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烯唑醇铜和银配合物的水热合成与晶体结构

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摘要：合成了 2 个新的烯唑醇铜和银配合物：$[CuL_4Cl_2]$ (**1**)，$[AgL_2]NO_3$ (**2**)(L=diniconazole)。通过元素分析、红外光谱和 X-ray 单晶衍射对其结构进行了表征。结构分析表明，**1** 属三斜晶系，$P\bar{1}$ 空间群，晶胞参数为 a=0.882 3(7) nm，b=1.370 5(10) nm，c=1.516 4(11) nm，α=91.507(11)°，β=97.356(9)°，γ=107.683(9)°。**2** 属单斜晶系，$P2_1/c$ 空间群，晶胞参数为 a=1.229 2(3) nm，b=1.272 1(3) nm，c=2.431 7(5) nm，β=98.694(3)°。**1** 和 **2** 都由分子间氢键连接成一维链结构。

关键词：铜配合物；银配合物；烯唑醇；水热合成；晶体结构
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Synthesis and Crystal Structures of Complexes of Copper, Silver Assembled by Diniconazole

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Abstract: Two new complexes $[CuL_4Cl_2]$ (**1**) and $[AgL_2]NO_3$ (**2**) (L=diniconazole) were synthesized by solvothermal condition and structurally characterized by element analysis, IR and single crystal X-ray diffraction. Complex **1** is the Triclinic system, space group $P\bar{1}$ with a=0.882 3(7) nm, b=1.370 5(10) nm, c=1.516 4(11) nm, α=91.507(11)°, β=97.356(9)°, γ=107.683(9)°. Complex **2** belongs to the Monoclinic system, space group $P2_1/c$ with a=1.229 2(3) nm, b=1.272 1(3) nm, c=2.431 7(5) nm, α=90°, β=98.694(3)°, γ=90°. **1** and **2** are linked into a one dimensional chain by intermolecular hydrogen bonds. CCDC: 805738, **1**; 818240, **2**.

Key words: copper complex; silver complex; diniconazole; hydrothermal synthesis; crystal structure

Diniconazole is a triazole-type fungicide developed by Japan′s Sumitomo Chemical Company. Diniconazole ((*E*)-(*RS*)-1-(2,4-dichlorophenyl)-4,4-dimethyl-2-(1*H*-1,2,4-triazol-1-yl)-pent-1-en-3-ol) is a highly active fungicide and plant growth regulator with low toxicity[1]. It is a specific inhibitor of the 14a-demethylation step of ergosterol biosynthesis in fungi. It shows excellent efficacy against various diseases and widely used in many crops, such as corn, wheat, peanut, grape and apple[2-4].

Copper and copper complexes are effective sterilization of pesticides to eliminate pests and diseases caused by mold or fungus. Copper fungicides can kill more than three hundred kinds of diseases of hundred kinds of crops. Meantime, copper is one of the essential trace minerals for animal, and involved in composition of superoxide dismutase and monoamine oxidase. Silver and silver complexes also can kill or

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inhibit various types of pathogenic microorganisms, such as the *G*+ bacteria, *G*− bacteria, spores, bacteria, fungi, viruses and mycoplasma. Because of the effect of against various diseases and no resistance, silver is also known as biophile metal.

Because of its strong antimicrobial activities and its wide applications, the synthesis of diniconazole and its derivatives have attracted much attention[5-9], but the the complexes of diniconazole are still rare[10-12]. Recently we have reported two cobalt and nickel complexes[11-12]. In order to find the new antibactericidal complexes with the efficiency, broad-spectrum and low toxicity, and further study the structural changes of diniconazole fungicides may occurred in the application process or remixed with other substances containing copper and silver complexes. We have been engaged in synthesising new metal complexes, and not long ago we obtained two new complexes with diniconazole. Herein we report the synthesis and structure of two new copper and silver complexes.

1 Experimental

1.1 Materials and measurements

Diniconazole, $AgNO_3$, $CuCl_2$ and other reactants of AR grade were obtained commercially and used without further purification. Elemental analysis of C, H and N was performed on a Perkin-Elmer 240C elemental analyzer. IR (KBr pellets) spectra were recorded in the 400~4 000 cm^{-1} range using a perkin-Elmer Spectrum One FTIR spectrometer.

1.2 Synthesis

Complex **1**: Diniconazole (0.062 5 g, 0.2 mmol) was dissolved in ethanol (10 mL). To this, $CuCl_2$ (0.017 g, 0.1 mmol) in ethanol (10 mL) was added slowly under stirring at room temperature. The mixture stirred well for 3 h at room temperature and some blue powders generated. The resulting solution was filtered and washed with ethanol. The filtrate was left undisturbed at room temperature, and the blue block crystal were obtained by slow evaporation of ethanol solution two weeks later. Yield 80% (base on $CuCl_2$). Elemental Anal. Calcd. for $C_{60}H_{68}Cl_{10}CuN_{12}O_4$ (1 439.30)(%): C, 50.07; H, 4.76; N, 11.68. Found (%): C, 49.98; H, 4.71; N, 11.65. IR (KBr, cm^{-1}): 3 313.92, 3 141.66, 2 967.57, 1 474.22, 1 400.07, 1 133.10, 1 100.41, 1 072.79, 1 053.08, 1 016.34.

Complex **2**: The procedure was the same as that for **2** except that $CuCl_2$ was replaced by $AgNO_3$ (0.017 g, 0.1 mmol). Yield: 60% (base on $AgNO_3$). Elemental Anal. Calcd. for $C_{30}H_{34}AgCl_4N_7O_5$ (822.31)(%): C, 43.82; H, 4.17; N, 11.92. Found (%): C, 43.79; H, 4.20; N, 11.90. IR (KBr, cm^{-1}): 3 400.15, 3 156.87, 2 958.92, 1 419.34, 1 399.90, 1 384.43, 1 101.95, 1 074.24, 1 053.75.

1.3 Structure determination

The crystal structures were determined by single-crystal X-ray diffraction. Reflection data were collected at room temperature on a Bruker APEX Ⅱ area detector diffractometer[13] equipped with a graphite-monochromatic Mo $K\alpha$ radiation (λ=0.071 073 nm) at 296(2) K with ω-2θ scan mode. Empirical adsorption corrections were applied to all date using SADABS. The structure were solved by direct methods and refined by full-matrix least squares on F^2 using SHELXTL 97 software[14].

All non-hydrogen atoms were located by direct methods and subsequent difference Fourier syntheses. The hydrogen atoms bound to carbon were located by geometrical calculations, and their positions and thermal parameters were fixed during the structure refinement, with O-H 0.082 nm in **1** and **2**. All calculations were carried out using SHELXTL 97[14] and PLATON[15]. Crystallographic date and pertinent information are givenin Table 1; selected bond lengths and angles in Table 2, and geometric parameters of hydrogen bonds in Table 3.

CCDC: 805738, **1**; 818240, **2**.

2 Results and dicussion

2.1 Crystal structure of 1

X-ray diffraction analysis shows that **1** is isomorphous to previously reported complexes constructed by the first-transition metal (Co, Ni, Zn) and diniconazole. Complex **1** is composed of one Cu(Ⅱ), four diniconazole, and two Cl ions (Fig.1). Each Cu(Ⅱ) adopts a distorted octahedral geometry where the basal plane is occupied by four triazole ring nitrogen atoms (N(1), N(1)#1, N(4), N(4)#1 from four equivalent diniconazole ligands; the axes are occupied by two Cl ions. The Cu-N bond distances are 0.202

Table 1　Crystal and structure refinement date for 1 and 2

Complex	**1**	**2**
Empirical fomula	$C_{60}H_{68}Cl_{10}CuN_{12}O_4$	$C_{30}H_{34}AgCl_4N_7O_5$
Fomula weight	1 439.30	822.31
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a / nm	0.882 3(7)	1.229 2(3)
b / nm	1.370 5(10)	1.272 1(3)
c / nm	1.516 4(11)	2.431 7(5)
α / (°)	91.507(11)	90
β / (°)	97.356(9)	98.694(3)
γ / (°)	107.683(9)	90
Volume / nm^3	1.728(2)	3.758 8(15)
Z	1	4
D_c / (g·cm^{-3})	1.383	1.453
Absorption coefficient / mm^{-1}	0.755	0.866
F(000)	743	1 672
Crystal size / mm	0.30×0.14×0.12	0.21×0.25×0.16
θ range for date collection / (°)	2.45 to 25.50	2.20 to 25.50
Reflections collected	8 620	28 415
Independent reflection (R_{int})	5 911 (0.018 1)	6 999 (0.042 2)
Goodness-of-fit on F^2	1.037	0.960
Final R indices ($I>2\sigma(I)$)	R_1=0.039 9, wR_2=0.086 1	R_1=0.050 0, wR_2=0.096 6
R indices (all date)	R_1=0.060 8, wR_2=0.096 3	R_1=0.099 9, wR_2=0.119 3

Table 2　Selected bond lengths (nm) and bond angles (°)

		1			
Cu(1)-N(1)	0.203 0(2)	Cu(1)-N(4)	0.202 1(2)	Cu(1)-Cl(5)	0.279 54(18)
N(1)-Cu(1)-N(4)	89.45(10)	N(1)-Cu(1)-N(1)#1	180.00(1)	N(4)-Cu(1)-N(4)#1	180.0
		2			
Ag(1)-N(1)	0.210 9(3)	Ag(1)-N(4)	0.211 1(4)	Ag(1)-O(3)	0.277 49(39)
N(1)-Ag(1)-N(4)	176.26(17)				

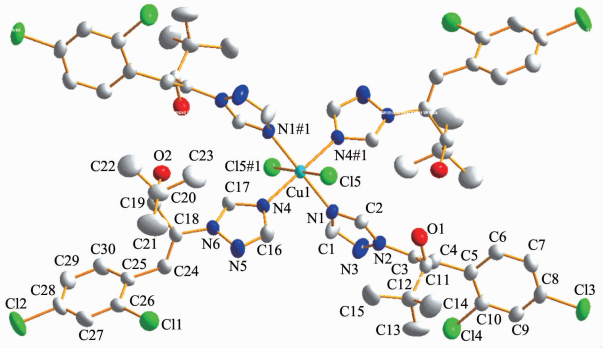
Symmetry transformation: **1**: #1: 1−x, −y, 1−z.

Table 3　Hydrogen bond lengths and bond angles of 1 and 2

D–H···A	d(D-H) / nm	d(H-A) / nm	d(D···A) / nm	∠DHA / (°)
1				
O(1)–H(3)···Cl(5)#2	0.082	0.229 5	0.3108	171.22
O(2)–H(2)···Cl(5)#2	0.082	0.227 7	0.3083	167.26
2				
O(2)–H(5)···N(7)#1	0.082	0.259	0.340 7(7)	171.3
O(2)–H(5)···O(4)#1	0.082	0.238	0.316 2(6)	158.6
O(2)–H(5)···O(5)#1	0.082	0.207	0.279 9(7)	147.0
O(1)–H(3)···N(7)#2	0.082	0.264	0.343 3(6)	164.4
O(1)–H(3)···O(4)#2	0.082	0.259	0.329 8(6)	144.9
O(1)–H(3)···O(3)#2	0.082	0.202	0.279 7(5)	157.1

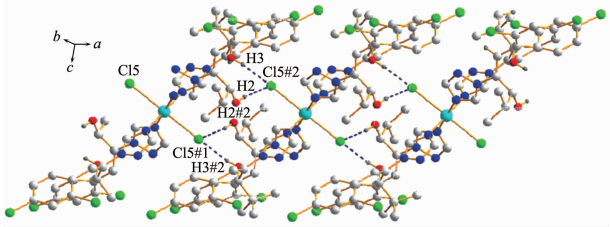
Symmetry codes: **1**: #2: 1+x, y, z; **2**: #1: −x+1, −y+2, −z; #2: −x+1, y−1/2, −z+1/2.

and 0.203 nm, the N-Cu-N bond angles are 89.45° and 180° (Table 1). These angles further confirm the octahedral geometry of Cu (II) in **1**. **1** is linked via intermolecular O–H···Cl hydrogen bonds (O(1)–H(3)···Cl(5)#2 and O(2)–H(2)···Cl(5)#2) between hydroxy and coordinated Cl ions (Table 3) to generate one dimensional chain (Fig.2).



Symmetry codes: #1: 1–*x*, –*y*, 1–*z*; H atoms omitted for clarity

Fig.1 Crystal structure of **1** with 50% thermal ellipsoids

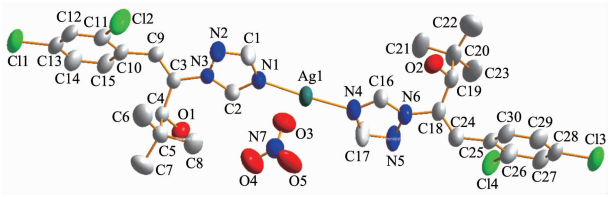


Symmetry codes: #1: 1–*x*, –*y*, 1–*z*; #2: 1+*x*, *y*, *z*; Some H atoms omitted for clarity

Fig.2 One-dimensional chain of **1**

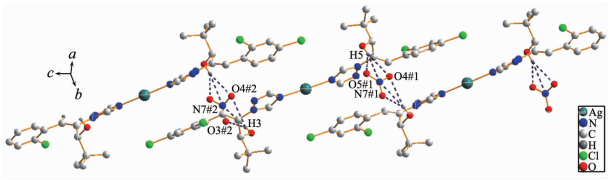
2.2 Crystal structure of 2

X-ray diffraction analysis shows that the structure of **2** is composed of one AgL_2 coordinated cation (L= diniconazole) and one nitrate ion (Fig.3). The Ag(I) atom is two-coordinated by two N atoms from two different diniconazoles in a linear mode. The Ag-N distances are 0.210 9 and 0.211 1 nm, the N-Ag-N bond angles is 176.26° (Table 1) and the dihedral angle of the triazole ring from two diniconazoles is 0.353 2(185) nm. There are intermolecular O–H···N and O–H···O hydrogen bonds between hydroxy and nitrate ion in the packing structure of **2** (Table 3) and intermolecular hydrogen bonds linked **2** to generate one dimensional chain (Fig.4).



H atoms omitted for clarity

Fig.3 Crystal structure of **2** with 50% thermal ellipsoids



Symmetry codes: #1: –*x*+1, –*y*+2, –*z*; #2: –*x*+1, *y*–1/2, –*z*+1/2; Some H atoms omitted for clarity

Fig.4 One-dimensional chain of **2**

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