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# Syntheses, crystal structures and luminescent properties of three new halogencuprate(I) complexes with 4-(trimethylammonio) phenyldisulphide

Jin-Xiang Chen<sup>a</sup>, Yong Zhang<sup>a</sup>, Zhi-Gang Ren<sup>a</sup>, Jian-Ping Lang<sup>a,b,\*</sup>

<sup>a</sup>Key Laboratory of Organic Synthesis of Jiangsu Province, School of Chemistry and Chemical Engineering, Suzhou University, 1 Shizi Street, Suzhou 215006, Jiangsu, P. R. China <sup>b</sup>State Key Laboratory of Structural Chemistry of FJIRSM, Chinese Academy of Sciences, Fuzhou 350002, Fujian, P. R. China

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#### Abstract

Reactions of CuX (X=I, Br) with TabHPF<sub>6</sub> (Tab=4-(trimethylammonio)benzenethiolate) under the existence of Et<sub>3</sub>N or Et<sub>4</sub>NI in open air gave rise to three novel halogencuprate(I) complexes with 4-(trimethylammonio)phenyldisulphide (Tab–Tab): [Tab–Tab][CuX<sub>3</sub>] (1: X = I; 2: X=Br) and {[Tab–Tab][Cu<sub>2</sub>I<sub>4</sub>]}<sub>n</sub> (3). Compounds 1–3 are characterized by elemental analysis, IR spectra and X-ray crystallography. It was found that the Tab–Tab dication in 1–3 serves as a counterion to maintain the electrical neutrality of 1–3. The dianions of 1 and 2 have planar triangular geometry with each halide atom being bound to the central trigonally coordinated copper atom. The dianion structure of 3 has a unique one-dimensional wavy chain composed of butterfly shaped [Cu<sub>2</sub>I<sub>3</sub>] units linked by  $\mu$ -I bridges. The luminescence properties of 1–3 along with [Tab–Tab]I<sub>2</sub> have also been investigated.

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Keywords: Synthesis; Crystal structure; Halogencuprate(I); 4-(Trimethylammonio)phenyldisulphide; Luminescence

#### 1. Introduction

As in past decades, much interest in the recognition of the disulphide continues to be motivated by its application as potential ligand for metal ions in biological system [1–3]. The stability of the metal/disulphide complexes has been studied and some of them are structurally determined [4–14]. These metal/disulphide complexes are often prepared through the reactions of metal salts with neutral organic disulphide [4–9]. However, only a few have been made from metal salts with thiolates [10–14]. In these cases, the thiolates used may be oxidized into cationic disulfides by various oxidizing agents such as oxygen, nitric acid, hydrogen peroxide, dimethyl sulfoxide and potassium ferricyanide.

On the other hand, we are interested in the preparation of metal/thiolate complexes from the unique cationic thiol

TabHPF<sub>6</sub> (Tab=4-(trimethylammonio)benzenethiolate), and so far several silver/Tab compounds have been isolated and structurally determined [15,16]. However, when Hg(II) salt was allowed to react with TabHPF<sub>6</sub>, no Hg/Tab complex but a Hg(II) complexes with Tab–Tab dication was isolated [12]. The resulting Tab–Tab dication in this compound was probably derived from the oxidation of Tab ligand by oxygen in open air. As an extension of this study, we carried out the reactions of CuX (X=I, Br) with TabHPF<sub>6</sub>, and three new halogencuprate complexes with the Tab–Tab dication, [Tab–Tab][CuX<sub>3</sub>] (1: X=I; 2: X=Br) and {[Tab–Tab][Cu<sub>2</sub>I<sub>4</sub>]}<sub>n</sub> (3), were obtained therefrom. Herein we report their syntheses, crystal structures and luminescent properties.

#### 2. Experimental

#### 2.1. General

TabHPF<sub>6</sub> and  $[Tab-Tab]I_2$  were prepared according to the literature method [17]. Other chemicals and reagents

<sup>\*</sup> Correspondence author. Tel.: +86 512 65213506; fax: +86 512 65224783.

E-mail address: jplang@suda.edu.cn (J.-P. Lang).

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were obtained from commercial sources and used as received. All solvents were predried over activated molecular sieves and refluxed over the appropriate drying agents under argon. The IR spectra were recorded on a Nicolet MagNa-IR 550 as KBr disk ( $4000-400 \text{ cm}^{-1}$ ). The elemental analyses for C, H, and N were performed on an EA1110 CHNS elemental analyzer. The photoluminescent spectra were performed on a Perkin–Elmer LS55 spectrofluorometer.

# 2.2. Syntheses

#### 2.2.1. Synthesis of $[Tab-Tab][CuI_3]$ (1)

To a suspension containing TabHPF<sub>6</sub> (125.2 mg, 0.4 mmol) in MeOH (5 ml) was added Et<sub>3</sub>N (0.25 ml). The resulting colorless solution was then treated with a solution of CuI (39 mg, 0.2 mmol) in MeCN (10 ml). The mixture was stirred for 0.5 h and then filtered. Diethyl ether (10 ml) was allowed to diffuse into the light yellow filtrate. After standing it at ambient temperature for several weeks, a large amount of insoluble gray materials were precipitated coupled with yellow block crystals of  $[Tab-Tab][CuI_3]$  (1), which were separated by decanting off the gray solids with large amount of MeOH/E2O (v/v=1:5), washed by Et<sub>2</sub>O and dried in vacuo. Yield: 19 mg (12% based on Cu). Anal. Calcd. for C<sub>18</sub>H<sub>26</sub>CuI<sub>3-</sub> N<sub>2</sub>S<sub>2</sub>: C, 27.76; H, 3.37; N, 3.60. Found: C, 27.53; H, 3.20; N, 3.32. IR (KBr disc): 1621 (w), 1489 (m), 1416 (w), 1126 (w), 1009 (w), 837 (w), 680(w), 548 (m),  $481(w) \text{ cm}^{-1}$ 

#### 2.2.2. Synthesis of $[Tab-Tab][CuBr_3]$ (2)

The preceding method was employed with TabHPF<sub>6</sub> (125.2 mg, 0.4 mmol), Et<sub>3</sub>N (0.25 ml), and CuBr (28.6 mg, 0.2 mmol) to form yellow platelets of [Tab–Tab][CuBr<sub>3</sub>] (**2**) . Yield: 32.8 mg (35% based on Cu). Anal. calcd for  $C_{18}H_{26}CuBr_{3}N_{2}S_{2}$ : C, 22.97; H, 2.78; N, 2.98. Found: C, 22.78; H, 2.53; N, 2.79. IR (KBr disc): 1621 (w), 1489 (m), 1413(w), 1126 (w), 1009 (w), 837 (w), 680 (w), 548 (m), 481 (w) cm<sup>-1</sup>.

#### 2.2.3. Synthesis of $\{[Tab-Tab][Cu_2I_4]\}_n$ (3)

To a solution containing CuI (78 mg, 0.4 mmol) in MeCN (15 ml) was added Et<sub>4</sub>NI (102.6 mg, 0.4 mmol). The resulting light yellow solution was treated with a solution of TabHPF<sub>6</sub> (125.0 mg, 0.4 mmol) in MeCN (15 ml). The mixture was stirred for 1 h and filtered to give a bright yellow solution. Diethyl ether (20 ml) was allowed to diffuse into the filtrate. After standing it at ambient temperature for about one week, yellow prisms of {[Tab–Tab][Cu<sub>2</sub>I<sub>4</sub>]}<sub>n</sub> (**3**) were formed, which were collected by filtration, washed by Et<sub>2</sub>O and dried in vacuo. Yield: 180.3 mg (93% based on Cu). Anal. calcd for C<sub>18</sub>H<sub>26</sub>Cu<sub>2</sub>I<sub>4</sub>N<sub>2</sub>S<sub>2</sub>: C, 22.30; H, 2.70; N, 2.89. Found: C, 22.45; H, 3.02; N, 3.12. IR (KBr disc): 1623 (w),

1485 (m), 1415 (w), 1126 (w), 1006 (w), 837 (s), 679 (w), 549 (m), 480 (w) cm<sup>-1</sup>.

#### 2.3. X-ray structure determination

All measurements were made on a Rigaku Mercury CCD X-ray diffractometer by using graphite monochromated Mo K $\alpha$  ( $\lambda$ =0.71070 Å). Crystals of 1-3 suitable for X-ray analysis were obtained directly from the above preparations. A yellow block crystal of 1 with dimensions  $0.45 \times 0.40 \times 0.10$  mm, a yellow platelet of 2 with dimensions of  $0.40 \times 0.36 \times 0.08$  mm and a yellow prism of **3** with dimensions of  $0.35 \times 0.20 \times 0.15$  mm were mounted at the top of a glass fiber, and cooled at 193 K in a liquid nitrogen stream. Diffraction data were collected at  $\omega$  mode with a detector-to-crystal distance of 34.63 mm (1), 34.52 mm (2) and 34.62 mm (3), respectively. Cell parameters were refined by using the program Crystalclear (Rigaku and MSc, Ver. 1.3, 2001) on all observed reflections between  $\theta$  of 3.2 and 25.3° (1) , 3.2 and 25.3° (2), 3.1 and 27.5° (3). A total of 720 (1, 2, 3) oscillation images were collected in the range 6.4 < $2\theta < 50.6^{\circ}$  for **1**,  $6.4 < 2\theta < 50.6^{\circ}$  for **2** and  $6.2 < 2\theta < 55^{\circ}$ for 3. The collected data were reduced by using the program CrystalClear (Rigaku and MSC, Ver.1.3, 2001), and an absorption correction (multiscan) was applied, which resulted in transmission factors ranging from 0.110 to 0.617 for 1, from 0.09 to 0.597 for 2, and from 0.235 to 0.385 for 3. The reflection data were also corrected for Lorentz and polarization effects. The largest electrondensity peak (1.314 e Å<sup>-3</sup>) in **1** was located 1.01(2) Å from atom I(2) while that  $(1.450 \text{ e} \text{ Å}^{-3})$  in 2 was 0.98 (1) Å from atom Br(2).

The crystal structures of 1-3 was solved by direct methods and refined on  $F^2$  by full-matrix least square methods with sheLXTL-97 program [18]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on their calculated positions and included in the refinement of the structure factors. The final refinement was based on 3815 (1), 2711 (2) and 5511 (3) reflections with  $I > 2.00\sigma(I)$ , and 242 (1), 242 (2) and 260 (3) variable parameters, and  $w = 1/[\sigma^2(F_a^2) + (0.0567P)^2]$ (1),  $w = 1/[\sigma^2(F_o^2) + (0.0600P)^2]$  (2),  $w = 1/[\sigma^2(F_o^2) +$  $(0.0416P)^2 + 20.424P$ ] (3) where  $P = (F_o^2 + 2F_c^2)/3$ . A summary of the key crystallographic information for 1-3 is tabulated in Table 1. Crystallographic data for the structural analysis have been deposited with Cambridge Crystallographic Data Centre, CCDC reference numbers 251149 (1), 267597 (2) and 251150 (3). These data can be obtained free of charge at www.ccdc.cam.ac.uk/ retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.)+44 1223/336 033; E-mail: deposit@ ccdc.cam.ac.uk].

Table 1
Crystallographic data for 1, 2 and 3

Compound	1	2	3
Molecular formula	$C_{18}H_{26}CuI_{3}N_{2}S_{2}$	$C_{18}H_{26}CuBr_3N_2S_2$	$C_{18}H_{26}Cu_2I_4N_2S_2$
Formula weight	778.80	637.80	969.25
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	P-1	P-1	Pbca
a (Å)	7.6778(6)	7.3652(6)	19.8478(8)
<i>b</i> (Å)	10.3539(9)	10.1272(9)	10.4870(4)
<i>c</i> (Å)	15.851(1)	15.4426(14)	25.7427(12)
$\alpha$ (degrees)	84.740(5)	84.016(5)	84.016(5)
$\beta$ (degrees)	79.653(4)	81.344(5)	
$\gamma$ (degrees)	84.621(4)	86.957(5)	
$V(\text{\AA}^3)$	1230.5(2)	1131.70(17)	
Ζ	2	2	8
<i>T</i> /K	193	193	193
$D_{\rm calc} ({\rm g}~{\rm cm}^{-3})$	2.102	1.872	2.403
$\lambda$ (Mo-K $\alpha$ ) (Å)	0.71070	0.71070	0.71070
$\mu$ (cm <sup>-1</sup> )	48.27	64.52	63.61
$2\theta_{\rm max}$ (degrees)	50.60	55.6	55.0
Total reflections	11953	11223	60622
Unique reflections	4449 ( $R_{\rm int} = 0.042$ )	$4119(R_{\rm int}=0.060)$	$6133 (R_{int} = 0.046)$
No. of observations	$3815(I > 2.00\sigma(I))$	$2711(I > 2.00\sigma(I))$	$5511(I > 2.00\sigma(I))$
No. of parameters	242	242	260
$R^{\mathrm{a}}$	0.0396	0.0684	0.0412
wR <sup>b</sup>	0.0952	0.1609	0.0942
GOF <sup>c</sup>	0.0972	1.052	1.109
$\Delta \rho_{\rm max}$ (e Å <sup>-3</sup> )	1.314	1.450	0.825
$\Delta \rho_{\min} (e \text{ Å}^{-3})$	-1.332	-1.844	-0.819

<sup>a</sup>  $R = \sum ||F_o| - |F_c|/|F_o|.$ 

 $\frac{1}{b} wR = \{\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2\}^{1/2}.$   $\frac{1}{c} GOF = \{\Sigma [w((F_o^2 - F_c^2)^2) / (n-p)\}^{1/2}, \text{ where } n = \text{number of reflections and } p = \text{total numbers of parameters refined.}$ 

# 3. Results and discussion

#### 3.1. Preparation and characterization of 1-3

Treatment of a suspension of TabHPF<sub>6</sub> in MeOH with excess Et<sub>3</sub>N afforded a colorless solution, to which was added a solution containing 1/2 equivalent of CuI in MeCN. The resulting yellow solution was stirred at room temperature for 0.5 h and then filtered. Diffusion of Et<sub>2</sub>O into the filtrate afforded yellow block crystals of [Tab-Tab]  $[CuI_3]$  (1) in 12% yield. The analogous bromide compound [Tab-Tab][CuBr<sub>3</sub>] (2) was prepared as starting from CuBr with 35% yield. On the other hand, reaction of CuI with Et<sub>4</sub>NI in MeCN afforded a homogenous yellow solution, which was treated with a solution of TabHPF<sub>6</sub> in MeCN. Similar workup to that used in the isolation of 1 or 2 led to the formation of  $\{[Tab-Tab][Cu_2I_4]\}_n$  (3) in 93% yield (Scheme 1). In the former reactions (1 and 2), the cationic thiol TabH<sup>+</sup> was deprotonated by Et<sub>3</sub>N into a zwitterionic species Tab, which may be further oxidized by  $O_2$  in air to generate the Tab-Tab disulfide dication. In the latter reaction (3), the proton of the thiol  $TabH^+$  may be removed during the oxidation of this thiol via O2 into the Tab-Tab dication. In all three cases, the resulting Tab-Tab dication acted as a counterion to stabilize the halogencuprate(I) anions in solution, e.g.  $[CuX_3]^{2-}$  in **1** or **2** and  $[Cu_2I_4]^{2-}$  in 3. Intriguingly, the formation of 1 or 2 was reproducible, but was always accompanied with a large amount of gray materials, which may be one main reason for the relatively low yield for 1 or 2. Such gray solids were insoluble in common organic solvents, which excluded their structural characterization. Currently it is very difficult to explain the formation of  $[CuX_3]^{2-}$  anions in **1** or **2**.

Compounds 1-3 were relatively stable toward oxygen and moisture. They were not soluble in common organic solvents but soluble in water. The elemental analyses of 1-3



Scheme 1.



Fig. 1. The perspective view of the structure of 1.

were consistent with their chemical formula. In the IR spectra of **1–3**, characteristic bands due to vibrations of Ph (1621, 1489, 1416 cm<sup>-1</sup>) and S–S bond (480–481 cm<sup>-1</sup>) were observed. The identities of **1–3** were finally confirmed by X-ray crystallography.

Table 2 Selected bond distances  $({\rm \AA})$  and angles (degrees) for  $1,\,2$ 

1		2	
Cu(1)–I(1)	2.5091(7)	Cu(1)–Br(1)	2.3771(15)
Cu(1)-I(2)	2.5465(7)	Cu(1)-Br(2)	2.3736(15)
Cu(1) = I(3) S(1) = S(2)	2.5555(7) 2.0538(17)	Cu(1) = Br(3) S(1) = S(2)	2.3498(14)
I(1)-Cu(1)-I(3)	120.79(3)	Br(3)-Cu(1)-Br(2)	118.16(6)
I(1)-Cu(1)-I(2)	122.09(3)	Br(3)–Cu(1)–Br(1)	123.73(6)
I(3)-Cu(1)-I(2)	117.11(3)	Br(2)- $Cu(1)$ - $Br(1)$	118.09(6)

## 3.2. Crystal structures of 1 and 2

Having a common chemical formula [Tab-Tab][CuX<sub>3</sub>], 1 and 2 both crystallize in the triclinic space group P-1, and the asymmetric unit contains one discrete Tab-Tab dication and one  $[CuX_3]^{2-}$  dianion (1: X=I; 2: X=Br). Their cell parameters are essentially identical, as are the crystal structures. Therefore only the perspective view of 1 is shown in Fig. 1. Selected bond lengths and angles for 1 and **2** are compared in Table 2. The  $[CuX_3]^{2-}$  dianions in **1** and 2 are common, and can be found in several compounds [19–23]. It has a planar triangular geometry with each halide atom being bonded to the central trigonally coordinated copper atom. This anion does not possess strict three-fold symmetry in the solid state in that the Cu-X bond lengths and X-Cu-X bond angles are not well equivalent. The mean Cu-I bond length and I-Cu-I bond angle of 1 are 2.530(7) Å and 119.99(3)°, which are comparable to those observed in



Fig. 2. One-dimensional double-chain formed via the hydrogen bonding interactions in 1.

Table 3	
Comparison on the S-S Bond Lengths (Å) and	CSSC torsion angle (degrees) in some disulphide compounds

Compounds	S-S Bond lengths	CSSC torsion angle	Ref.	
$\{ [C_{10}H_{10}N_2S_2] [Cu_2Cl_6] [BF_4]_2 \}_n^a$	2.032(1)	81.5(2)	[4]	
$[C_{12}H_{26}N_2S_2][CuCl_4]^b$	2.02(2)	90.0(1)	[10]	
$[{Me_2NH(CH_2)_3S}_2][CdBr_4]$	2.013(3)	74.83(1)	[11]	
[C <sub>10</sub> H <sub>22</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub> ]Cl <sub>2</sub> <sup>c</sup>	2.049(3)	114.71(2)	[24]	
$L-L\cdot 0.5C_6H_5CH_3^d$	2.0628(5)	86.3(2)	[25]	
$[C_8H_{22}N_2S_2]Cl_2^e$	2.075(5)	82.39(2)	[26]	
1	2.0538(17)	82.1(4)	This work	
2	2.049(3)	81.9(5)	This work	
3	2.026(2)	80.4(4)	This work	

<sup>a</sup>  $C_{10}H_{10}N_2S_2 = bis(4-pyridinium)disulfide.$ 

<sup>b</sup>  $C_{12}H_{26}N_2S_2 = bis[4-N-methylpiperidinium]disulfide$ 

<sup>c</sup>  $[C_{10}H_{22}N_2O_4S_2][Cl]_2 = 3, 3, 3', 3'$ -tetramethyl<sub>-D</sub>-cystin (D-penicillamine disulfide) dihydrochloride.

<sup>d</sup> L-L=2,2'-bis[6-(2,2'-bipyridyl)]diphenyldisulfide.

<sup>e</sup>  $C_8H_{22}N_2S_2 = bis-[2-(N,N-dimethylamino)ethyl]disulfide dihydrochloride.$ 

 $[PPh_3Me]_2[CuI_3]$  (2.554(3) Å, 120.03(1))° [19] and  $[Cp_2-Co]_2[CuI_3]$  (2.545(2) Å, 120.38(5))° [21]. The mean Cu–Br bond length and Br–Cu–Br bond angle of **2** are 2.3668(14) Å and 119.99(6)°, respectively, which are close to those reported in  $[PMe_4]_2[CuBr_3]$  (2.365(3) Å, 120.00(1))° [22] and  $[PPh_3Me]_2[CuBr_3]$  (2.355(4) Å,

Table 4 Selected bond distances (Å) and angles (degrees) for 3

$Cu(1)\cdots Cu(2)$	2.6368(11)	Cu(1)–I(1)	2.5417(8)
Cu(1)–I(2)	2.6758(9)	Cu(1)–I(3)	2.7366(9)
Cu(1)–I(4B)	2.7577(9)	Cu(2)–I(2)	2.5422(9)
Cu(2)–I(3)	2.5633(8)	Cu(2)–I(4)	2.5232(8)
S(1)–S(2)	2.026(2)		
Cu(2)–I(2)–Cu(1)	60.64(3)	Cu(2)–I(3)–Cu(1)	59.57(2)
Cu(2B)–I(4B)–Cu(1)	157.74(3)	I(1)-Cu(1)-I(2)	116.64(3)
I(1)-Cu(1)-I(3)	114.71(3)	I(2)-Cu(1)-I(3)	104.54(3)
I(1)-Cu(1)-I(4B)	108.08(3)	I(2)-Cu(1)-I(4B)	106.53(3)
I(3)-Cu(1)-I(4B)	105.54(3)	I(4)-Cu(2)-I(2)	124.90(3)
I(4)-Cu(2)-I(3)	119.32(3)	I(2)–Cu(2)–I(3)	113.95(3)

## 119.99(1))° [23] (Table 2).

Table 3 lists comparison on the S–S bond lengths and CSSC torsion angles of the disulfides in some known complexes. The S(1)–S(2) bond lengths of **1** and **2** are 2.0538(17) Å and (2.049(3) Å), respectively, which are similar to those reported in  $[C_{10}H_{22}N_2O_4S_2]Cl_2$  (2.049(3) Å;  $C_{10}H_{22}N_2O_4S_2$ =D-penicillamine disulfide dihydrochloride) [24], and L–L·0.5C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> (2.0628(5) Å; L–L=2,2'-bis[6-(2,2'-bipyridyl)]diphenyldisulfide) [25], but in-between those observed in [{Me<sub>2</sub>NH(CH<sub>2</sub>)<sub>3</sub>S}<sub>2</sub>][CdBr<sub>4</sub>]

(2.013(3) Å) [11] and  $[C_8H_{22}N_2S_2]Cl_2$  (2.075(5) Å;  $C_8H_{22}N_2S_2$ =bis-[2-(*N*,*N*-dimethylamino)ethyl]disulfide dihydrochloride) [26]. The CSSC torsion angles of **1** and **2** are 82.1(4) and 81.9(5)°, respectively, which are comparable to that found in { $[C_{10}H_{10}N_2S_2][Cu_2Cl_6][BF_4]_2$ }, (81.5(2)°;  $C_{10}H_{10}N_2S_2$ =bis(4-pyridinium)disulfide) [4], but in-between those reported in [{ $Me_2NH(CH_2)_3S$ }\_2]-[CdBr<sub>4</sub>] (74.83(1)°) [11] and [ $C_8H_{22}N_2S_2$ ]Cl<sub>2</sub> (114.71(2)°;  $C_8H_{22}N_2S_2$ =bis-[2-(*N*,*N*-dimethylamino)ethyl]disulfide dihydrochloride) [26].

Having positive charges located on the NMe<sub>3</sub> groups, the Tab-Tab dications in the crystals of 1 and 2 are arranged parallel to each other and the [CuX<sub>3</sub>]<sup>-</sup> dianions are positioned among the dications. Such an arrangement leads to interactions of halogen atoms with H atoms of the methyl group of the Tab–Tab dication. The halogen atoms are hydrogen-bond acceptor while H atoms of the methyl are hydrogen-bond donor. As shown in Fig. 2, two hydrogen bonding interactions between I(2) and the methyl group with C(18) [C(18)····I(2) (-x, -y+1, -z+1) 3.07 Å] and between I(3) and the methyl group with C(9)  $[C(9)\cdots I(3)]$ (x-1, y-1, z) 3.07 Å] led to the formation of a onedimensional zigzag chain extended along the c-axis. In addition, the I(1) atom of the  $[CuI_3]^{2-}$  dianion has hydrogen bonding interaction with the methyl group with C(7) $[C(7)\cdots I(1) (x-1, y, z) 3.09 \text{ Å}]$  in neighboring parallel chain, thus forming a one-dimensional double-chain structure. In the case of 2, however, only a one-dimensional zigzag chain is stacked along c-axis by the hydrogen bonding interactions between Br(1) and the methyl group



Fig. 3. One-dimensional chain formed via the hydrogen bonding interactions in 2.



Fig. 4. The perspective view of the structure of 3.

with C(18) [C(18)...Br(1) (-x+1, -y+1, -z+1)2.84 Å] and between Br(2) and the methyl group with C(7) [C(7)...Br(2) (-x+2, -y+1, -z+2) 2.88 Å] (Fig. 3).

## 3.3. Molecular structure of 3

Compound **3** crystallizes in the orthorhombic space group *Pbca* and the asymmetric unit contains one Tab– Tab dication and one  $[Cu_2I_4]^{2-}$  dianion. As shown in Figs. 4–6, the I(4) atom serves a bridge to interconnect  $[Cu_2I_3]$  fragments, forming an interesting 1D wavy chain extended along the *b*-axis. The neighboring chains are 9.47 Å apart, and separated by Tab–Tab dications. Although iodide-bridged copper(I) polymers are ubiquitous in halogencuprate(I) complexes, those having a wavy chain structure is uncommon. As shown in Table 4, the Cu(2)–I(4)–Cu(1A) angle of 157.74(3)° is quite bent. The  $[Cu_2I_3$  fragment consists of a butterfly like  $[Cu(\mu-I)_2Cu]$  fragment with a terminal I(1) atom



Fig. 5. The perspective view of the neighboring chains containing hydrogen bonding interactions in 3.



Fig. 6. The unit cell packing diagram of **3** looking down the *b*-axis.

coordinated to Cu(1). In this fragment, Cu(1) adopts a distorted tetrahedral coordination geometry while Cu(2) has a trigonal planar geometry. The Cu(1)…Cu(2) separation (2.6368(11) Å) within the  $[Cu(\mu-I)_2Cu]$ rhomb is comparable to that in  $[CuIL]_2$  (2.609(2) Å; L=1,10-phenanthroline) [27], but shorter than those observed in  $[CuIL]_2$  (2.803(2) Å; L=2,6-bis(3-pyridyloxy)pyrazine) [28] and  $[PPh_4]_2[Cu_2I_4]$  (2.957(1) Å) [29]. The mean Cu-µ-I bond length for trigonally coordinated Cu(2) is 2.542(8) Å, which is similar to those of other trigonally coordinated Cu complexes such as [PPh<sub>4</sub>]<sub>2</sub>[- $Cu_2I_4$ ] (2.589(1) Å) [29], [PPh<sub>3</sub>Me]<sub>2</sub>[Cu<sub>2</sub>I<sub>4</sub>] (2.572(2) Å) [30]. The average Cu-µ-I bond distance for tetrahedrally coordinated Cu(1) is 2.7233(9) Å, which is close to that in other tetrahedrally coordinated Cu complexes such as  $[CuIL]_2$  (2.7297(9) Å, L=2,6-bis(3-pyridyloxy)pyrazine) [28], but longer than that of  $[PyH]_2[Cu_3I_5]$  (2.6795(5) Å) [31]. The terminal Cu(1)–I(1) distance (2.5417 (8) Å) is comparable to that of 1. The S-S bond length and CSSC torsion angle in **3** are 2.026(2) and  $80(4)^{\circ}$ , respectively, which are somewhat smaller than those of the corresponding ones of 1 and 2.

As shown in Figs. 5 and 6, I(2) atom in the  $[Cu_2I_4]^{2-}$  dianion has H-bonding interaction with the methyl group of C(17) [C(17)…I(2) (-*x*, *y*+3/2, -*z*+3/2) 2.90 Å], thus affording a one-dimensional chain with Tab–Tab dications covering on its one side.

#### 3.4. Luminecent properties of 1-3

Compounds 1, 2 and 3 exhibit luminescence in solid state at ambient temperature as shown in Fig. 7. Their lifetimes (11.32 µs (1), 11.46 µs (2) and 9.73 µs (3)) were measured by time-resolved spectroscopy at room temperature and calculated through the mono-exponential decay method. In the emission spectra of 1–3, they have a broad band at ca. 566 nm ( $\lambda_{ex}$ =397), which is quite similar to that of the free compound [Tab–Tab]I<sub>2</sub> ( $\lambda_{em}$ =566 nm,  $\lambda_{ex}$ =397). Therefore, the possible origin of the emissions of 1–3 may be



Fig. 7. The emission spectra of  $1\!-\!3$  and  $[{\rm Tab}\!-\!{\rm Tab}]{\rm I}_2$  in the solid state at ambient temperature.

attributable to the ligand-charge (LC) transition from S (non-bonding 3p) to benzene ring ( $\pi^*$ ) or from benzene ring ( $\pi^*$ ) to benzene ring ( $\pi^*$ ) of the Tab–Tab dication.

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