Hydrothermal Synthesis and Characterization of a One-Dimensional Copper(I) Halide Cluster with 1,10-Phenanthroline

YU, Jie-Hui(于杰辉)   SHI, Zhan(施展)   XU, Ji-Qing*(徐吉庆)   CUI, Xiao-Bing(崔小兵)
DING, Hong(丁红)   JING, Wei-Jie(荆维杰)   CHU, De-Qing(储德清)   HUA, Jia(华佳)
XU, Jia-Ning(徐家宁)   WANG, Tie-Gang(王铁钢)
*College of Chemistry and State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University,
Changchun, Jilin 130023, China*

The title compound Cu_2Cl_2phen (phen = 1,10-phenanthroline, $C_{12}H_8N_2$) 1 was synthesized from $CuCl_2 \cdot 2H_2O$, CuCl and phen by hydrothermal method and its structure was determined by single crystal X-ray analysis. With phen, CuCl forms one-dimensional chains, which comprise two zigzag chains based on fused Cu-X units and connected via covalent bonds. The compound contains two crystallographically unique monovalent copper ions, Cu(1) and Cu(2). The Cu(1) atom in the tetrahedral site, is coordinated to two bridging Cl^- and two N atoms in phen. The Cu(2) atom with a slightly distorted triangular planar geometry, is coordinated to three Cl^-. The compound 1 was crystallized in monoclinic, space group $P2_1/n$ with a = 0.37338(4), b = 1.9510(2), c = 1.68008(19) nm, β = 95.605 (3)°, R = 0.0458, and was characterized by elemental analysis, IR spectrum and TGA analysis.

Keywords   hydrothermal synthesis, crystal structure, copper(I) halide, 1,10-phenanthroline

Introduction

Copper(I) halides can form oligomeric (normally dimers or tetramers) and polymeric frameworks themselves. All the copper(I) halide polymeric species are based on one-dimensional chains, no examples of two-dimensional sheets have been found so far. In order to increase the dimensions of copper(I) halide framework structures, bidentate bridging N-donor ligands such as 4,4'-Bipyridyl(Bpy), Pyrazine(Pyz), Quinoxaline(Quin), and Phenazine(Phz), and so on, may be used as cooperated ligands. Blake et al.[1] and Graham et al.[2] have given a good review of results of copper(I) halides with monodentate or bidentate bridging ligands, respectively. Different topologies and arrangements of CuX clusters or infinite chains were discussed for this type of solid in their papers. The basic motifs in these complexes are the cyclic Cu_2X_2 dimer and the $[CuX]_\infty$ zigzag polymer. But the review on the syntheses and structures of copper(I) halides with bidentate chelate ligands has not been described.

The copper(I) halide frameworks were reported with bidentate chelate ligands containing N or P as auxiliary ones, which include from mononuclear species to tetranuclear discrete clusters, as well as polymeric structure. The mononuclear species are ionic such as $[Cu(phen)_2]$-ClO_4, $[Cu(phen)_2][CuBr_2]$ etc..[3] The dinuclear species are based on rhomboidal dimers of stoichiometry $[Cu_2X_2L_2]$[4,5] and the tetranuclear species on stepped cubane tetramers of stoichiometry $[Cu_4X_4L_2]$[6], respectively, while trinuclear species are very rare.[7] The copper (I) halide polymeric species are based on one-dimensional chains comprising a linear array of hexagons.[8] Here, we report the synthesis and the structure of a one-dimensional copper(I) halide cluster Cu_2Cl_2phen (1).

Experimental

Preparation

Reaction of CuCl (0.30 g), $CuCl_2 \cdot 2H_2O$ (0.51 g), phen$\cdot H_2O$ (0.89 g) and H_2O in a molar ratio of 1 : 1 : 1.5 : 300 in a 30 mL of Teflon-lined autoclave at 160 ℃ for 4 days afforded red needle crystals suitable for X-ray diffraction studies. The yield of **1** was *ca*. 20% based on CuCl.

Elemental analysis

Elemental analysis was determined by a Perkin-Elmer 240C elemental analyzer. Anal. calcd for Cu_2Cl_2-phen C 38.09, H 2.12, N 7.41, found C 37.71, H 2.13, N 7.08.

Infrared spectrum

Infrared spectrum of the title compound was recorded with a Nicolet 400 spectrophotometer in 4000—400 cm^{-1} region using a powdered sample on a KBr plate.

Thermogravimetric analysis

Thermogravimetric analysis was performed on a Perkin-Elmer TGA-7 instrument with a heating rate of 20 ℃·min^{-1} in air.

Crystal structure determination

The crystals used for X-ray work are obtained as described in preparation section. Crystal data and structure refinement details for **1** are given in Table 1. Selected bond lengths and angles for **1** are given in Table 2. Data were collected with Mo Kα radiation ($\lambda = 0.071073$ nm) using a Siemens SMART CCD diffractometer. The sample selected for investigation has dimensions of $0.06 \times 0.06 \times 0.30$ mm^3. A total of 5737 reflections were measured to give 1684 independent reflections ($R_{int} = 0.1525$). The structure was solved using direct methods with SHELXTL program[9] and refined by full-matrix least-squares techniques. The non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement (Table 3). The hydrogen atoms were treated using a riding model. The structure was then refined on F^2 using

SHELXL-97.[10] The final R value (on F) was 0.0458.

Table 1 Crystal data and structure refinement for Cu_2Cl_2phen

Empirical formula	$C_{12}H_8Cl_2Cu_2N_2$
Formula weight	378.18
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimension	$a = 0.37338(4)$ nm
	$b = 1.9510(2)$ nm
	$c = 1.68008(19)$ nm
	$\beta = 95.605(3)°$
Volume, Z	1.218(2) nm^3, 3
Density	1.547 g/cm^3
F (000)	558
Absorption coefficient	2.931 mm^{-1}
Crystal size	0.06 mm × 0.06 mm × 0.30 mm
θ range	1.60° to 23.22°
T (K)	293(2)
Reflections collected/unique	5737/1684 ($R_{int} = 0.1525$)
Data/restraints/parameters	1684/0/163
Goodness of fit indicator	0.800
Final R indicates $[I > 2\sigma(I)]$	$R_1 = 0.0458$, $wR_2 = 0.0923$
Largest diff. peak and hole	357 e/nm^3 and -406 e/nm^3

Table 2 Selected bond lengths (nm × 10^{-1}) and angles (°) for Cu_2Cl_2phen

Cu(1)—N(1)	2.027(5)
Cu(1)—N(2)	2.091(5)
Cu(1)—Cl(2)	2.2312(19)
Cu(1)—Cl(2) # 1	2.6829(18)
Cu(2)—Cl(2)	2.2263(18)
Cu(2)—Cl(1) # 2	2.235(2)
Cu(2)—Cl(1)	2.325(2)
N(1)-Cu(1)-N(2)	81.2(2)
N(1)-Cu(1)-Cl(2)	141.79(17)
N(2)-Cu(1)-Cl(2)	123.33(15)
N(1)-Cu(1)-Cl(2) # 1	109.01(15)
N(2)-Cu(1)-Cl(2) # 1	94.60(14)
Cl(2)-Cu(1)-Cl(2) # 1	98.48(6)
Cl(2)-Cu(2)-Cl(1) # 2	130.30(8)
Cl(2)-Cu(2)-Cl(1)	118.87(8)
Cl(1) # 2-Cu(2)-Cl(1)	109.91(9)
Cu(2) # 1-Cl(1)-Cu(2)	109.91(9)
Cu(2)-Cl(2)-Cu(1)	86.64(7)
Cu(2)-Cl(2)-Cu(1) # 2	80.26(6)
Cu(1)-Cl(2)-Cu(1) # 2	98.48(6)

Symmetry transformations used to generate equivalent atoms: # 1 $x - 1$, y, z; # 2 $x + 1$, y, z.

Table 3 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($nm^2 \times 10^1$) for Cu_2Cl_2phen

| Atoms	X	Y	Z	$U_{eq}{}^a$
Cu(1)	2075(3)	6257(1)	1222(1)	67(1)
Cu(2)	6603(3)	7482(1)	786(1)	69(1)
Cl(1)	1534(5)	8135(1)	963(1)	57(1)
Cl(2)	5871(4)	6426(1)	294(1)	45(1)
N(1)	1298(14)	6503(3)	2365(3)	43(1)
N(2)	736(14)	5284(3)	1626(3)	43(1)
C(1)	1610(18)	7097(4)	2738(4)	55(2)
C(2)	890(20)	7194(4)	3542(5)	65(2)
C(3)	−210(20)	6660(5)	3944(4)	60(2)
C(4)	−553(17)	6009(4)	3584(4)	49(2)
C(5)	−1714(17)	5417(4)	3979(4)	53(2)
C(6)	−1979(18)	4801(4)	3611(4)	59(2)
C(7)	−1211(16)	4730(4)	2801(4)	46(2)
C(8)	−1525(18)	4110(4)	2369(5)	58(2)
C(9)	−719(19)	4079(4)	1604(5)	61(2)
C(10)	394(19)	4678(4)	1260(4)	58(2)
C(11)	−85(15)	5302(3)	2386(4)	39(2)
C(12)	220(15)	5956(3)	2783(3)	40(2)

$^a U_{eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

Results and discussion

The title compound Cu_2Cl_2phen is constructed via a self-assembly process under mid-temperature hydrothermal conditions. Hydrothermal reactions are often sensitive to certain experimental parameters, such as temperature, solvent, stoichiometry and pH value. Using a mixture of Cu(I)/(II) as starting materials to synthesize the mixed-valence copper halide clusters, but only Cu(I) is present at the end of the reaction. Maybe $CuCl_2 \cdot 2H_2O$ plays a role in adjusting pH value of this system. The chain structure of Cu_2Cl_2phen is displayed in Fig. 1. With phen, CuCl forms [Cu_2Cl_2phen] chains that comprise a linear array of hexagons based on fused Cu_3Cl_3 units. Compound **1** contains two crystallographically unique monovalent copper ions, Cu(1) and Cu(2). The Cu(1) atom in the tetrahedral site, has a 2-fold coordination with Cl^-, leaving two sites available for the third and the fourth bonds with an additional ligand. Phen is one of the more reactive chelate rigid ligands and is just a good choice for other two sites of Cu(1). The Cu(2) atom with a slightly distorted triangular planar geometry, is coordinated to three Cl^-. Therefore, these copper atoms share corners via μ_2-Cl and μ_3-Cl to form an extended one-di-

mensional chain along the *a*-axis, as shown in Fig. 1. The Cu(1)—Cl distances, 0.22312(19)—0.26829(18) nm, the Cu(2)—Cl distances, 0.22263(18)—0.2325 (2) nm, and the Cu(1)—N distances, 0.2027(5)— 0.2091 (5) nm, are comparable with those found in [Cu_2Cl_2(dpiz)].[8] In fact, Cu_2Cl_2phen has a common motif with [Cu_2Cl_2(dpiz)], and the difference between the two compounds is that the two N atoms of the ligand are coordinated to one Cu atom in the former while two Cu atoms in the latter. The tetrahedrally coordinated copper is quite distorted, with Cl-Cu-Cl angles of 98.48(6)° and Cl-Cu-N angles range of 94.60 (14)°—141.79 (17)°. The Cl-Cu-Cl angles for the triangular copper are 109.91(9)°, 118.87(8)° and 130.30(8)°, respectively.
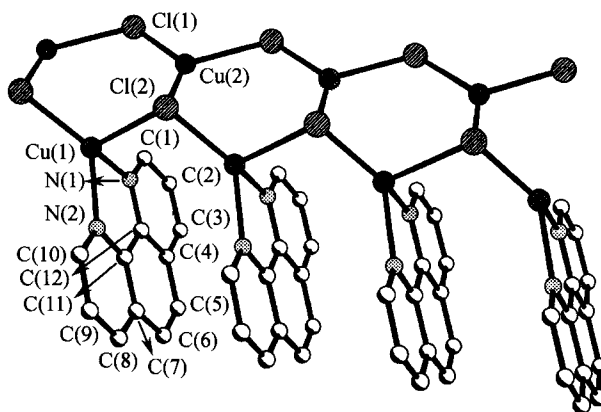
Fig. 1 Chain structure of compound **1**.

The packing diagram of unit cell of compound **1** is given in Fig. 2. It is obvious that the crystal structure contains two types of hydrogen bonds among $(CuX)_{2, \infty}$ chains: C—H···Cl [C(3A)—Cl(1) = 0.3734 nm][11] and C—H···Cu [C(3A)—Cu(2) = 0.3525 nm][12], respectively. The one-dimensional chains are connected via these hydrogen bonds along *c*-axis, and the compound is constructed to two-dimensional supramolecular network.

The IR spectrum of **1** displays the complex absorption corresponding to coordinated phen[13] at 3043, 1618, 1506, 1419 cm^{-1}. The thermal behavior of **1** was studied from 30 ℃ to 700 ℃. The TGA curve indicates only one stage of weight-loss. In fact, it is not one-step decomposition. Compound **1** was thermally stable up to around 360 ℃, and then began to decompose. Before ligand phen did not completely decompose, copper halides (m.p. 430 ℃[14]) had begun to vaporize, meanwhile copper ions were oxidized. After decomposition of **1** at high temperature,

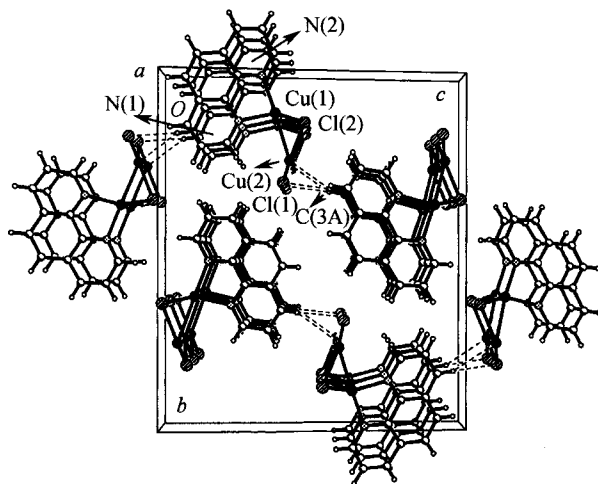the residues were copper oxides, which is also comparable with the result found in [Cu₂Cl₂(dpiz)].

Fig. 2   Packing diagram of unit cell for Cu₂Cl₂phen.

References

1   Blake, A. J.; Brooks, N. R.; Champness, N. R.; Cooke, P. A.; Deveson, A. M.; Fenske, D.; Hubberstey, P.; Li, W.-S.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1999**, 2103.

2   Graham, P. M.; Pike, R. D.; Sabat, M.; Bailey, R. D.; Pennington, W. T. *Inorg. Chem.* **2000**, *39*, 5121.

3   Healy, P. C.; Engelhardt, L. M.; Partrick, V. A.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1985**, 2541.

4   Healy, P. C.; Pakawatchai, C.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1985**, 2531.

5   Skelton, B. W.; Waters, A. F.; White, A. H. *Aust. J. Chem.* **1991**, *44*, 1207.

6   Nardin, G.; Randaccio, L. *Acta Cryst.* **1974**, B*30*, 1377.

7   Nardin, G.; Randaccio, L.; Zangrando, E. *J. Chem. Soc., Dalton Trans.* **1975**, 2566.

8   Lu, J. Y.; Cabrera, B. R.; Wang, R.-J.; Li, J. *Inorg. Chem.* **1998**, *37*, 4480.

9   *SHELXTL*, version 5.1; Siemens. Industrial Automation, Inc., **1997**.

10   Sheldrick, G. M. *SHELXL97*. Program for the Refinement of Crystal Structures. University of Göttingen, Germany, **1990**.

11   Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

12   Braga, D.; Grepioni, F.; Tedesco, E.; Biradha, K.; Desiraju, G. R. *Organometallics* **1997**, *16*, 1846.

13   Vinikii, D. M.; Solntsev, K. A.; Kuznetsov, N. T.; Goeva, L. V. *Zh. Neorg. Khim.* **1986**, *31*, 2326.

14   Bailar, J. C.; Emeleus, H. J.; Nyholm, S. R.; Trotman-dickenson, A. F. *Comprehensive Inorganic Chemistry*. Toronto, Sydney, Braunschweig, Pergamon press, Oxford, New York, **1973**, *3*, 27.