

Synthesis and Crystal Structure of a New Diamine Complex CuCl₄(H₂tn)[†]

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In an attempt to synthesize a new pyrimidine complex of copper(II) in a solution reaction of CuBr₂ with 2,2'-bis(hexahydropyrimidine) and hydro-chloric acid, we unexpectedly obtained a bright yellow chip-like crystal of CuCl₄(H₂tn) [H₂tn=(H₃NCH₂CH₂CH₂NH₃)²⁺]. Its structure was determined by single-crystal X-ray diffraction analysis. The crystal belongs to orthorhombic system, space group *Pnma*, with cell parameters: *a*=0.7216(2) nm, *b*=1.8308(6) nm, *c*=0.7553(3) nm, *V*=0.9953(6) nm³, *Z*=4, *F*(000)=564, *M_r*=281.49, *D_c*=1.879 g/cm³. *μ*(Mo K α)=3.204 mm⁻¹, *R*₁=0.0248, *wR*₂=0.0575. The analysis of the crystal structure indicates that the complex has a three-dimensional network structure, which is formed by hydrogen bonds and electrostatic interaction.

Keywords copper(II) complex, synthesis, three-dimensional network structure

Introduction

During the past several decades, diamines and their derivatives have been extensively investigated in both basic research and their application. The result shows that they can form stable complexes with many transition metals. These complexes would be widely applied in various fields such as biotechnology,¹ synthesis,² food processing industry,³ environmental science,⁴ biochemistry,⁵ etc. Especially, in recent years, more and more attention is placed on their other peculiarities. For example, protonated 1,3-diaminopropane is interleaved among the sheets of [Al₂(PO₄)(OH, F)₅]²⁻ to ensure the cohesion of the structure by hydrogen bonds.⁶ The similar property for diaminobutane was also reported.⁷ In an attempt to synthesize a new pyrimidine complex of copper(II) in a solution reaction of CuBr₂ with 2,2'-bis(hexahydropyrimidine) and hydrochloric acid, we obtained a bright yellow chip-like crystal of CuCl₄(H₂tn) [H₂tn=(H₃NCH₂CH₂CH₂NH₃)²⁺]. Its structure was determined by single-crystal X-ray diffraction analysis. In the present paper, the synthesis and crystal structure of the title complex are reported.

Experimental

Apparatus and reagents

Elemental analysis was performed on a Germany

Vario EL III CHNOS analyzer. Copper contents were determined on a SOLLAR M6 Dual Zeeman atomic absorption instrument. IR spectra were measured with KBr pellets on an EQUINO×55 spectrometer. ¹H NMR spectra were recorded on an INOVA-400 NMR spectrometer using TMS as internal standard. Mass spectra were determined on an HP-5800A mass spectrometer. X-ray intensity data were measured on a Bruker Smart-1000CCD diffractometer. All reagents were of A.R. grade. 1,3-Diaminopropane was purchased from Fluka Chemical Co. 2,2'-Bis(hexahydropyrimidine) was prepared following the literature method.⁸

Preparation of ligand

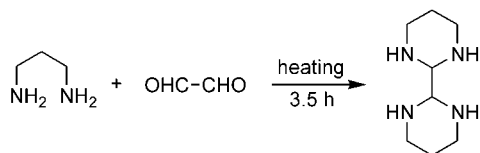
2,2'-Bis(hexahydropyrimidine) was prepared following the literature method.⁸ Needles were formed. Yield 49%, m.p. 120—122 °C; ¹H NMR (400 MHz, CDCl₃) δ : 3.32 (s, 2H), 3.10 (ddd, *J*=13.0, 4.3, 2.0 Hz, 4H), 2.71 (ddd, *J*=13.0, 4.3, 2.0 Hz, 4H), 1.41 (dt, *J*=13.2, 2.9, 2.0 Hz, 2H), 1.48 (dt, *J*=13.2, 12.0, 4.3 Hz, 2H); IR (KBr) *v*: 3283, 3227, 1635, 1513, 1427, 1313, 1229, 1184, 1112, 1001 cm⁻¹; MS *m/z* (%): 170 (M⁺, <1), 85 (100), 50 (31), 36 (11). Anal. calcd for C₈H₁₈N₄: C 56.49, H 10.66, N 32.94; found C 56.84, H 10.43, N 32.47. The equation of the reaction can be written as follows:

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Preparation of complex

A solution of CuBr_2 (0.11 g, 0.0005 mol) in 4 mL of ethanol was dropped into a solution of 2,2'-bis(hexahydropyrimidine) (0.17 g, 0.001 mol) in 3 mL of ethanol under stirring at room temperature. After mixing, 0.16 g of grass-green complex **1** $\text{Cu(L)Br}_2 \cdot 0.5\text{H}_2\text{O}$ [L = 2,2'-Bis(hexahydropyrimidine)] was produced. Yield 79.5%, m.p. 132—133 °C. Anal. calcd for $\text{C}_8\text{H}_{19}\text{N}_4\text{O}_{0.5}\text{CuBr}_2$: C 23.87, H 4.76, Cu 15.77, N 13.91; found C 24.17, H 4.95, Cu 15.38, N 13.60. The complex **1** was dissolved in 15 mL of 4 mol·L⁻¹ hydrochloric acid, the reaction solution turned green and was left standing for a month. Bright yellow chip-like crystals (complex **2**) suitable for X-ray diffraction analysis were formed. Yield 44.7%, m.p. 228—229 °C. Anal. calcd for $\text{C}_3\text{H}_{12}\text{N}_2\text{CuCl}_4$: C 12.84, H 4.29, N 9.95; found C 13.24, H 4.17, N 10.01.

X-ray diffraction study

A single crystal with dimensions 0.50 mm × 0.40 mm × 0.15 mm was selected for data collection, using a Bruker Smart-1000CCD diffractometer with graphite monochromatized Mo K α radiation ($\lambda = 0.071073$ nm). Data were collected by ω -2 θ scan technique. The total reflections of 5058 were collected, of which 1104 unique reflections could be observed and used in the structure analysis. The structure was solved by direct methods. The positions of all remaining non-H atoms were obtained from successive Fourier syntheses. The positions of all non-H atoms were refined anisotropically with full-matrix least-squares on F^2 . In the final difference map, the residual densities are 375 and -408 e/nm³, respectively. The crystallographic data and analysis parameters are showed in Table 1. The crystal belongs to orthorhombic system, space group *Pnma* with cell parameters: $a = 0.7216(2)$ nm, $b = 1.8308(6)$ nm, $c = 0.7553(3)$ nm, $V = 0.9953(6)$ nm³, $Z = 4$, $F(000) = 564$, $M_r = 281.49$, $D_c = 1.879$ g/cm³, $\mu(\text{Mo K}\alpha) = 3.204$ mm⁻¹, $R_1 = 0.0248$, $wR_2 = 0.0575$.

Results and discussion

Crystal structure

The non-H atomic coordinates and thermal parameters of the title complex are listed in Table 2, and the selected bond lengths and angles are listed in Table 3. All of the data in brackets are standard deviation. The structure unit cell of the complex consists of $[\text{CuCl}_4]^{2-}$ and $(\text{H}_2\text{tn})^{2+}$. The copper atom lies at the inversion center. At the same time, one of the carbon atoms of the protonated 1,3-diaminopropane is located on the symmetrical plane (Figure 1). The bond length data:

Table 1 Crystal data and structure analysis parameters

Formula	$\text{CuCl}_4(\text{H}_2\text{tn})$
Crystal size/mm ³	$0.50 \times 0.40 \times 0.15$
Empirical formula	$\text{C}_3\text{H}_{12}\text{Cl}_4\text{CuN}_2$
Temperature/K	298(2)
Wavelength/nm	0.071073
Formula weight	281.49
Crystal system	orthorhombic
Space group	<i>Pnma</i>
a/nm	0.7216(3)
b/nm	1.8308(6)
c/nm	0.7553(3)
V/nm^3	0.9953(9)
Z	4
$D_c/(\text{g}\cdot\text{cm}^{-3})$	1.879
$F(000)$	564
Scan mode	ω -2 θ
θ range for data collection/(°)	2.92—27.08
Scan speed/(°)·min ⁻¹	16
Reflections collected	5058
Reflections unique	1104

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (nm² × 10⁵)

	x	y	z	$U(\text{eq})$
Cu(1)	0	5000	10000	25(1)
N(1)	136(3)	6142(1)	4725(3)	35(1)
Cl(1)	197(1)	3746(1)	9574(1)	34(1)
Cl(2)	2250(1)	5169(1)	7899(1)	30(1)
C(1)	-356(4)	6826(1)	5622(4)	40(1)
C(2)	273(5)	7500	4663(5)	39(1)

Table 3 Selected bond lengths (nm) and bond angles (°)

Cu(1)—Cl(2)	0.22885(7)	Cu(1)—Cl(2) ^{#1}	0.22885(7)
Cu(1)—Cl(1)	0.23231(9)	Cu(1)—Cl(1) ^{#1}	0.23231(9)
N(1)—C(1)	0.1467(3)	C(1)—C(2)	0.1501(3)
C(2)—C(1) ^{#2}	0.1501(3)		
Cl(2)—Cu(1)—Cl(2) ^{#1}	180.0	Cl(2)—Cu(1)—Cl(1)	89.673(19)
Cl(2) ^{#1} —Cu(1)—Cl(1)	90.326(19)	Cl(2)—Cu(1)—Cl(1) ^{#1}	90.327(19)
Cl(2) ^{#1} —Cu(1)—Cl(1) ^{#1}	89.674(19)	Cl(1)—Cu(1)—Cl(1) ^{#1}	180.0
N(1)—C(1)—C(2)	114.0(2)	C(1) ^{#2} —C(2)—C(1)	110.7(3)

#1: $-x, -y+1, -z+2$; #2: $x, -y+3/2, z$.

Cu(1)—Cl(1) 0.23231(9) nm, Cu(1)—Cl(1A) 0.23231(9) nm, Cu(1)—Cl(2) 0.22885(7) nm, Cu(1)—Cl(2A) 0.22885(7) nm and bond angle data Cl(2)—Cu(1)—Cl(2A) 180.0°, Cl(2)—Cu(1)—Cl(1) 89.673(19)°, Cl(2A)—Cu(1)—

Cl(1) 90.326(19)°, Cl(2)-Cu(1)-Cl(1A) 90.327(19)°, Cl(2A)-Cu(1)-Cl(1A) 89.674(19)°, Cl(1)-Cu(1)-Cl(1A) 180.0°. These data suggest that copper atom has a quadrangle planar coordination geometry with four chlorine atoms. However, the unit quite often gives tetrahedral structure. In the title complex, the structure of the unit $[\text{CuCl}_4]^{2-}$ is distorted because of the existing of the $(\text{H}_2\text{tn})^{2+}$, which accords with principal.⁹ In Figure 2, the chlorine atom of the $[\text{CuCl}_4]^{2-}$ forms hydrogen bond with one of the hydrogen atoms of $(\text{H}_2\text{tn})^{2+}$. The other hydrogen atom of $(\text{H}_2\text{tn})^{2+}$ forms hydrogen bond with another $[\text{CuCl}_4]^{2-}$. So there are not only intramolecular hydrogen bonds but also intermolecular hydrogen bonds in the complex $\text{CuCl}_4(\text{H}_2\text{tn})$. Protonated 1,3-diaminopropane is interleaved between the units $[\text{CuCl}_4]^{2-}$ to ensure the cohesion of the structure by hydrogen bonds. The hydrogen bond length data: N(1)—H(1)···Cl(1) 0.3377 nm, N(1)—H(2)···Cl(1) 0.3253 nm, N(1)—H(3)···Cl(2) 0.3273 nm, H(1)···Cl(1) 0.2520 nm, H(2)···Cl(1) 0.2471 nm, H(3)···Cl(2) 0.2454 nm and bond angle data: N(1)—H(1)···Cl(1) 163.63°, N(1)—H(2)···Cl(1) 163.73°, N(1)—H(3)···Cl(2) 143.80°. The data of hydrogen bond length and hydrogen bond angle are in the scope of the system described by Jeffrey.¹⁰ In the meantime, the $[\text{CuCl}_4]^{2-}$ unit, which has been bonded to $(\text{H}_2\text{tn})^{2+}$ through hydrogen bond, interacts with another $(\text{H}_2\text{tn})^{2+}$ by electrostatic interaction. On the other hand, there is another

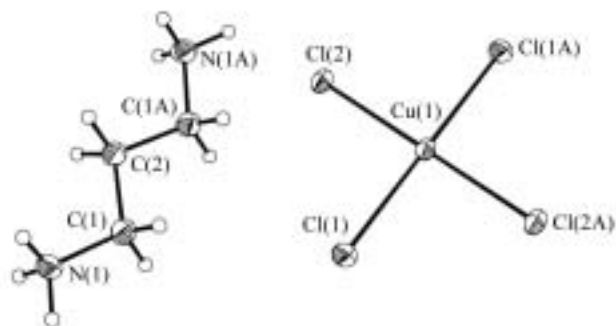


Figure 1 Crystal structure of $\text{CuCl}_4(\text{H}_2\text{tn})$.

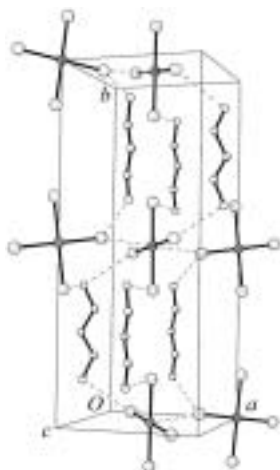


Figure 2 Cell packing of $\text{CuCl}_4(\text{H}_2\text{tn})$.

bond of $\text{Cu}-\text{Cl}\cdots\text{H}-\text{N}$ in the structure. The $\text{Cu}-\text{Cl}$ bond is almost vertical to the $\text{Cl}\cdots\text{H}$ bond. The similar structure was found in the complex $\text{trans}[\text{PtCl}_2(\text{NH}_3)_2]$, with a $\text{Cl}\cdots\text{N}$ distance of 3.41 nm and a $\text{Pt}-\text{Cl}\cdots\text{N}$ angle of 78°. In crystals, $\text{M}-\text{Cl}\cdots\text{H}-\text{N}$ hydrogen bonds, which are roughly perpendicular to the $\text{M}-\text{Cl}$ bond, are almost exclusively donated.¹¹⁻¹³ Because of the hydrogen bonds and electrostatic interaction, the complex forms three-dimensional network structure (Figure 3).

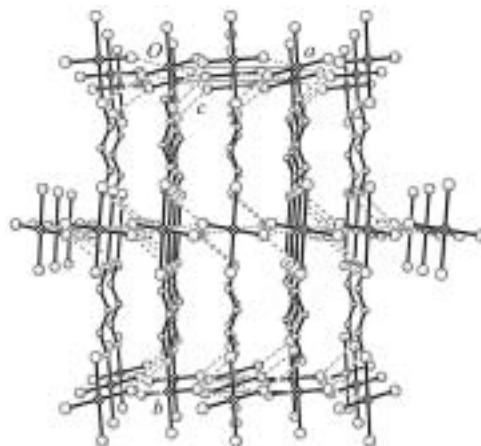
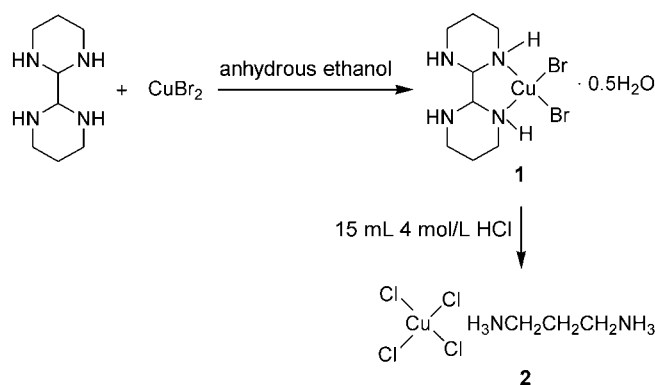


Figure 3 Space filling model of $\text{CuCl}_4(\text{H}_2\text{tn})$ molecules in the crystal cell.

Discussion of the reaction mechanism

In terms of the experiment, the possible reaction procedure is presumed as Scheme 1.

Scheme 1



After mixing ligand 2,2'-bis(hexahydropyrimidine) and copper(II) bromide, grass-green complex **1** was produced, m.p. 132—133 °C. The complex was dissolved after 15 mL of 4 mol·L⁻¹ HCl was dropped into the mixture. The reaction solution changed to bright green. The crystal is bright yellow chip-like, m.p. 228—229 °C. That is to say, the complex **1** underwent apparently changing. We think that the reasons for the change are: (1) the complex **1** was decomposed in the acid solution. 2,2'-Bis(hexahydropyrimidine) was dissociated to form 1,3-diaminopropane, then 1,3-diaminopropane was acidified. (2) The ability of the protonated 1,3-diamio-

propane coordinating to the metal atom declined. On the other hand, the ability of acting on chloride anion increased. (3) The intensity of ligand field of the ligands Cl^- and $(\text{H}_2\text{tn})^{2+}$ was $\text{Cl}^- > (\text{H}_2\text{tn})^{2+}$, at the same time, there were a lot of free chloride anions in solution, therefore, it was easier for Cl^- to coordinate to copper(II) than $(\text{H}_2\text{tn})^{2+}$. Cl^- occupied the original coordination points of two nitrogen atoms and two bromine atoms. Then the unit $[\text{CuCl}_4]^{2-}$ bonded to the protonated 1,3-diaminopropane, and the new complex **2** was formed.

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