



## Solvothermal Synthesis, Characterization and Crystal Structure of a New Supramolecular Compound Composed by 1,10-Phenanthroline Ligand with Bi(III) and Cu(II)

YI-SHENG YANG<sup>1</sup>, WEN-XIANG CHAI<sup>1,2,\*</sup>, LI SONG<sup>3</sup>, HONG-SHENG SHI<sup>1</sup> and LAI-SHUN QIN<sup>1</sup>

<sup>1</sup>College of Materials Science and Engineering, China Jiliang University, Hangzhou 310018, P.R. China

<sup>2</sup>State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P.R. China

<sup>3</sup>Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou 310018, P.R. China

\*Corresponding author: Fax: +86 571 86835608; Tel: +86 571 86835738; E-mail: wxchai\_cm@yahoo.com.cn

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The solvothermal reaction of bismuth(III) iodide, 1,10-phenanthroline (phen) and copper(I) iodide in ethanol solution yielded the supramolecular compound, namely  $[\text{Cu}^{\text{I}}(\text{phen})_2] \cdot [\text{Bi}^{\text{III}}(\text{phen})_4\text{I}_4]$  (**1**). The crystallizing sample was characterized by elementary analysis. Its structure was determined by single crystal X-ray diffraction experiment. The compound crystallizes in the monoclinic system and adopts a centrosymmetric space group of  $P2_1/c$ . The asymmetric unit contains one  $[\text{Cu}^{\text{I}}(\text{phen})_2]^+$  cation and one  $[\text{Bi}^{\text{III}}(\text{phen})_4\text{I}_4]^-$  anion. The Cu(I) is coordinated by two 1,10-phenanthroline ligands with a tetrahedral geometry. In the anion, the Bi(III) adopt a octahedral coordination sphere constructed by two N atoms from one phen ligand and four I<sup>-</sup>. By virtue of  $\pi$ - $\pi$  stacking interaction, all adjacent cations connect each other along c axis direction and form a column-like supramolecular structure. And along the crystal plane group of  $\{1\ 0\ 0\}$ , these columns are fused together by all  $[\text{Bi}(\text{phen})_4\text{I}_4]^-$  anions through other  $\pi$ - $\pi$  stacking interactions to form a wave-like supramolecular layer.

**Key Words:** Solvothermal synthesis,  $\pi$ - $\pi$  Stacking interaction, Supramolecular structure.

### INTRODUCTION

During the past few decades, supramolecular compounds have received much more attentions due to their importance for the study of biological systems and their potential applications in material research, as sensors, gas storage, *etc.*<sup>1-3</sup>. Usually, in all supramolecular systems, hydrogen bonding and aromatic stacking interactions are two main cohesions to form supramolecules. Previously, organic-inorganic hybrid materials based on heavy *p*-block metal halide (SnI<sub>2</sub>, PbI<sub>2</sub>, BiCl<sub>3</sub>, BiI<sub>3</sub>, *etc.*) have received considerable attention due to their fascinating variety of structures and properties including semiconducting, nonlinear optical, luminescent, photochromic, *etc.*<sup>4-6</sup>. The halide metalate anions is the key component of these hybrid materials for their properties<sup>5</sup>. There are often some halide-halide supramolecular interactions between halide metalate anions. So far, many supramolecular systems containing halometallate groups as their main component have been reported<sup>4,7-9</sup>. For synthesizing new supramolecular compound containing halometallate groups, we have employed some aromatic ligands, *e.g.*, 1,10-phenanthroline, to assemble with Bi-I system. Here, we report the synthesis and crystal structure of a supramolecular compound  $[\text{Cu}(\text{phen})_2][\text{Bi}(\text{phen})_4\text{I}_4]$  (**1**).

### EXPERIMENTAL

All chemicals were obtained from commercial sources and used as received. Elemental analysis for C, H and N were performed on an Elementar Vario MICRO analytic instrument.

**Synthesis of  $[\text{Cu}(\text{phen})_2][\text{Bi}(\text{phen})_4\text{I}_4]$  (**1**):** The compound **1** was synthesized by solvothermal reaction of BiI<sub>3</sub> (60 mg, 0.1 mmol), Cu<sub>2</sub>I<sub>2</sub> (19 mg, 0.1 mmol) and 1,10-phenanthroline monohydrate (60 mg, 0.3 mmol) in 7 mL ethanol. The mixture was heated to 413 K at the rate of 20 K/h and kept at this temperature for 2 days and then cooled to room temperature at the rate of 2 K/h. The red crystals of compound **1** were obtained in a yield of 57 % (75 mg). Anal. calcd. for C<sub>36</sub>H<sub>24</sub>N<sub>6</sub>I<sub>4</sub>BiCu (%): C, 32.74; H, 1.83; N, 6.36. Found: C, 32.46; H, 1.63; N, 6.87.

**Single crystal structure determination:** X-ray intensity data of compound **1** were collected on a red prism crystal (0.23 mm × 0.20 mm × 0.20 mm) at 293 ± 2 K on a Rigaku RAXIS-RAPID CCD area detector diffractometer using graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.071075$  nm). The structure was solved using direct methods and refined by full-matrix least-squares techniques. All non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement. All hydrogen atoms were added at calculated positions and

refined using a riding model. The structure was refined on  $F^2$  using SHELXTL-97 software package<sup>10</sup> without any unusual events. The crystal and refinement details for compound **1** are listed in Table-1. Selected bond lengths and angles are given in Table-2.

TABLE-1  
CRYSTAL DATA, COLLECTION AND STRUCTURE  
REFINEMENT PARAMETERS FOR COMPOUND **1**

Parameters	<b>1</b>
Empirical formula	$C_{24}H_{16}N_4Cu \cdot C_{12}H_8N_2BiI_4$
Formula weight	1320.73
Temperature (K)	$293 \pm 2$
Crystal system	Monoclinic
Space group	$P2_1/c$
Crystal size ( $mm^3$ )	$0.23 \times 0.20 \times 0.20$
Crystal description	Prism, red
a (Å)	14.964 (3)
b (Å)	17.253 (3)
c (Å)	15.662 (3)
$\beta$ (°)	100.74 (3)
Volume V (Å <sup>3</sup> )	3762.0 (12)
Z	4
Dcalc (Mg m <sup>3</sup> )	2.332
$\mu$ (mm <sup>-1</sup> )	8.55
F(000)	2424
Final R indices [ $I > 2\sigma(I)$ ] <sup>#</sup>	R1 = 0.0518, wR2 = 0.1569
R indices (all data) <sup>#</sup>	R1 = 0.0600, wR2 = 0.1661
Goodness-of-fit <sup>#</sup> on $F^2$	1.065
<sup>#</sup> $R1 = \sum ( F_o  -  F_c ) / \sum  F_o $ ; $wR2 = \left\{ \sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \right\}^{0.5}$	

TABLE-2  
SELECTED BOND LENGTHS (Å) AND  
ANGLES (°) OF THE COMPOUND **1**

Bi1-I1	3.0390(10)	Bi1-I2	3.0140(9)
Bi1-I3	3.0610(7)	Bi1-I4	3.0194(8)
Bi1-N1	2.527(7)	Bi1-N2	2.519(7)
Cu1-N3	2.015(6)	Cu1-N4	2.065(8)
Cu1-N5	2.079(7)	Cu1-N6	1.991(7)
I1-Bi1-I2	102.27(3)	I1-Bi1-I3	96.47(2)
I1-Bi1-I4	96.74(2)	N1-Bi1-I1	158.18(16)
N2-Bi1-I1	93.54(16)	I2-Bi1-I3	93.52(2)
I2-Bi1-I4	96.91(3)	N1-Bi1-I2	99.31(17)
N2-Bi1-I2	163.97(17)	I4-Bi1-I3	161.030(19)
N1-Bi1-I3	85.31(15)	N2-Bi1-I3	81.96(16)
N1-Bi1-I4	77.41(15)	N2-Bi1-I4	83.69(16)
N2-Bi1-N1	65.1(2)	N3-Cu1-N4	82.7(3)
N3-Cu1-N5	130.2(3)	N6-Cu1-N3	132.3(3)
N6-Cu1-N4	123.2(3)	N4-Cu1-N5	108.6(3)
N6-Cu1-N5	82.6(3)	-	-

## RESULTS AND DISCUSSION

We have synthesized the supramolecular compound  $[Cu(phen)_2][Bi(phen)_4I_4]$  (**1**) (Fig. 1). In compound **1**, the Bi atom is located in a distorted octahedral environment of four iodine atoms and two nitrogen atoms from the 1,10-phenanthroline ligand. In this  $BiN_2I_4$  octahedron, the Bi1-N1 = 2.527 (7) Å, Bi1-N2 = 2.519 (7) Å, Bi1-I1 = 3.039 (1) Å, Bi1-I2 = 3.0140 (9) Å, Bi1-I3 = 3.0610 (7) Å, Bi1-I4 = 3.0194 (8) Å. All bond lengths are within commonly accepted values in the literature<sup>8,9,11</sup>. A  $[Cu(phen)_2]^+$  cation balances charge in the salt. This coordinated cation has been reported elsewhere<sup>12</sup>, with

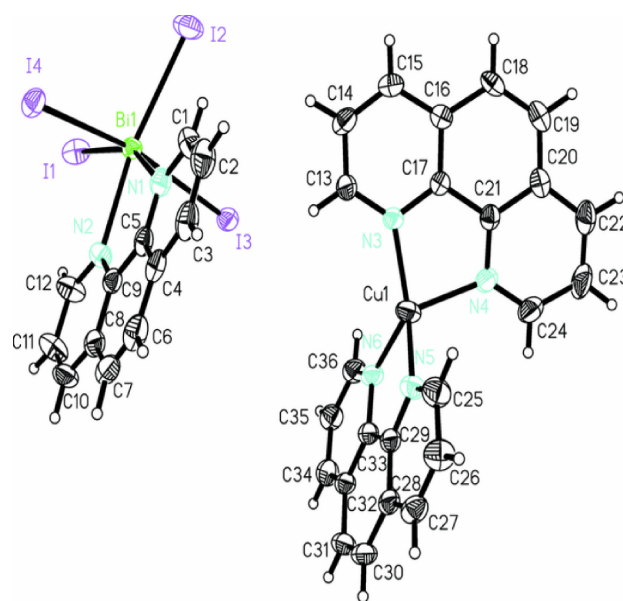


Fig. 1. Structure and labeling of the compound **1**, with displacement ellipsoids drawn at the 30 % probability level and H atoms shown as small spheres of arbitrary radii

the copper(I) also located in a distorted tetrahedral coordination sphere. In this  $CuN_4$  distorted tetrahedron, the Cu1-N3 = 2.015 (6) Å, Cu1-N4 = 2.065 (8) Å, Cu1-N5 = 2.079 (7) Å, Cu1-N6 = 1.991 (7) Å, which are all similar to that of the previous reports. In the crystal structure of **1**, three pairs of offset face-to-face aromatic  $\pi$ - $\pi$  stacking interactions lead to the formation of a two-dimensional supramolecular wave-like layer. Firstly, along the c axis direction, all adjacent cations of  $[Cu(phen)_2]^+$  are joined each other by virtue of one pair of  $\pi$ - $\pi$  stacking interaction between two 1,10-phenanthroline ligands to form a 1-D supramolecular column structure<sup>13</sup>. The phen skeletons are arranged in a almost parallel fashion; ring 1 (C28-C33) [symmetry code: (x, y, z)] of one cation stacks with ring 2 (C16A-C21A) [symmetry code: (x, 1/2 - y, 1/2 + z)] of a neighbouring cation with an interplanar distance of 3.311 (6) Å and angle of 3.9°. Two adjacent  $[Bi(phen)_4I_4]^-$  connect each other *via* the second pair of  $\pi$ - $\pi$  stacking interaction between two phen ligands to form a centrosymmetric anionic pair. The phen skeletons are arranged in a absolute parallel fashion; ring 3 (C4-C9) [symmetry code: (x, y, z)] of one anion stacks with ring 4 (C4B-C9B) [symmetry code: (1 - x, 1 - y, 2 - z)] of a neighbouring anion with an interplanar distance of 3.304 (9) Å. And then, along the crystal plane group of  $\{1\ 0\ 0\}$ , adjacent supramolecular columns are fused together by the anionic pair of two  $[Bi(phen)_4I_4]^-$  through the third pair of  $\pi$ - $\pi$  stacking interaction between some phen ligands form cationic columns and anionic pairs. The phen skeletons are arranged in a almost parallel fashion; ring 2 (C16A-C21A) [symmetry code: (x, 1/2 - y, 1/2 + z)] of one cation stacks with ring 3 (C4-C9) [symmetry code: (x, y, z)] of a neighbouring anion with an interplanar distance of 3.258 (8) Å and angle of 5.7°. As a result, through these  $\pi$ - $\pi$  stacking interactions, the supramolecular columns stack one by one to present a two-dimensional supramolecular layer (Fig. 2). The packing diagram of **1** viewed along the c-direction is shown in Fig. 3.

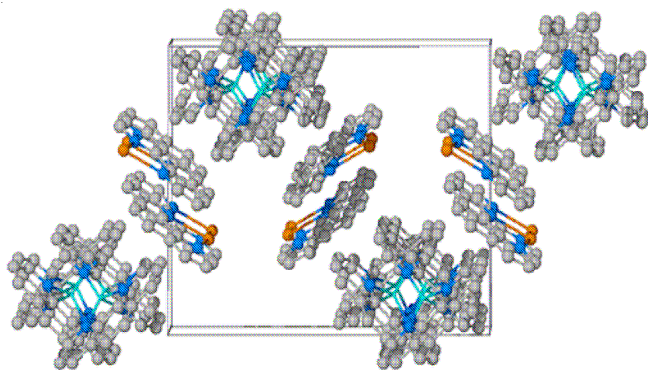


Fig. 2. Supramolecular organic-inorganic hybrid wave-like layer constructed by  $\pi$ - $\pi$  stacking interactions, viewed along the c-direction

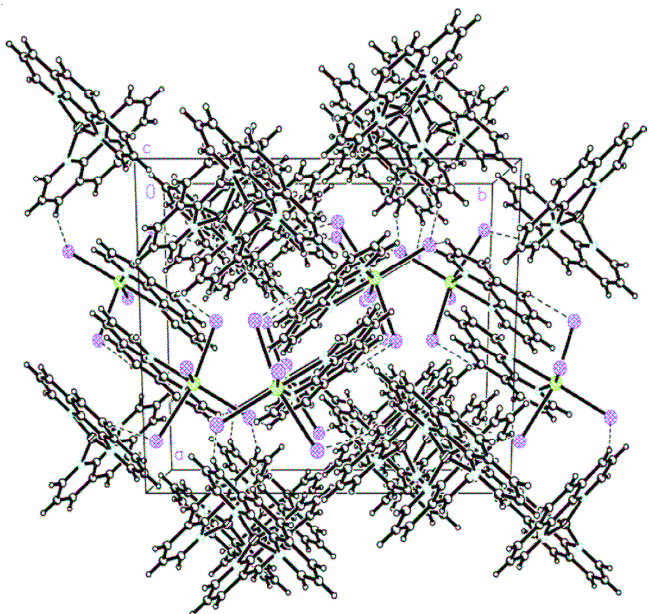


Fig. 3. Packing diagram viewed along the c-direction

## Conclusion

In conclusion, we have synthesized the supramolecular compound  $[\text{Cu}(\text{phen})_2][\text{Bi}(\text{phen})\text{I}_4]$ . All adjacent cations connect each other to give out a supramolecular column through a pair of  $\pi$ - $\pi$  stacking interaction. And all anions fused these columns together by other  $\pi$ - $\pi$  stacking interactions to form a wave-like supramolecular layer structure.

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