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

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ABSTRACT
The 1:2 M-ratio reaction between cuprous bromide and pyrazole derivatives in toluene results in mononuclear Cu(I) complexes [CuBr(pyrazole)2]. The complexes have been characterized by 1H 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 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.

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1. Introduction

Photoluminescent metal complexes have been the focus of many scientific investigations, owing to their potential use as organic light-emitting diodes (OLEDs) [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 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. CuX₃L) to polymeric (e.g. (CuXL)₅) networks, although the most common are dinuclear (CuₓX₂L₄), tetranuclear (CuₓX₄L₄), and polymeric ((CuXL)₅) 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(μ-X)dppb]₂ with CuX [12]. This is probably because the CuₓX₂ diamond core in [Cu(μ-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

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 ¹H 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 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 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°–110.71°.

2.3. Thermogravimetric analysis

Thermogravimetric analyses (TGA) of the complexes were carried out in nitrogen with a heating rate of 15 °C min⁻¹. 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 the increase in steric hindrance on the pyrazole unit. For instance, the emission maximum of \( \text{B3} \) was blue-shifted 6 and 17 nm related to \( \text{B2} \) and \( \text{B1} \), 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 metal-to-ligand charge-transfer (MLCT) state, which may narrow the energy gap between excited and ground states [17]. Moreover, \( \text{B4} \) 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

\[ R_1 = \sum F_o - F_c / \sum F_o, \quad wR_2 = \left( \sum w(F_o^2 - F_c^2)^2 / \sum wF_o^2 \right)^{1/2}. \]

\[ \theta_\text{max}(\text{deg}) = 2 \theta_\text{max}(\text{deg}) = 20.4, 25.05. \]

Figure 2. Perspective view of the structure of \( \text{B4} \). Thermal ellipsoids are drawn at 50% probability level. Hydrogens are omitted for clarity.

Table 1. Summary of crystallographic data.

| Param.                     | \( \text{B3} \) | \( \text{B4} \) |
|----------------------------|----------------|----------------|
| Formula                    | \( \text{C}_2\text{H}_6\text{BrCuN}_4 \) | \( \text{C}_3\text{H}_9\text{BrCuN}_4 \) |
| \( F_w \) (K)              | 504.03         | 581.97         |
| Crystal system             | Triclinic      | Triclinic      |
| Space group                | \( \text{P}1 \) | \( \text{P}1 \) |
| \( a \) (Å)                | 10.748(5)      | 9.8233(19)     |
| \( b \) (Å)                | 10.882(5)      | 11.112(2)      |
| \( c \) (Å)                | 13.607(6)      | 13.813(3)      |
| \( \alpha \) (°)           | 88.526(9)      | 109.948(2)     |
| \( \beta \) (°)            | 69.546(7)      | 98.825(3)      |
| \( \gamma \) (°)           | 65.110(8)      | 108.938(3)     |
| \( V \) (Å³)               | 1338.8(11)     | 1280.1(4)      |
| \( Z \)                    | 2              | 2              |
| \( \rho_{\text{calcd}} \) (g cm⁻³) | 1.250          | 1.510          |
| \( \mu \) (mm⁻¹)           | 2.321          | 2.440          |
| \( F(000) \)               | 528            | 588            |
| Crystal size (mm³)         | 0.32 × 0.30 × 0.25 | 0.49 × 0.45 × 0.40 |
| \( \theta_{\text{min}}, \theta_{\text{max}}(°) \) | 2.04, 25.05 | 2.08, 25.05 |
| Limiting indices           | \( -12 < h < 12, -12 < k < 12, -16 < l < 16 \) | \( -11 < h < 11, -13 < k < 13, -16 < l < 16 \) |
| No. refin. collected       | 7342           | 13,723         |
| No. unique refin.          | 4726           | 4544           |
| \( R \)                    | 0.0242         | 0.0218         |
| Data/restraints/parameters | 4713/0/265     | 4544/0/326     |
| GOOF on \( F^2 \)          | 0.983          | 1.387          |
| Final \( R \), \( wR_2 \) [\( I > 2\sigma(I) \)] | 0.0404, 0.0824 | 0.0269, 0.0717 |
| \( R \), \( wR_2 \) (all data) | 0.0744, 0.0947 | 0.0356, 0.0745 |
| Largest diff. peak/hole (e Å⁻³) | 0.424/−0.244 | 0.546/−0.369 |

[17]
to the related work [18], the highest occupied molecular orbitals of the complexes were believed to most likely spread over the Cu(I) ion and the halide ligand, while their lowest unoccupied molecular orbitals were thought to be basically localized on the pyrazole ligands. Therefore, the emissive excited states of the complexes are perhaps best regarded as the MLCT excited states, probably with some halide-to-ligand charge-transfer character.

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

|          | B3                     | B4                     |
|----------|------------------------|------------------------|
| 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(8)              |
| 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)             |

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

Figure 4. Emission spectra of Cu(I) complexes in the solid at room temperature.
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 μs, 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 dπ orbital of the Cu center to the unoccupied π* 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 1H were referenced to tetramethylsilane (δ = 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-N2 laser system (PTI Time Master) with λ_ex = 337 nm. TGA were performed on a Perkin-Elmer thermal analyzer.

Table 3. Photophysical and thermal properties of solid complexes.

| Complex | λ_ex, a (nm) | λ_em, b (nm) | τ, b (μs) | T_dec, c (°C) |
|---------|--------------|--------------|-----------|---------------|
| B1      | 289          | 445          | 21        | 154           |
| B2      | 277          | 434          | 34        | 156           |
| B3      | 279          | 428          | 48        | 154           |
| B4      | 358          | 493          | 15        | 160           |

aMeasurements were done with λ_em of the complexes in the solid at room temperature.

bMeasured at the excitation of 300 nm in powder.

cDefined as the temperature of 10% weight loss.

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

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 μs, indicating that the emission may stem from the triplet state.
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 a N₂ 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%, ¹H NMR (400 MHz, CDCl₃): δ/ppm 2.21 (s, 12H, CH₃), 5.95 (s, 2H, H₄-pz), 12.49 (s, 2H, NH). Anal. Calcd for C₁₀H₁₆BrCuN₄: C, 35.78; H, 4.80; N, 16.69. Found: C, 35.93; H, 4.92; N, 16.78.

**B2.** Yield 90%, ¹H NMR (400 MHz, CDCl₃): δ/ppm 1.21 (d, 24H, CH₃-3,5-pz), 2.93 (m, 4H, CH-3,5-pz), 5.99 (s, 2H, H₄-pz), 12.48 (s, 2H, NH). Anal. Calcd for C₁₈H₃₂BrCuN₄: C, 48.27; H, 7.20; N, 12.51. Found: C, 49.13; H, 7.32; N, 12.75.

**B3.** Yield 90%, ¹H NMR (400 MHz, CDCl₃): δ/ppm 1.29 (s, 36H, CH₃-3,5-pz), 6.02 (s, 2H, H₄-pz), 12.59 (s, 2H, NH). Anal. Calcd for C₂₂H₄₀BrCuN₄: C, 52.42; H, 8.00; N, 11.12. Found: C, 53.36; H, 8.78; N, 12.07.

**B4.** Yield 90%, ¹H NMR (400 MHz, CDCl₃): 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 C₃₀H₂₄BrCuN₄: 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 the slow evaporation of a dichloromethane-hexane solution of the complex at room temperature. Data were measured using Mo-Kα 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 multiscan method (SADABS). The crystal structure of B₃ and B₄ was solved by direct methods and refined by full-matrix least squares on F² using the SHELXTL program package.

### 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 Center via www.ccdc.cam.ac.uk/data_request/cif.

### Disclosure statement

No potential conflict of interest was reported by the authors.

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