

水熱合成含銅(I)-氯二維配位 錯合物及結構分析

Hydrothermal Synthesis and Crystal Structure of a Two-dimensional Copper(I)-chloride Coordination Polymer

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摘 要：將 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ 、2,6-吡啶雙羧酸及 1,2-雙吡啶乙烷加水混合，利用水熱合成反應，得到含銅(I)-氯的高分子配位化合物，其化學式為 $[\text{Cu}_2(\mu_2\text{-bpe})(\mu_3\text{-Cl})_2]_n$ ，(bpe = 1,2-雙吡啶乙烷)。利用元素分析儀、FT-IR 光譜儀及 X-Ray 晶體繞射儀測定產物晶體結構及性質。錯合物以銅(I)離子為配位中心，配位三個氯離子及一個氮原子，氮原子來自 1,2-雙吡啶乙烷，配位鍵結構成四配位具些微扭曲的正四面體型(CuCl_3N)幾何結構。每個氯離子當橋鍵 ($\mu_3\text{-Cl}$)，同時鄰接三個銅(I)離子，而每個銅(I)離子尾端臨接 1,2-雙吡啶乙烷的氮原子，延著 a 軸方向形成星型的鏈狀結構。配位中心銅(I)離子經由 1,2-雙吡啶乙烷配位基的相互連結，形成平行於向量 $[001]$ 方向之二維空間層狀結構。

關鍵詞：水熱合成、1,2-雙吡啶乙烷、銅(I)-鹵化物、 $\pi \cdots \pi$ 吸引力

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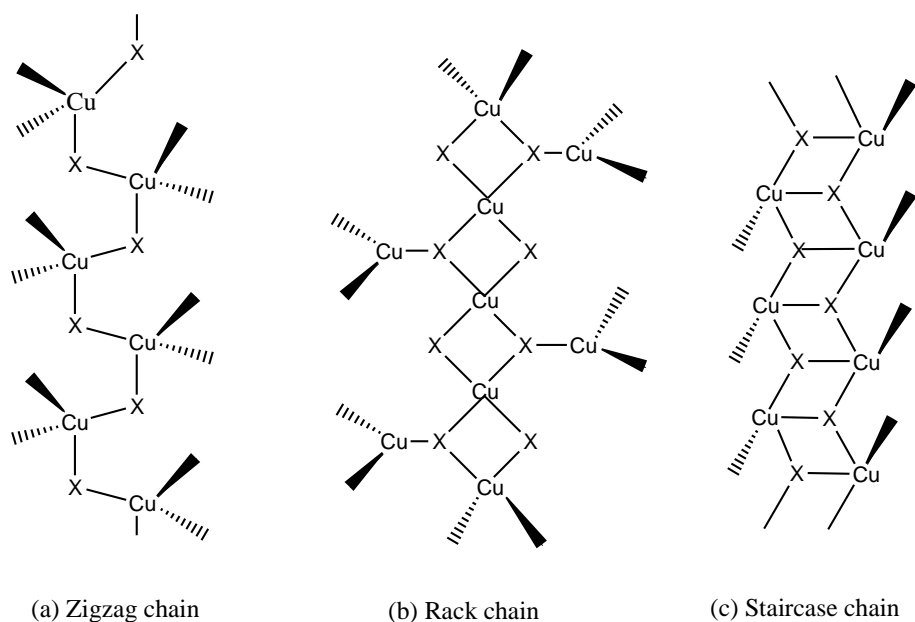
Abstract : A metal-organic coordination polymer, $[\text{Cu}_2(\mu_2\text{-bpe})(\mu_3\text{-Cl})_2]_n$ (bpe=1,2-bis(4-pyridyl)ethene), has been hydrothermally synthesized from the reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 1,2-bis(4-pyridyl)ethane and 2,6-pyridinedicarboxylic acid. The complexes have been characterized by elemental analyses, FT-IR spectroscopy and single-crystal X-ray diffraction. The title compound, Cu (I) cation is coordinated by an N atom from the bpe ligand and three Cl^- anions in a distorted tetrahedral CuCl_3N coordination geometry. Each Cl^- anion bridges ($\mu_3\text{-Cl}$) three Cu cations related by inversion centers, forming a stair-case polymeric chain along the *a* axis, and the terminal N atoms of the bpe ligand, located across an inversion center, coordinate the Cu cations from neighboring chains, forming two-dimensional polymeric sheets parallel to $[001]$.

Key words : Hydrothermal Reaction, 1,2-bis(4-pyridyl)ethene, Copper (I)-halide, $\pi \cdots \pi$ stacking interactions

I . Introduction

In recent years, many studies groups have been devoted to the investigation of new synthetic strategies, with the use of novel rigid or flexible spacer ligand¹⁻³. In a previous attempt to investigate the design and control of the self-assembly of coordination polymers with flexible bridging ligands, such as 4,4'-bipyridine, 1,2-bis(4-pyridyl)ethane, 1,2-bis(4-pyridyl)thene, 4,4'-trimethylenedipyridine and other flexible ligands. The 1,2-bis(4-pyridyl)ethane is a versatile building block for purposes of crystal engineering. Copper(I)-halide motifs, including zigzag chains⁴, rack chains⁵ and staircases⁶⁻⁸(Scheme1), which can be propagated through the coordination of organic N-donor ligands to form network structures. It has been demonstrated that the ligand geometry can affect the type of Cu(I)-halide framework. In the structural investigation of compounds with general formula $[(\text{Cu-X})_2\text{L}]_n$, ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{L} =$ flexible linker ligand), has been found⁹⁻¹⁴. The coordinate covalent bonds or non-covalent interactions, such as hydrogen bonds and $\pi \cdots \pi$ interactions, are useful tools to connect inorganic and organic components. Here we report the syntheses, crystal structures and characterization of a copper(I)-halide polymer, $[\text{Cu}_2(\mu_2\text{-bpe})(\mu_3\text{-Cl})_2]_n$, (bpe = 1,2-bis(4-pyridyl)ethene) which exhibits an organic-inorganic layered structure formed by the assembly of a one-dimensional CuCl staircase and the bridging ligand.





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cheme 1. Structure motifs observed for copper (I) halides. X= halide anion.

II . Experimental Section

Materials and methods

All chemicals purchased were reagent grade and used without further purification. Elemental analysis (C, H and N) was performed on a Heraeus CHN-O-Rapid elemental analyzer. FT-IR spectra were recorded in the range 400-4000 cm^{-1} on a *JASCO 6200 Micro-FT-IR* spectrophotometer using a KBr pellet. All measurements were performed at room temperature.

X-ray Crystallographic Analysis

Diffraction data of the title compound were collected on a Bruker SMART CCD area detector diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) in ψ and ω scan modes. All the structures were solved by direct methods using the program SHELXS 97 and refined by full-matrix least-squares methods on F^2 using the program¹⁵ SHELXL 97. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions. The crystallographic data and experimental details for structural analyses are summarized in **Table 1**. Selected bond lengths and Bond angles for the title compound are listed in **Table 2** and **Table 3**.



Table 1. Crystal data, experimental details and refinement parameters for the structure of $[\text{Cu}_2(\mu_2\text{-bpe})(\mu_3\text{-Cl})_2]_n$.

Chemical formula	$\text{Cu}_2\text{Cl}_2(\text{C}_{12}\text{H}_{10}\text{N}_2)$
Molecular weight	380.22
Temperature, K	296(2)
Wavelength, Å	0.71073
Crystal system	Monoclinic
Crystal description color	Orange
Space group	P2(1)/n
Unit cell parameters, a, b, c, Å	3.7842 (3), 15.0547 (12), 10.8993 (9)
Volume, Å ³	617.06 (9)
β (deg)	96.401 (2)
Z	4
d_x , g/cm ³	2.046
Extinction coefficient, mm ⁻¹	3.86
F(000)	376
Crystal size, mm	0.50 x 0.30 x 0.15
h, k, l limits	$-4 \leq h \leq 4$, $-17 \leq k \leq 17$, $-10 \leq l \leq 12$
Data completeness on θ , %	2.5-25.0, 99.8%
Measured/independent reflections	3199/1100 [$R_{\text{int}} = 0.037$]
Reflections with $I > 2\sigma(I)$	1000
Number of parameters	82
Transmission	0.98517-1.00000
Refinement	Full-matrix least squares against F^2
Final R factor [$I > 2\sigma(I)$]	$R_1 = 0.0343$, $wR_2 = 0.0948$
R factor (all data)	$R_1 = 0.0378$, $wR_2 = 0.0967$
Residual electron density, e. Å ⁻³	-0.60 and 0.81

Table 2. Bond lengths d , Å in the structure of $[\text{Cu}_2(\mu_2\text{-bpe})(\mu_3\text{-Cl})_2]_n$.

Bond	$d(\text{Å})$	Bond	$d(\text{Å})$
Cu1—Cl1	2.5410 (12)	Cu1—Cu1 ⁱ	2.966(2)
Cu1—N1	1.995 (3)	Cl1—Cu1 ⁱ	2.323(2)



Cu1—Cl1 ⁱ	2.3957 (11)	Cl1—Cu1 ⁱⁱ	2.396(2)
Cu1—Cl1 ⁱⁱ	2.3230 (11)	C1—C2	1.377(4)
N1—C1	1.340 (5)	C2—C3	1.395(3)
N1—C5	1.336 (5)	C3—C4	1.392(3)
Cu1—Cu1 ⁱⁱ	2.966(2)	C4—C5	1.379(4)
C6—C6 ^{ix}	3.432(6)	C6—C6 ⁱⁱⁱ	1.322(6)

Symmetry codes: (i) $-x, -y+1, -z+2$; (ii) $-x+1, -y+1, -z+2$; (iii) $-x, 2-y, 2-z$; (ix) $1-x, 2-y, 2-z$.

Table 3. Bond angles ω , deg. in the structure of $[\text{Cu}_2(\mu_2\text{-bpe})(\mu_3\text{-Cl})_2]_n$.

Angle	ω	Angle	ω
Cl1—Cu1—N1	103.11 (10)	C1—N1—C5	116.6 (3)
Cu1—Cl1—Cu1 ⁱⁱ	74.98 (3)	Cl1 ⁱ —Cu1—N1	111.43 (10)
Cl1—Cu1—Cl1 ⁱ	106.25 (4)	Cl1 ⁱⁱ —Cu1—N1	123.04 (10)
Cu1 ⁱ —Cl1—Cu1 ⁱⁱ	106.63 (5)	Cl1 ⁱ —Cu1—Cl1 ⁱⁱ	106.63 (4)
Cl1—Cu1—Cl1 ⁱⁱ	105.02 (4)	Cu1—Cl1—Cu1 ⁱ	73.75 (3)
Cu1—N1—C1	121.6 (3)	N1—C1—C2	123.8 (4)
Cu1—N1—C5	121.8 (3)	N1—C5—C4	123.5 (4)
C3—C6—C6 ⁱⁱⁱ	125.32(41)	C6 ⁱⁱⁱ —C6—H6A	117.33(42)

Symmetry codes: (i) $-x, -y+1, -z+2$; (ii) $-x+1, -y+1, -z+2$; (iii) $-x, 2-y, 2-z$.

Synthesis

A mixture of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.0856g, 0.50mmol), pyridine-2,6-dicarboxylic acid (0.0836g, 0.50mmol), 1,2-bis(4-pyridyl)ethane (0.0934g, 0.50mmol) and distilled water (7 mL) was sealed in a 23 mL Teflon-lined stainless autoclave was heated to 418 K under autogenous pressure for 48 h then allowed cooling slowly to room temperature. Orange crystals were obtained (yield 25.05 %, based on Cu). IR (KBr, cm^{-1}): 1599(s), 1552(m), 1495(m), 1419(s), 1335(w), 1330(w), 1200(w), 1020(m), 977(s), 828(s), 531(s). Elemental analysis calcd. for $\text{Cu}_2\text{Cl}_2(\text{C}_{12}\text{H}_{10}\text{N}_2)$ ($M_r = 380.22$): C, 37.87; N, 7.36; H, 2.65 %. Found: C, 36.98; N, 7.15; H, 2.70 %.

Results and discussion

The title compound has been prepared by hydrothermal reactions under nearly neutral conditions (the pH value was adjusted to 6.8~7.0). Copper (II) chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) reacts with 2,6-pyridinedicarboxylic acid and 1,2-bis(4-pyridyl)ethane at 418 K. We have successfully applied to synthesis of Cu(I)-halide coordination polymer. The product is stable in air and insoluble in water and common organic solvents such as ethanol, acetonitrile, tetrahydrofuran,



1,2-dichloroethane, acetone and DMF. When the preparation of the title compound was tried in the absence of 2,6-pyridinedicarboxylic acid, only gave very poor crystalline products, and therefore we gave up further characterizations.

The valence sum calculations give the average value of 0.903 for Cu atom, suggesting that all Cu centers are in the +1 oxidation state ($[\text{Ar}] 3d^{10}4s^04p^0$)^{16,17}. The title polymeric structure is shown in Fig 1. The title compound, Cu(I) cation is coordinated by an N atom from the bpe ligand and three Cl⁻ anions in a distorted tetrahedral CuCl_3N coordination geometry. Each Cl⁻ anion bridges three Cu cations related by inversion centers, forming a stair-case polymeric chain along the a axis, and the terminal N atoms of the bpe ligand, located across an inversion center, coordinate the Cu cations from neighboring chains, forming two-dimensional polymeric sheets layed on the ab-plane (Fig 2). We have recently reported the crystal structure $[\text{Cu}_2(\mu_2\text{-bpe})(\mu_3\text{-Br})_2]_n$ ¹⁸, the compound $[\text{Cu}_2(\mu_2\text{-bpe})(\mu_3\text{-Br})_2]_n$ and title compound are iso-structural. All interatomic distances and angles are very similar for the two structures. The polymer framework has four-member $\text{Cu}\text{-Cl}\text{-Cu}\text{-Cl}$ units that form the step of a stair and bpe ligand across those stairs,^{19,20} shown as Fig. 2. $\text{Cu}\cdots\text{Cu}$ distances are between 2.966(2)~3.784(1) Å and $\text{Cu}\text{-Cl}\text{-Cu}$ angles are 73.75(3)~106.63(5)°, respectively (Table 2 and Table 3).

The crystal structure is further consolidated by $\pi\cdots\pi$ stacking between nearly parallel pyridine ring systems, the centroid \cdots centroid distances between $\text{Cg1}(\text{N1/C1}\text{-}\text{C5})\cdots\text{Cg1}^{(\text{iii})}$ and $\text{Cg2}(\text{N1a/C1a}\text{-}\text{C5a})\cdots\text{Cg2}^{(\text{iv})}$ are 3.784(2) and 3.354(2) Å [symmetry code : (iii) 1-X, 1-Y, 2-Z, (iv) -X, 1-Y, 2-Z], respectively (Fig 3)^{21,22}.

III. Conclusions

In summary, we have successfully isolated a cuprous chloride open-framework with the flexible linker ligand bpe connects $[\text{Cu}_2\text{Cl}_2]_n$ polymeric staircase ladders to form a 2-D hybrid inorganic-organic sheet ; This study not only proves the hydrothermal reaction in preparing metal-organic hybrid materials but also shows weak intermolecular interactions ($\pi\cdots\pi$ stacking interactions) contributed to the formation of higher-dimensional network.

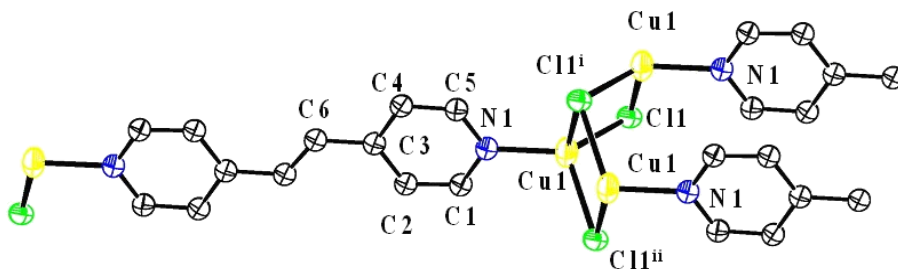


Fig 1. The asymmetric unit of the compound $[\text{Cu}_2(\mu_2\text{-bpe})(\mu_3\text{-Cl})_2]_n$, showing the atom-



numbering scheme, the H atoms are omitted for clarity. Symmetry codes:
(i) $-x, -y+1, -z+2$; (ii) $-x+1, -y+1, -z+2$.

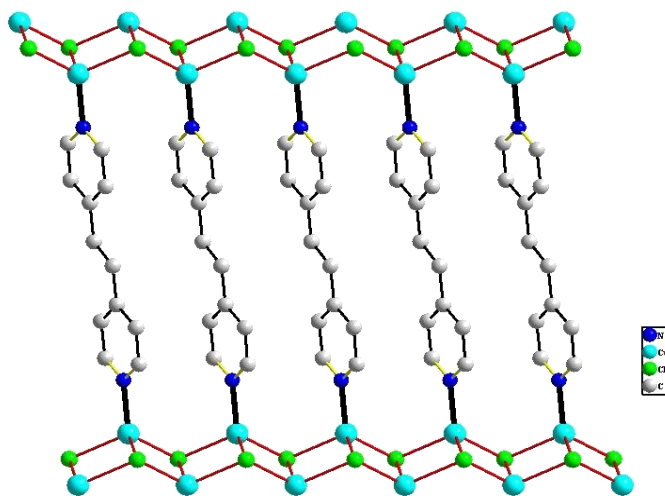


Fig. 2. Part of a polymeric sheet in the structure of $[\text{Cu}_2(\mu_2\text{-bpe})(\mu_3\text{-Cl})_2]_n$.
H atoms are omitted for clarity.

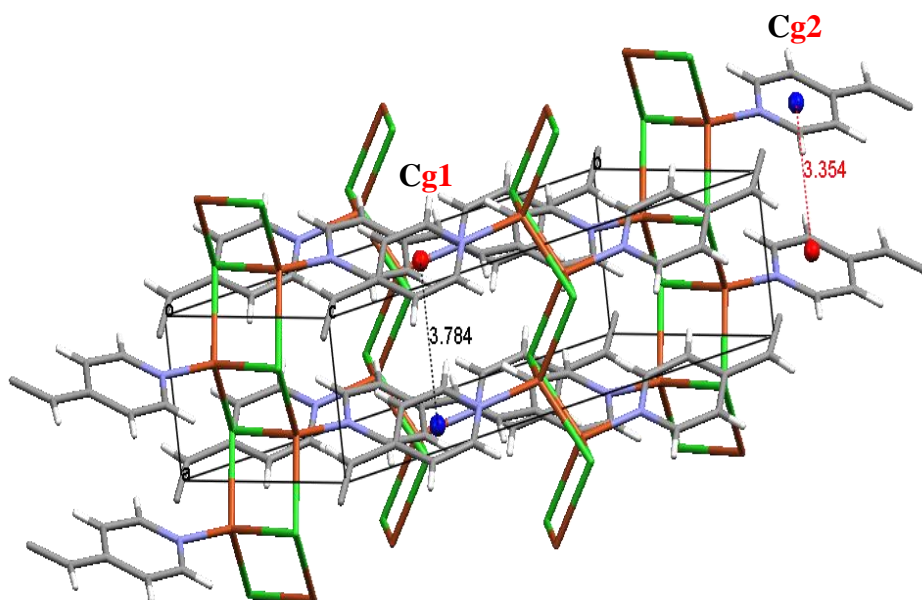


Fig 3. Fragment of the structure of $[\text{Cu}_2(\mu_2\text{-bpe})(\mu_3\text{-Cl})_2]_n$ that illustrates the $\pi \cdots \pi$ stacking interactions.



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