2(CH_3COO)_2(\mu_{1,1}\text{-}N_3)_4]$ (**2**) (L = 4-chloro-2-[(2-dimethylaminoethylimino)methyl]phenolate), have been obtained from the same Schiff base ligand and an identical synthetic procedure using anions of the metal salts as the only independent variable. Complex **1** was synthesized using copper(II) nitrate, while complex **2** was synthesized using the copper(II) acetate as the salt. Both of the complexes show novel supramolecular structures in their crystals as elucidated by X-ray analyses. The polynuclear complex **1** contains $[CuL(\mu_{1,1}\text{-}N_3)]_n$ units as the building blocks, crystallizes in the *P*bca space group. The tetra-nuclear complex **2** contains $[Cu_4L_2(CH_3COO)_2(\mu_{1,1}\text{-}N_3)_4]$ units as the building blocks, crystallizes in the $P\bar{1}$ space group.

Keywords: Copper(II) complexes; Polynuclear complexes; Schiff bases; Crystal structure; Supramolecular assembly

Introduction

Metal-organic complexes containing bridging ligands are of great interest because of their interesting molecular topologies as well as the fact that they may be designed with specific functionalities [1−3]. Among pseudohalogens, azide has become the most extensively studied building blocks in the multi-dimensional complexes due to its versatility and probability in functioning as a bridging ligand to give varieties of coordination modes [4−6]. 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 [7−9]. Furthermore, the design and syntheses of novel coordination modes controlled by varying the reaction conditions (including temperature [10−12], metal/ligand ratio [13], pH values [14], solvents [15], and counter anions [16, 17]) are of great interest in coordination chemistry. Appropriate control of the reaction conditions makes it possible to construct new materials with useful properties. In this paper, we report the syntheses of a pair of novel azide-bridged polynuclear copper(II) complexes, $[CuL(\mu_{1,1}\text{-}N_3)]_n$ (**1**) and $[Cu_4L_2(CH_3COO)_2(\mu_{1,1}\text{-}N_3)_4]$ (**2**) (L = 4-chloro-2-[(2-dimethylaminoethylimino)methyl]phenolate), from an identical synthetic procedure and the same Schiff base ligand but with different copper(II) salts.

Experimental Section

Materials and measurements

All chemicals (reagent grade) were commercially available and were used without further purification. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded on a Nicolet AVATAR 360 spectrometer as KBr pellets in the 4000-400 cm^{-1} region.

Preparation of the ligand HL

To a MeOH solution (20 mL) of 5-chlorosalicylaldehyde (157.7 mg, 1.0 mmol) was added a MeOH solution (10 mL) of *N,N*-dimethylethane-1,2-diamine (88.2 mg, 1.0 mmol) with stirring. The mixture was stirred for 10 min at room temperature to give a clear orange solution. The ligand was not isolated from the solution. The MeOH solution was used for the syntheses of the complexes.

Preparation of the complexes

$[CuL(\mu_{1,1}\text{-}N_3)]_n$ (1). To a MeOH solution (5 mL) of $Cu(NO_3)_2 \cdot 3H_2O$ (48.5 mg, 0.2 mmol) was added a MeOH solution (10 mL) of HL (22.7 mg, 0.1 mmol) and an aqueous solution (5 mL) of NaN_3 (13.1 mg, 0.2 mmol), with stirring. The mixture was stirred for 30 min at room temperature and filtered. Diffraction quality single crystals of **1** were obtained after a few days by slow evaporation of the filtrate in open atmosphere. The crystals were isolated, washed three times with cold MeOH and dried in a vacuum desiccator containing anhydrous $CaCl_2$. Analysis: Calcd. for

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$C_{11}H_{14}ClCuN_5O$: C, 39.88; H, 4.26; N, 21.14 %. Found: C, 40.12; H, 4.32; N, 21.33 %. Yield: 50.3 % on the basis of HL.

$[Cu_4L_2(CH_3COO)_2(\mu_{1,1}\text{-}N_3)_4]$ (2). Complex **2** was prepared by the similar synthetic procedure as described for **1**, with $Cu(NO_3)_2{\cdot}3H_2O$ replaced by $Cu(CH_3COO)_2{\cdot}H_2O$ (39.8 mg, 0.2 mmol). Analysis: Calcd. for $C_{26}H_{34}Cl_2Cu_4N_{16}O_6$: C, 31.49; H, 3.46; N, 22.60 %. Found: C, 31.20; H, 3.53; N, 22.78 %. Yield: 45.9 % on the basis of HL.

Caution! Although our samples never exploded during handling, metal azide complexes are potentially explosive. Only a small amount of material should be prepared and it should be handled with care.

Crystal structure determination

X-ray intensities of complexes **1** and **2** were collected using a Bruker Smart Apex 1000 CCD area detector equipped with graphite-monochromated Mo-*Kα* radiation ($\lambda = 0.71073$ Å) at 298(2) K. Empirical absorption corrections were applied to the data using the SADABS program [18]. Structures were solved by the direct method and refined by full-matrix least squares on F^2 using the SHELXTL version 5.1 [19]. All of the non-hydrogen atoms were refined anisotropically. All H atoms were placed in calculated positions and constrained to ride on their parent atoms. The crystallographic data for the two complexes are summarized in Table 1. Selected bond lengths and angles are given in Table 2. Crystallographic data for **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre (CCDC 614212, 614213).

Results and Discussion

To design novel structures of transition metal complexes, the ligands used in the synthesis are important. Based on the above considerations, we used the tridentate Schiff base ligand HL to synthesize the complexes. The reason we use HL as the ligand is that it could adopts versatile coordination modes through the donor atoms [20, 21]. The second ligand, *viz.* azide, is a well known bridging group. It readily bridges different metal ions through the terminal donor atoms, forming polynuclear complexes. Copper(II) is a good candidate of square-pyramidal coordination. Complexes **1** and **2** (as illustated in schemes 1 and 2, respectively) were synthesized simply under similar synthetic procedures. The syntheses of the two complexes here demonstrate that the anions of the copper(II) salts can severely influence the structures of the complexes.

Table 1 Crystallographical and experimental data for **1** and **2**

Compound	**1**	**2**
Formula	$C_{11}H_{14}ClCuN_5O$	$C_{26}H_{34}Cl_2Cu_4N_{16}O_6$
Mr	331.26	991.75
T /K	298(2)	298(2)
Radiation(Mo-*Kα*) /*λ*	0.71073	0.71073
Crystal shape/color	block/blue	block/blue
Crystal size/mm^3	0.32×0.29×0.23	0.27×0.23×0.20
Crystal system	orthorhombic	triclinic
Space group	*P*bca	$P\bar{1}$
a /Å	6.744(2)	9.829(2)
b /Å	19.885(4)	10.504(2)
c /Å	20.572(4)	10.934(3)
α /°	90.00	99.285(2)
β /°	90.00	115.562(2)
γ /°	90.00	102.573(2)
V /Å^3	2758.8(9)	951.3(7)
Z	8	1
Dc /(g/cm^{-3})	1.595	1.731
μ /mm^{-1}	1.776	2.408
F(000)	1352	500
θ range/°	1.98/27.50	2.16/25.50
Index range (*h*, *k*, *l*)	−8/8, −25/25, −26/26	−11/11, −12/12, −13/13
Measured reflections	3159	3280
Observed reflections I ≥ 2σ(I)	2704	2193
Absorption correction	empirical	empirical
Min. and max. transmission	0.6003/0.6855	0.5625/0.6445
Data/restraints/parameters	3159/0/174	3280/0/247
Goodness-of-fit on F^2	1.045	1.032
R$_1$, *wR$_2$* [I ≥ 2σ(I)]	0.0281, 0.0697	0.0808, 0.1943
R$_1$, *wR$_2$* (all data)	0.0350, 0.0735	0.1144, 0.2253

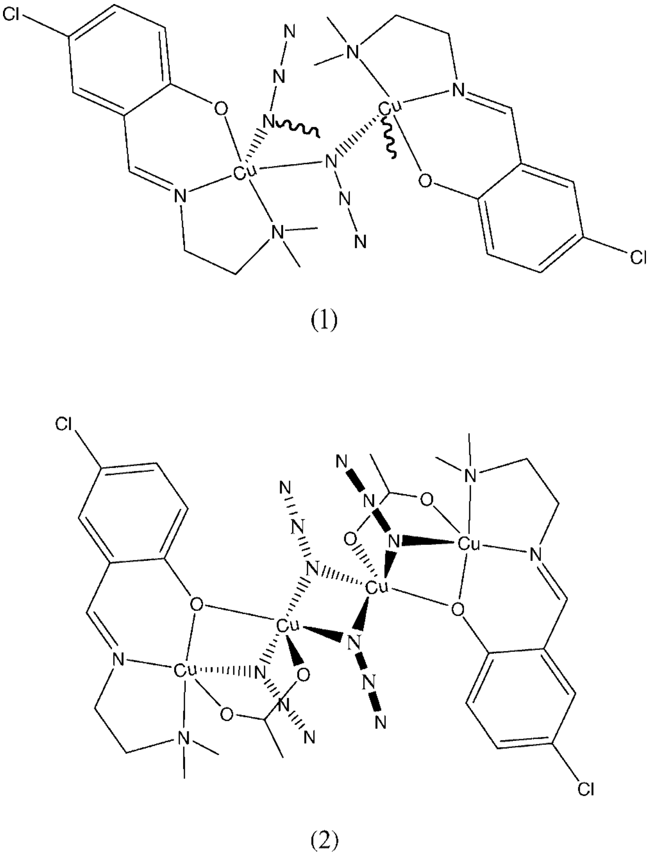
Table 2 Selected bond lengths/Å and angles/° for **1** and **2**

1			
Cu1-O1	1.911(2)	Cu1-N1	1.950(2)
Cu1-N3	1.978(2)	Cu1-N2	2.079(2)
Cu1-N3A	2.631(2)		
O1-Cu1-N1	93.0(1)	O1-Cu1-N3	89.3(1)
N1-Cu1-N3	172.2(1)	O1-Cu1-N2	177.5(1)
N1-Cu1-N2	84.5(1)	N3-Cu1-N2	93.1(1)
O1-Cu1-N3A	87.6(1)	N1-Cu1-N3A	87.2(1)
N2-Cu1-N3A	92.8(1)	N3-Cu1-N3A	100.3(1)
2			
Cu1-O1	1.922(5)	Cu1-N1	1.941(7)
Cu1-O2	1.952(6)	Cu1-N2	2.044(7)
Cu1-N3	2.464(9)	Cu2-O3	1.932(6)
Cu2-N6A	1.980(7)	Cu2-N3	1.991(9)
Cu2-N6	2.012(7)	Cu2-O1	2.317(6)
O1-Cu1-N1	92.7(3)	O1-Cu1-O2	91.3(3)
N1-Cu1-O2	164.0(3)	O1-Cu1-N2	174.2(3)
N1-Cu1-N2	84.6(3)	O2-Cu1-N2	89.9(3)
O1-Cu1-N3	82.9(3)	N1-Cu1-N3	101.3(3)
O2-Cu1-N3	94.5(3)	N2-Cu1-N3	102.7(3)
O3-Cu2-N6A	164.1(3)	O3-Cu2-N3	95.8(3)
N6A-Cu2-N3	95.2(3)	O3-Cu2-N6	89.4(3)
N6-Cu2-N6A	79.3(3)	N3-Cu2-N6	174.6(3)
O3-Cu2-O1	95.2(2)	N6A-Cu2-O1	97.0(3)
N3-Cu2-O1	85.4(3)	N6-Cu2-O1	95.3(3)

The Schiff base ligand HL was soluble in MeOH. Complexes **1** and **2** are two novel polynuclear complexes. They are stable in air at room temperature, soluble in DMF, DMSO, MeOH, EtOH, MeCN and Me_2CO; poorly soluble in water and Et_2O.

Structure description of 1

The single-crystal X-ray structural analysis shows that complex **1** is an interesting azide-bridged polynuclear copper(II) compound. The neutral $[CuL(\mu_{1,1}\text{-}N_3)]$ units in **1** are linked through the single $\mu_{1,1}$-N_3 ligand, forming an infinite one-dimensional polymeric chain (Scheme 1 and Figure 1). The Cu atom is five-coordinated by the NNO donor set of the Schiff base ligand and two bridging azide anions, forming a square pyramidal coordination. The basal plane of the square pyramidal coordination is defined by the two N atoms and one phenolate O atom of L and one terminal N atom of the bridging azide ligand. The apical position is occupied by one terminal N atom of the bridging azide ligand from the symmetry related unit (symmetry code:



Scheme 1

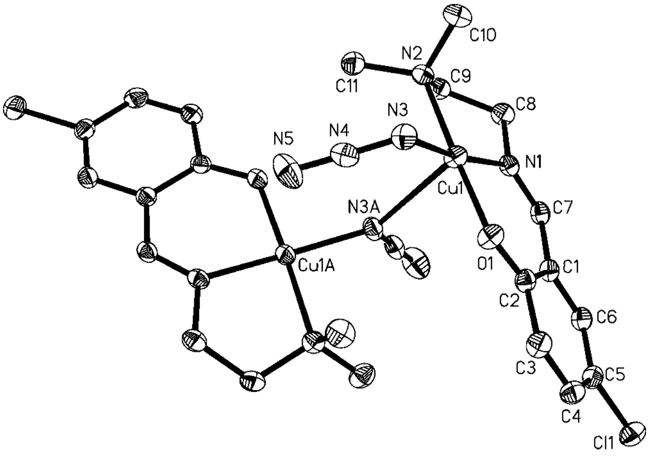


Figure 1 Molecular structure of **1**. Displacement ellipsoids are drawn at the 30 % probability level and H atoms have been omitted for clarity. Atoms labeled with the suffix A or unlabeled are at the symmetry position −1/2 + x, 1/2 − y, 1 − z.

−1/2 + x, 1/2 − y, 1 − z). Each azide ligand bridges adjacent copper(II) ions through basal-apical linkage mode. The apical Cu-N bond length is much longer than usual. The other bond lengths and angles are within normal values. The Cu···Cu distance is found to be 4.167(2) Å. The Cu-$\mu_{1,1}$-N_3-Cu chains are propagated along the crystallographic *a*-axis (Figure 2). There are no short intermolecular contacts among the chains from the crystallographic study.

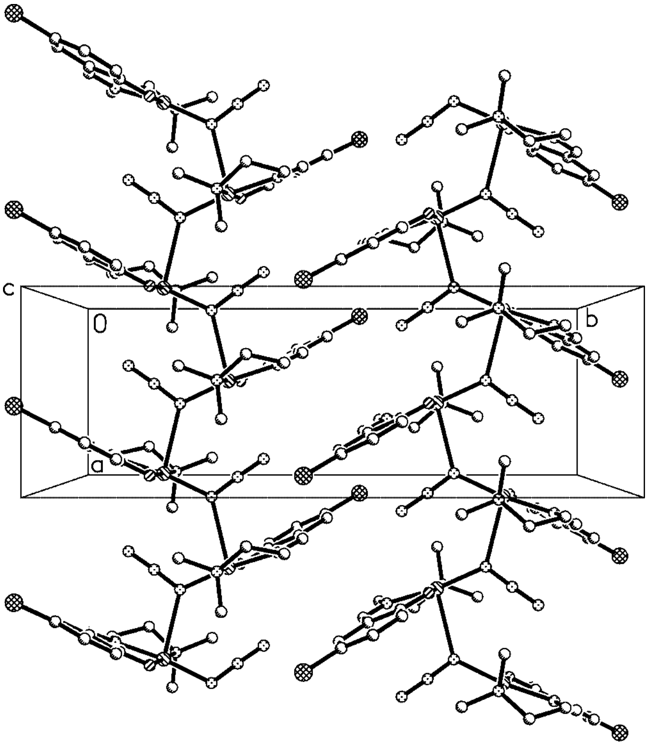


Figure 2 The molecular packing of **1**, viewed along the *c* axis.

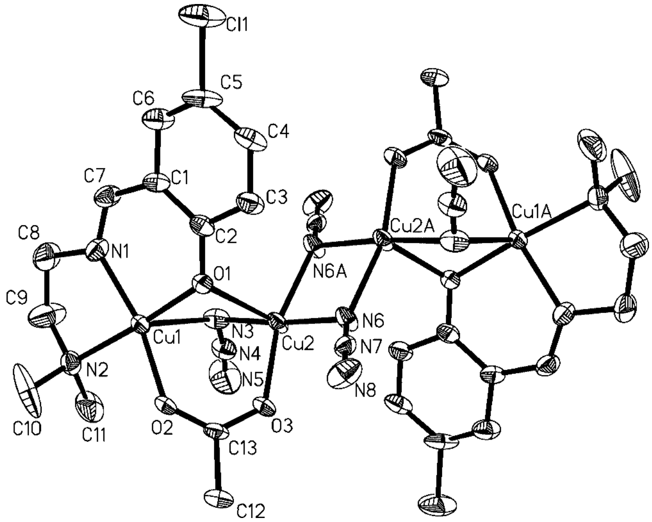


Figure 3 Molecular structure of **2**. Displacement ellipsoids are drawn at the 30 % probability level and H atoms have been omitted for clarity. Atoms labeled with the suffix A or unlabeled are at the symmetry position 1−x, 1 − y, − z.

Structure description of 2

The single-crystal X-ray structural analysis shows that complex **2** is an interesting acetate- and azide-bridged tetranuclear copper(II) compound with inversion centre (Scheme 1 and Figure 3). The asymmetric unit of **2** consists of one half of the molecule, with the other half generated by the inversion ($\bar{1}$) symmetry. Each asymmetric unit is a dinuclear copper(II) complex moiety, within which the Cu atoms are connected by three bridging groups: one phenolate O atom, one $\mu_{1,1}$-N_3 ligand, and one acetate ligand. The two asymmetric units are further linked through another two $\mu_{1,1}$-N_3 ligands, forming a tetranuclear copper(II) complex. Each of the symmetry related two outermost Cu atoms is five-coordinated by one Schiff base ligand, one bridging azide ligand, and one bridging acetate ligand, forming a square pyramidal coordination. The basal plane of the square pyramidal coordination for the outermost Cu atom is defined by the two N atoms and one phenolate O atom of L and one O atom of the bridging acetate ligand. The apical position is occupied by one terminal N atom of the bridging azide ligand. Each of the symmetry related two central Cu atoms is five-coordinated by one phenolate O atom, one acetate ligand, and three bridging azide ligands, forming a square pyramidal coordination. The basal plane of the square pyramidal coordination for the central Cu atom is defined by the three terminal N atoms from the three bridging azide ligands and one O atom of the bridging acetate ligand. The apical position is occupied by the phenolate O atom of L. Each azide ligand in the asymmetric unit bridges adjacent copper(II) ions through basal-apical linkage mode, while the azide ligands located between the symmetry units bridges the central copper(II) ions only through the basal linkage mode. The apical Cu-N and Cu-O bond lengths are much longer than usual. The other bond lengths and angles are within normal values. The Cu···Cu distances are found to be 3.066(2) Å for Cu1 and Cu2 and 3.072(2) Å for Cu2 and Cu2A, respectively. In the crystal structure, molecules are stacked along the *b* axis, with no short intermolecular contacts (Figure 4).

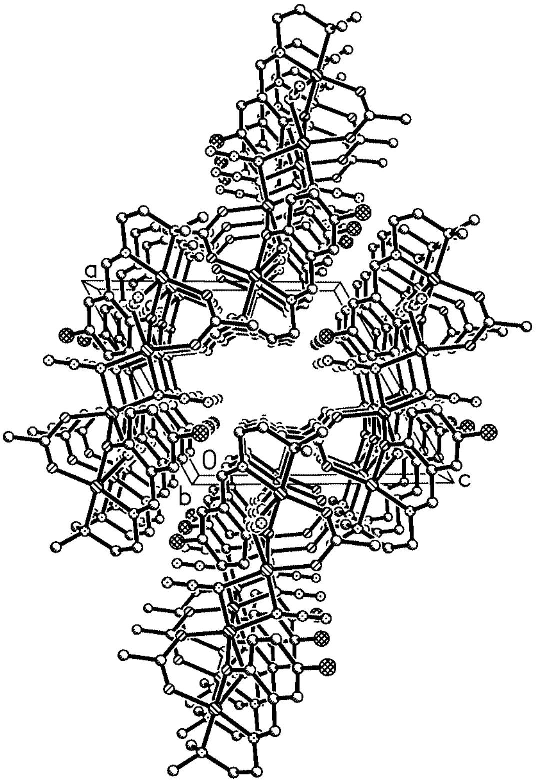


Figure 4 The crystal packing of **2**, viewed along the *a* axis.

I.r. spectra

Complexes **1** and **2** show strong absorption bands at 2054 and 2072 cm^{-1}, respectively, consistent with the presence of azide ligands in the structures. The lower frequency of the stretching vibration for the azide ligands in **1** than that in **2** may be attributed to the highly asymmetrical nature of the azide bridges in **1** [22]. The bands corresponding to the azomethine (C=N) groups in the complexes appear at 1612 and 1617 cm^{-1} for **1** and **2**, respectively [23]. Complex **2** exhibits the typical acetate vibrations $\nu_{asym}(CO_2)$ at 1531 cm^{-1} and $\nu_{sym}(CO_2)$ at 1443 cm^{-1}. While for **1**, there are no vibrations for the nitrate groups, indicating that they were not participate in the coordination.

Conclusions

It is evident from the above discussion that we have successfully synthesized two novel azide-bridged copper(II) complexes, $[CuL(\mu_{1,1}\text{-}N_3)]_n$ (**1**) and $[Cu_4L_2(CH_3COO)_2(\mu_{1,1}\text{-}N_3)_4]$ (**2**), with different coordination modes using the same NNO donor Schiff base ligand under the same synthetic procedure, only with different copper(II) salts, *viz.* copper(II) nitrate for **1** and copper(II) acetate for **2**. The different anions of the copper(II) salts used in the preparation of the complexes can severely influence the structures of the final products.

Acknowledgment. This work was supported by the **National Natural Science Foundation of China** (20571037).

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