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## Synthesis, crystal structure and photophysical study of luminescent three-coordinate cuprous bromide complexes based on pyrazole derivatives

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The 1:2 molar-ratio reaction between cuprous bromide and pyrazole derivatives in toluene results in mononuclear Cu(I) complexes [CuBr(pyrazole)<sub>2</sub>]. The complexes have been characterized by <sup>1</sup>H NMR spectroscopy and elemental analysis. The molecular structure, established by single-crystal X-ray diffraction, features a trigonal planar geometry around copper, with monodentate pyrazole derivatives. All the Cu(I) complexes are luminescent in the solid state at ambient temperature. Intense blue or blue-green emission in the solid state is observed for these complexes, with the maxima ranging from 431 nm to 493 nm. The observed photoluminescence could be ascribed to the metal-to-ligand charge-transfer excited states, probably mixed with some halide-to-ligand character. The microsecond lifetime scale of the complexes implies that these transitions arise from the triplet excited states.

Keywords: Cuprous bromide; Luminescence; Crystal structures; Three-coordinate

#### 1. Introduction

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Photoluminescent metal complexes have been the focus of many scientific investigations, owing to their potential use as organic light-emitting diodes [1], solar cells [2], and chemical sensors [3]. For example, complexes of heavy metal ions, such as cyclometalated iridium(III) complexes, are applied as particularly useful emitter materials for efficient light generation in electroluminescent devices. Unfortunately, iridium, as well as platinum which also forms luminescent cyclometalated complexes, is relatively rare and costly, so that an impetus exists to find suitable emitters based on less expensive metals. Luminescent copper(I) complexes, as a new class of electroluminescence materials for organic light-emitting diode (OLED) applications, have been studied for many years [4]. Over the past two decades, phosphorescent and delayed-fluorescent tetrahedral copper(I) complexes containing two bidentate ligands (bisimine and/or bisphosphine ligands) have received attention as dopants because of the low cost and stable supply of copper [5]. Reaction of Cu(I) halides with monodentate aliphatic and aromatic N donors led, depending on the reaction conditions, to remarkable structural diversity, ranging from monomeric (e.g.,  $CuX_3L$ ) to polymeric (e.g.,  $(CuXL)_{\infty}$ ) networks, although the most common are dinuclear  $(Cu_2X_2L_4)$ , tetranuclear  $(Cu_4X_4L_4)$ , and polymeric  $((CuXL)_{\infty})$  clusters [6]. The stereochemistry of copper(I) complexes is dominated by four-coordination, whereas three-coordinate species are less common [7].

Though the luminescence behavior of copper(I) complexes is rich, tetrahedral copper(I) complexes tend to display weak emission and short-lived excited states [8]. Strong evidence indicates a Jahn-Teller based distortion (flattening) in the excited state, and consequent formation of a five-coordinate exciplex, that accelerates nonradiative decay [9]. The generally accepted approach to alleviate this problem is to increase the bulk of ligands in order to block excited state geometrical distortion and non-emissive relaxation pathways [10]. Recently, Osawa *et al.* reported a new series of highly emissive three-coordinate copper(I) complexes, (dtpb)CuIX [X = Cl(1), Br(2), I(3); dtpb = 1,2-bis(o-ditolylphosphino)benzene] [11]. The *o*-methyl groups of dtpb are required for formation of three-coordinate complexes because 1,2-bis-(diphenylphosphino)benzene (dppb), which lacks methyl groups, forms only the

halogen-bridged binuclear copper complexes  $[Cu(\mu-X)dppb]_2$  with CuX [12]. This is probably because the Cu<sub>2</sub>X<sub>2</sub> diamond core in  $[Cu(\mu-X)dtpb]_2$  would be unstable as a result of steric hindrance of the *o*-methyl groups located on the sides of the metal centers, causing the unusual monomeric three-coordinate structures.

Herein, we describe the syntheses, crystal structures and photophysical properties of a series of luminescent Cu(I) complexes formed upon reacting pyrazole derivatives with cuprous bromide in toluene. The complexes are emissive in the solid state, and their emission properties can be controlled by proper choice of different groups on the pyrazole.

#### 2. Results and discussion

#### 2.1. Synthesis and characterization



Scheme 1. Synthetic routes for the cuprous bromide complexes.

Pyrazole derivatives, as a class of important precursors, were prepared in almost quantitative yields from volatile 1,3-diones and hydrazine hydrate according to the literature methods [13]. Then the reactions of cuprous bromide with pyrazole derivatives in dry toluene afforded the corresponding Cu(I) complexes in good yields, as shown in scheme 1. Analytically pure Cu(I) complexes were obtained by further purification through precipitation and washing steps under nitrogen. The Cu(I) complexes are air-stable in the solid state but will be oxidized by several days' air exposure in solution inducing the formation of more stable water coordinated Cu(II) complexes. The Cu(I) complexes were characterized by <sup>1</sup>H NMR spectroscopy and elemental analysis.

#### 2.2. Description of structures

The single crystals of **B3** and **B4** suitable for X-ray diffraction analysis were obtained by slow evaporation of the respective saturated solutions of dichloromethane-hexane (1:3, v/v) and both were characterized by crystallographic analyses. Perspectives views of **B3** and **B4** are shown in figures 1 and figure 2, respectively. Pertinent crystallographic data and other experimental details are summarized in table 1, and selected bond lengths and angles are given in table 2. The single crystal structures reveal that copper exhibits a monomeric three-coordinate geometry, surrounded by two nitrogens from two pyrazole ligands, and one bromide from cuprous bromide, as shown in figures 1 and 2. The Cu-Br distances in **B3** and **B4** are 2.561 Å and 2.532 Å, respectively, similar with those of four-coordinate Cu(I) bromide complexes (2.536 Å) [14], but longer than that of two-coordinated complex (2.201 Å) [15], probably attributed to the steric hindrance around the Cu center. The Cu-N bond lengths of the complexes are similar to each other, 1.943-1.969 Å, comparable to the literature values [16]. The N1-Cu-N3 angles in **B3** and **B4** are 142.97° and 140.25°, respectively, deviating significantly from the ideal trigonal value of 120°, probably attributed to the sterically congested pyrazole ligands around Cu. Accordingly, the N1-Cu-Br and N3-Cu-Br angles are smaller than 120°, in the range of 107.31° to 110.71°.

## 2.3. Thermogravimetric analysis

Thermogravimetric analyses of the complexes were carried out in nitrogen with a heating rate of  $15 \,^{\circ}$ C min<sup>-1</sup>. As depicted in figure 3, all Cu(I) complexes have low decomposition temperatures, with 10% weight loss between 154 and 160 °C. On further heating, a two-step weight loss was observed between 160 and 900 °C, in which the first loss between 250 and 380 °C is assigned to the removal of pyrazole ligands, and the second step in the range 380-900 °C corresponds to gradual loss of bromide. Compared to other complexes, **B4** is slightly more stable, probably due to the more bulky group around the copper center.

#### 2.4. Photophysical properties

The photoluminescence properties of the complexes in the solid state were recorded at ambient temperature (figure 4). Upon exposure to UV radiation, B1-B4 show a broad emission spectrum with the maxima at 445, 434, 428 and 493 nm, respectively (table 3). The emission maximum of the complexes is blue-shifted with increase of steric hindrance on the pyrazole unit. For instance, the emission maximum of **B3** was blue-shifted 6 nm and 17 nm related to **B2** and **B1** respectively, when the substituents on pyrazole change from tertbutyl to isopropyl and methyl group. The reason for this is that incorporation of the bulky substituents around the copper center can sterically prevent structural relaxation in the MLCT state, which may narrow the energy gap between excited and ground states [17]. Moreover, B4 displayed a significant red-shifted emission relative to the other three complexes, probably due to the stronger conjugation because of the phenyl group. With reference to the related work [18], the highest occupied molecular orbitals (HOMO) of the complexes were believed to most likely spread over the Cu(I) ion and the halide ligand, while their lowest unoccupied molecular orbitals (LUMO) were thought to be basically localized on the pyrazole ligands. Therefore, the emissive excited states of the complexes are perhaps best regarded as the metal-to-ligand charge-transfer (MLCT) excited states, probably with some halide-to-ligand charge-transfer (XLCT) character.

The excitation spectra of the Cu(I) complexes in the solid at room temperature are shown in figure 5. All the complexes display similar excitation bands with maxima at 289, 277, 279 and 358 nm, respectively. In addition, the lifetimes of the emitting species are 15-48  $\mu$ s, indicating that the emission may stem from the triplet state.

## 3. Conclusion

A series of cuprous bromide complexes based on pyrazole ligands have been synthesized and characterized. Single crystal X-ray analyses reveal that copper exhibits a monomeric three-coordinate geometry. The Cu(I) complexes are luminescent in the solid state at ambient temperature. The emissive excited states of the complexes are assigned to the transition from the  $d_{\pi}$  orbital of the Cu center to the unoccupied  $\pi^*$  orbital of the pyrazole ligand, probably mixed with some XLCT character. The blue and blue-green emitters obtained are particularly interesting for OLED and OLEC applications. Benefiting from the cheap and nontoxic copper meal, ease of structural variation, and the synthetic simplicity, the new approach opens a new perspective for the development of blue phosphorescent materials.

#### 4. Experimental

#### 4.1. Materials and methods

NMR spectra were recorded on a Bruker Ultrashield 400 Plus NMR spectrometer. The NMR chemical shifts for <sup>1</sup>H were referenced to tetramethylsilane ( $\delta$ = 0.00 ppm). Luminescence properties of the complexes in solid were investigated at ambient temperature. Steady-state visible fluorescence and PL-excitation spectra were measured with a Photon Technology International (PTI) Alphascan spectrofluorimeter. Visible-decay spectra were recorded with a pico-N<sub>2</sub> laser system (PTI Time Master) with  $\lambda_{ex}$  = 337 nm. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer thermal analyzer.

All experiments were carried out without special treatments. The cuprous bromide was purchased from Aldrich Chemical Co. Solvents were freshly distilled over appropriate drying regents under an N<sub>2</sub> atmosphere.

### 4.2. General procedure for the preparation of Cu(I) complexes

To a dry and degassed toluene (10 mL) solution of pyrazole (2 mmol) was added CuBr (143.5 mg, 1 mmol). The mixture was kept at reflux under nitrogen for 12 h. Upon cooling, a precipitate formed. The solid was filtered off, washed with toluene, diethyl ether, and hexane. The white product obtained was recrystallized from dichloromethane:hexane (1:3).

B1. Yield 90%, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ/ppm 2.21 (s, 12H, CH<sub>3</sub>), 5.95 (s, 2H, H4-pz),
12.49 (s, 2H, NH). Anal. Calcd for C<sub>10</sub>H<sub>16</sub>BrCuN<sub>4</sub>: C, 35.78; H, 4.80; N, 16.69. Found: C, 35.93; H, 4.92; N, 16.78.

**B2**. Yield 90%, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ/ppm 1.21 (d, 24H, CH<sub>3</sub>-3,5-pz), 2.93 (m, 4H, CH-3,5-pz), 5.99 (s, 2H, H4-pz), 12.48 (s, 2H, NH). Anal. Calcd for C<sub>18</sub>H<sub>32</sub>BrCuN<sub>4</sub>: C, 48.27; H, 7.20; N, 12.51. Found: C, 49.13; H, 7.32; N, 12.75.

B3. Yield 90%, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ/ppm 1.29 (s, 36H, CH<sub>3</sub>-3,5-pz), 6.02 (s, 2H, H4-pz), 12.59 (s, 2H, NH). Anal. Calcd for C<sub>22</sub>H<sub>40</sub>BrCuN<sub>4</sub>: C, 52.42; H, 8.00; N, 11.12. Found: C, 53.36; H, 8.78; N, 12.07.

**B4**. Yield 90%, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ/ppm 7.24 (s, 2H, H4-pz), 7.48 (m, 12H, *m*,*p*-Ph), 7.88 (m, 8H, *o*-Ph), 13.54 (s, 2H, NH). Anal. Calcd for C<sub>30</sub>H<sub>24</sub>BrCuN<sub>4</sub>: C, 61.70; H, 4.14; N, 9.59. Found: C, 62.27; H, 4.77; N, 10.48.

#### 4.3. X-ray crystallography

Single crystals suitable for crystal structure analysis were obtained by slow evaporation of a dichloromethane-hexane solution of the complex at room temperature. Data were measured using Mo-K $\alpha$  radiation on a Bruker SMART 1000 CCD diffractometer. Data collection at 296 K and reduction were performed using SMART and SAINT software. Absorption correction was applied using the multi-scan method (SADABS). The crystal structure of **B3** and **B4** was solved by direct methods and refined by full matrix least-squares on F<sup>2</sup> using the SHELXTL program package.

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#### Supplementary material

CCDC-1411709 (**B3**) and CCDC-1411708 (**B4**) 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.

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Param.	B3	<b>B4</b>
Formula	$C_{22}H_{40}BrCuN_4$	$C_{30}H_{22}BrCuN_4$
Fw	504.03	581.97
Т (К)	296(2)	296(2)
Crystal system	Triclinic	Triclinic
Space group	Pī	Pī
a (Å)	10.748(5)	9.8233(19)
b (Å)	10.882(5)	11.112(2)
c (Å)	13.607(6)	13.813(3)
α (°)	88.526(9)	109.948(2)
β (°)	69.546(7)	98.825(3)
γ (°)	65.110(8)	108.938(3)
V (Å <sup>3</sup> )	1338.8(11)	)1280.1(4)
Z	2	2
$\rho_{\text{calcd}} (\text{g cm}^{-3})$	1.250	1.510
$\mu (mm^{-1})$	2.321	2.440
F(000)	528	588
Crystal size (mm <sup>3</sup> )	$0.32 \times 0.30 \times 0.25$	$0.49\times0.45\times0.40$
$\theta_{\min}, \theta_{\max}$ (°)	2.04, 25.050	2.08, 25.05
Limiting indices	)) -12 < h <12,	-11 < h <11,
	-12< k < 12,	-13< k < 13,
	-16 < 1 < 16	-16 < 1 < 16
No. reflns. collected	7342	13723
No. unique reflns.	4726	4544
R <sub>int</sub>	0.0242	0.0218
Data / restraints / parameters	4713 / 0 / 265	4544 / 0 / 326
GOOF on F <sup>2</sup>	0.983	1.387
Final $R_1$ , w $R_2$	0.0404, 0.0824	0.0269, 0.0717
$[I > 2\sigma(I)]^{[a]}$		
$R_1$ , w $R_2$ (all data)	0.0744, 0.0947	0.0356, 0.0745
Largest diff. peak / hole (e·Å <sup>-3</sup> )	0.424 / -0.244	0.546 / -0.369

Table 1. Summary of crystallographic data.

	B3	<b>B4</b>
Cu-Br	2.561(4)	2.5328(5)
Cu-N(1)	1.961(4)	1.9608(19)
Cu-N(3)	1.969(4)	1.9432(18)
N(1)-Cu-N(3)	142.97(17)	140.25(8)
N(1)-Cu-Br	108.02(16)	108.82(6)
N(3)-Cu-Br	107.31(15)	110.71(6)
N(2)-N(1)-Cu	115.62(12)	116.11(14)
N(4)-N(3)-Cu	116.08(12)	117.17(14)
C(1)-N(1)-Cu	138.92(11)	137.29(17)
C(16)-N(3)-Cu	138.57(14)	136.96(16)

Table 2. Selected bond lengths (Å) and angles (°).

Complex	$\lambda_{ex}^{a}$ (nm)	$\lambda_{em}^{b}$ (nm)	τ <sup>b</sup> (μs)	T <sub>dec</sub> <sup>c</sup> (°C)
<b>B</b> 1	289	445	21	154
B2	277	434	34	156
<b>B3</b>	279	428	48	154
<b>B4</b>	358	493	15	160

Table 3. Photophysical and thermal properties of solid complexes.

<sup>*a*</sup> Measurements were done with  $\lambda_{em}$  of the complexes in the solid at room temperature; <sup>*b*</sup> Measured at the excitation of 300 nm in powder; <sup>*c*</sup> Defined as the temperature of 10% weight loss.



Figure 1. Perspective view of the structure of **B3**. Thermal ellipsoids are drawn at 50% probability level. Hydrogens are omitted for clarity.

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Figure 2. Perspective view of the structure of **B4**. Thermal ellipsoids are drawn at 50% probability level. Hydrogens are omitted for clarity.

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Figure 3. TGA traces of the Cu(I) complex.



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



Figure 5. Excitation spectra of the Cu(I) complexes in the solid at room temperature.

## Graphical abstract

Cu N Br