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#### Luminescent Monomeric and Polymeric Copper(I) Halides

#### Complexes with 1,2-Bis(3,5-dimethylpyrazol-1-ylmethyl)-

#### **Benzene as Ligand**

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#### **ABSTRACT:**

bromide of copper(I) with of Reaction equimolar amounts 1,2-bis(3,5-dimethylpyrazol-1-ylmethyl)-benzene (dpb) afforded a mononuclear three-coordinated complex [CuBr(dpb)] (F2) with dpb acting as a chelating ligand. In contrast, copper(I) iodide under the same conditions gave the polymeric compound  $[Cu_2I_2(dpb)]_n$  (F1) which contains double-bridging iodine atoms. The complexes were characterized by element analysis and <sup>1</sup>H NMR spectroscopy, and the crystal structures were determined by single-crystal X-ray diffraction methods. The Cu(I) complexes are luminescent in the solid state at ambient temperature. Intense orange emission for complex F1 is observed, with maxima at 593 nm, probably ascribed to a combination of a halide-to-metal charge transfer and copper-centered  $d \rightarrow s$ , p transitions. F2 exhibits a blue photoluminescence, with emission maximum at 515 nm, assigned to metal-to-ligand charge-transfer excited states, probably mixed with some halide-to-ligand characters.

Key Words: Cu(I) halides, luminescence, crystal structures, coordination polymers

Copper(I) complexes have attracted considerable interest because of their rich structural and photophysical properties [1] and potential applications as inexpensive, abundant materials in

optoelectronics [2], catalysis [3], and biological systems [4]. Copper(I) halide aggregates constitute a large family of compounds studied mainly for their photochemical and photophysical properties [5] which are at the forefront of coordination chemistry and crystal engineering research [6]. To date, a large number of mono- and polynuclear copper(I) halides with various aggregates, such as rhomboid dimer, cubane tetramer, stepped cubane tetramer, open cubane tetramer and diamondoid tetramer have been synthesized by self-assembly reactions [7]. This variability arises from the many possible combinations of coordination numbers (two, three and four) available for copper(I) and geometries that can be adopted by the halide ions (from terminal to  $\mu_2$  and up to  $\mu_8$  bridging) [8].

Based on our earlier observations on a series of copper (I) chain polymers and dimeric complex [9], the coordination behavior (terminal or bridging mode) has been supposed to depend on the nature of the halide ligand. In particular, formation of halide bridges has been found to be favored for the "soft" iodide but not for the "harder" chloride ligands, whereas both bridging and terminal bonding modes were observed for the bromide ligands since bromide lies on the borderline between soft and hard bases [10]. The luminescent properties of copper(I) halide aggregates have been extensively studied by Ford et al., who showed that luminescent behaviour and geometries of the aggregate are strictly related [11]. Among the various clusters acting as connecting nodes, dimeric and tetrameric units have been seen to be the most common. In the case of the cluster Cu4l4py4, the emissions have been assigned to XLCT (halide to ligand charge-transfer) and CC (cluster-centered) excited states on the basis of experimental and theoretical studies [12]. Herein, we report the preparation, crystal structures and photophysical properties of two novel coordination compounds, namely  $[Cu_2I_2(dpb)]_n$  (F1) and [CuBr(dpb)] (F2), formed upon reacting copper(I) halides with 1,2-bis(3,5-dimethylpyrazol-1-ylmethyl)-benzene (dpb) [13] in toluene. Both of the two complexes are photoluminescent in the solid state, and the emissive properties of the complexes are very dependent on their structures.

The ligand and Cu(I) complexes were prepared according to the literature method with minor revisions [14]. As shown in Scheme 1, 1,2-bis(3,5-dimethylpyrazol-1-ylmethyl)-benzene was synthesized by condensing of 1,2-bis(bromomethyl) benzene with two equivalent of 3,5-dimethylpyrazole through a phase-transfer catalyzed reaction. Subsequently, the reactions of Cu(I) halides with dpb in dry toluene afforded the corresponding Cu(I) complexes in good yields.

The analytically pure Cu(I) complexes were obtained by further purification through precipitation and washing steps. The complexes are stable in the atmosphere in the solid state, but will be oxidized by several days' air exposure in solution. The ligand and Cu(I) complexes were characterized by <sup>1</sup>H NMR, elemental analysis and MALDI-TOF spectroscopy.

The crystals of F1 and F2 suitable for X-ray diffraction analysis were obtained by diffusion of hexane into the dichloromethane solution of the complexes and both of them were characterized by crystallographic analyses. Perspectives views of F1 and F2 are shown in Fig.1 and Fig.2, respectively. The crystallographic data of the complexes are given in Table 1. Remarkably, the single crystal structures of the complexes significantly depend on the cuprous halides used for coordination. As shown in Fig.2, treatment of equimolar quantities of cuprous bromide and 1,2-bis(3,5-dimethylpyrazol-1-ylmethyl)-benzene in dry toluene solution affords a monomeric complex [CuBr(dpb)] (F2). The three-coordinated Cu(I) atom was surrounded by two nitrogen atoms from one dipyrazole ligand, and one bromide to generate a trigonal configuration with the N3-Cu-N1, N3-Cu-Br and N1-Cu-Br angles falling in the range of 115.47(9)° to 124.57(10)°. The Cu-Br distance is 2.3472 Å, which is shorter than that of four-coordinated Cu(I) bromide complexes (2.5369 Å) [10], but a slightly longer than that of two-coordinated complex (2.2012 Å) [9], probably attributed to the steric hindrance around Cu center. The Cu-N bond lengths of the complex localize in a region of 2.007-1.973 Å, which are comparable to the literature values [15]. In contrast, reaction of cuprous iodide under the same experimental conditions displays a very different coordination mode, where two dipyrazole ligands were bridged by a rhombus  $Cu_2I_2$  to afford a 1-D linear coordination polymer  $[Cu_2I_2(dpb)]_n$  (F1), as shown in Fig.1. The copper and  $\mu_2$ -iodide ions each occupy the opposite corners of the distorted square plane (Cu<sub>2</sub>I<sub>2</sub>), which displays a much closer Cu1-Cu2 distance (2.565 Å), much separated I1-I2 distance (4.472 Å), Cu1-I1 2.568(6) Å, I1-Cu1-I2 120.61(2)°, and Cu1-I1-Cu2 59.225(17)°. It should be noted that the relatively short Cu1-Cu2 distance in F1 is less than twice the van der Waals radius (1.4 Å) of Cu(I), implying a strong metal-metal interaction may exist between the two Cu atoms [16]. The phenomenon of Cu-Cu interaction has been extensively observed for Cu<sub>4</sub>I<sub>4</sub> clusters and other multinuclear Cu(I) complexes [9, 17].

The UV–vis absorption spectra of the Cu(I) complexes in  $CH_2Cl_2$  solution at room temperature are shown in Fig.3. Both of **F1** and **F2** display intense absorption bands around 250 nm, which can

be attributed to the  $\pi$ - $\pi$ \* transitions inside the dipyrazole ligand [1a]. In addition, the complexes display additional bands between 200 and 350 nm, which can be assigned to the low-lying metal-to-ligand charge-transfer (MLCT) bands involving mainly the 3d orbitals of Cu(I) and the unoccupied  $\pi$ \* orbital of the dipyrazole ligand, probably mixed with some halide-to-ligand charge-transfer (XLCT) character [18].

The photoluminescence properties of the complexes in the solid state were recorded at ambient temperature. Upon exposure to UV radiation, **F1** exhibits an orange luminescence, and a broad emission spectrum was observed with the maximum located at 593 nm, as shown in Fig.4. **F2** emits an intense blue light under UV irradiation with maximum peak at 515 nm. The distinct photoluminescence behaviors of the cuprous halide complexes are probably attributed to their different crystal structures. According to the previous papers [19], the excited states in Cu(I) halide complexes possibly include ligand-based ( $\pi$ - $\pi$ \*), metal-to-ligand charge transfer (MLCT), halogen-to-ligand charge transfer (XLCT) and cluster-centered (CC). Since **F1** shows a strong interaction between the two Cu atoms, the photoluminescence of **F1** could be attributed to a combination of a halide-to-metal charge transfer (XMCT) and copper-centered d $\rightarrow$ s, p transitions (<sup>3</sup>CC). The crystal structure of **F2** indicates no Cu–Cu interactions. Accordingly, the photoluminescence of **F2** was assigned to the transition from the d<sub>π</sub> orbital (3d<sup>10</sup>) of the Cu center to the unoccupied  $\pi$ \* orbital of the dipyrazole ligand, probably mixed with some XLCT character [20]. Besides, the microsecond lifetime scale of the emitting species implies that the transitions may arise from the triplet excited states, as shown in Table 2.

The thermogravimetric analysis of the complexes was carried out in nitrogen atmosphere with a heating rate of 15 °C min<sup>-1</sup>. As depicted in Fig.5, both of the two Cu (I) complexes have high decomposition temperatures, with 10% weight loss up to 250 °C. On further hearting, a two-step weight loss was observed for **F2** between 250 and 900 °C, in which the first weight loss between 250 and 350 °C is assigned to the removal of dipyrazole ligand, and the second step in the range 350-900 °C corresponds to the gradually loss of bromide. As expected, the cuprous iodides complex **F1** containing Cu<sub>2</sub>I<sub>2</sub> cluster show higher thermal stability than that of **F2**, with decomposition temperature up to 268 °C.

In summary, the coordination behavior of Cu(I) bromide and iodide in the presence of 1,2-bis(3,5-dimethylpyrazol-1-ylmethyl)-benzene (dpb) as ligand have been established.

Single-crystal structure analyses revealed that two different types of compounds, namely, monomeric with three-coordinated Cu(I) complex for X = Br (F2) and polymeric with double-bridging iodo ligands for X = I (F1), have been isolated under the same reaction conditions. The Cu-Cu distance of F1 (2.56 Å) is shorter than the sum of the van der Waals radii of copper(I) (2.80 Å), indicating a strong metal-metal bonding interaction. The Cu(I) complexes are luminescent in the solid state at ambient temperature. The blue and orange emitters obtained are particularly interesting for OLED and OLEC applications. On the basis of this work, further synthesis and structural and photophysical studies of novel heteronuclear coordination polymers will be also underway in our laboratory.

#### Acknowledgment

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#### **Appendix. Supplementary material**

CCDC-1054226 (**F1**) and CCDC-1054225 (**F2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article, including synthetic details of ligand and complexes, and excitation spectrum can be found in the online version.

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- [14] Synthesis of Cu(I) complexes. To a dry and degassed toluene (10 mL) solution of dpb (1 mmol) was added CuX (143.5 mg, 1 mmol). The mixture was kept at reflux under nitrogen for 12 h. Upon cooling, a precipitate was formed. The solid was filtered off, washed with toluene, diethyl ether and hexane and then recrystallised from dichloromethane/hexane (1: 3) solution as white crystals. For F1, <sup>1</sup>H NMR (400MHz, DMSO-d<sub>6</sub>): δ/ppm 2.21 (s, 6H, Me5-pz), 2.27 (s, 6H, Me3-pz), 5.43 (s, 4H, CH<sub>2</sub>), 6.00 (s, 2H, H4-pz), 7.03-7.06 (m, 2H, H3,6-ph) and 7.26-7.28 (m, 2H, H4,5-ph). Anal.Calcd for C<sub>18</sub> H<sub>22</sub> Cu<sub>2</sub> I<sub>2</sub> N<sub>4</sub>: C, 32.01; H, 3.28; N, 8.30. Found: C, 33.87; H, 3.42; N, 8.45. For F2, <sup>1</sup>H NMR (400MHz, DMSO-d<sub>6</sub>): δ/ppm 2.16 (s, 6H, Me5-pz), 2.36 (s, 6H, Me3-pz), 5.44 (s, 4H, CH2), 6.04 (s, 2H, H4-pz), 7.03-7.07 (m, 2H, H3,6-ph) and 7.25-7.28 (m, 2H, H4,5-ph). Anal.Calcd for C<sub>18</sub> H<sub>22</sub> Br Cu N<sub>4</sub>: C, 49.38; H, 5.06; N, 12.80. Found: C, 50.24; H, 5.18; N, 13.25.
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Scheme 1. The synthetic routes for the Cu(I) halides complexes.



**Fig.1.** Perspective view of the structure of **F1**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Cu1-N1 1.975(3), Cu1-Cu2 2.5659(7), Cu1-II 2.5687(6), Cu2-II 2.6233(6), N1-Cu1-Cu2 175.90(9), N1-Cu1-II 121.68(9), Cu2-Cu1-II 61.447(19), N1-Cu1-I2, 117.71(9), Cu2-Cu1-I2 59.251(18), I1-Cu1-I2 120.61(2), N3-Cu2-II, 114.99(9), Cu1-I1-Cu2 59.225(17), I2-Cu2-II 119.88(2), Cu2-I2-Cu1 60.104(18).



**Fig.2**. Perspective view of the structure of **F2**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Cu-N1 2.007(3), Cu-N3 1.973(4), Cu-Br 2.3472(12), N3-Cu-N1 119.94(13), N3-Cu-Br 124.57(10), N1-Cu-Br 115.47(9), N2-N1-Cu 123.2(3).



Fig.3. Absorption spectrum of Cu(I) complexes in DCM solution at room temperature.



Fig.4. Emission spectra of Cu(I) complexes in the solid at room temperature.



Fig.5. TGA traces of complexes F1 and F2.

Parameter	<b>F1</b>	<b>F2</b> C <sub>18</sub> H <sub>22</sub> BrC	
Formula	$C_{18}H_{22}Cu_2I_2N_4$		
Fw	675.28	437.85	
T (K)	296(2)	296(2)	
Radiation ( $\lambda$ , Å)	0.71073	0.71073	
cryst syst	monoclinic	orthorhom	
space group	P2(1)/n	Pna2(1)	
a( Å )	10.3576(8)	14.387(6)	
b ( Å )	14.0032(10)	12.587(5)	
c ( Å )	15.4409(11)	10.200(5)	
a(deg)	90.00	90.00	
β (deg)	105.0690(10)	90.00	
γ (deg)	90.00	90.00	
$V(Å^3)$	2162.5(3)	1847.0(14)	
Z	4	4	
$\rho_{calcd}$ (g cm <sup>-3</sup> )	2.074	1.575	
absorption coefficient (mm <sup>-1</sup> )	4.831	3.352	
F(000)	1288	888	
crystal size (mm <sup>3</sup> )	0.36 x 0.33 x 0.33	0.35 x 0.25	
$\theta_{\min}, \theta_{\max}$ (deg)	2.00, 25.05	2.15, 25.05	
limiting indices	-12 < h <12,	-17 < <i>h</i> < 1	
	-14< k < 16,	-10 < <i>k</i> < 1	
	-18 < 1 < 17	-11 < <i>l</i> < 12	
no. reflns collected	11874	9958	
no. unique reflns	3835	3218	
R <sub>int</sub>	0.0315	0.0484	
data/restr/params	3835 / 0 / 240	3218/ 1/ 22	
GOOF on $F^2$	1.019	1.079	
final R <sub>1</sub> , wR <sub>2</sub>	0.0282, 0.0584	0.0345, 0.0	
$[I > 2\acute{o}(I)]^{[a]}$			
$R_1$ , w $R_2$ (all data)	0.0390, 0.0624	0.0540, 0.0	
largest diff peak and hole $(e^{-A^{-3}})$	0.889 and -0.423	0.307 and-	
Flack number		0.105	

Complex	$\lambda_{abs}{}^a$ (nm)	$\lambda_{em}^{b}$ (nm)	$\tau^{b}(\mu s)$	$T_{dec}^{c}(^{\circ}C)$
F1	250,300~340	593	13.6	268
F2	250,300~340	515	5.2	250

Table 2. Photophysical and thermal properties of F1 and F2 at room temperature.

<sup>a</sup> Measurements were done in  $1 \times 10^{-6}$  mol L<sup>-1</sup> solution in DCM at 298 K; <sup>b</sup> Measured at the excitation of 300 nm in powder; <sup>c</sup> Defined as the temperature of 10% weight loss.

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#### **Graphical Abstract**



The preparation, crystal structures and photophysical properties of two novel coordination compounds, namely  $[Cu_2I_2(dpb)]_n$  and [CuBr(dpb)], formed upon reacting copper(I) halides with 1,2-bis(3,5-dimethylpyrazol-1-ylmethyl)-benzene (dpb) were reported. Both of the two complexes are photoluminescent in the solid state, and their emissive properties are very dependent on their structures.



#### Highlights

- Two novel coordination compounds, namely  $[Cu_2I_2(dpb)]_n$  and [CuBr(dpb)] were prepared and characterized.
- Crystal structures of the monomeric and polymeric Cu(I) halides complexes were presented.
- The Cu(I) complexes are luminescent in the solid state at ambient temperature.

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