Inorganic Chemistry Communications 58 (2015) 113–116

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Luminescent monomeric and polymeric cuprous halide complexes with 1,2-bis(3,5-dimethylpyrazol-1-ylmethyl)-benzene as ligand

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ARTICLE INFO

Article history:
Received 6 May 2015
Received in revised form 9 June 2015
Accepted 13 June 2015
Available online 16 June 2015

Keywords:
Cuprous halides
Luminescence
Crystal structures
Coordination polymers

ABSTRACT

Reaction of cuprous bromide with equimolar amounts of 1,2-bis(3,5-dimethylpyrazol-1-ylmethyl)-benzene (dpb) affords a mononuclear three-coordinated complex [CuBr(dpb)] (F2) with dpb acting as a chelating ligand. In contrast, using cuprous iodide instead under the same conditions gives the polymeric compound $[Cu_2I_2(dpb)]_n$ (F1) which contains double-bridging iodine atoms. The complexes were characterized by element analysis and ^1H 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 → 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.

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]. Cuprous 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 cuprous 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 Cu(I) and geometries that can be adopted by the halide ions (from terminal to μ_{2-} and up to μ_{8-} bridging) [8].

Based on our earlier observations on a series of Cu(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 cuprous halide aggregates have been extensively studied by Ford et al., who showed that luminescent behavior 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 Cu4I4py4, 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 complexes are photoluminescent in the solid state, and their emissive properties 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 after several

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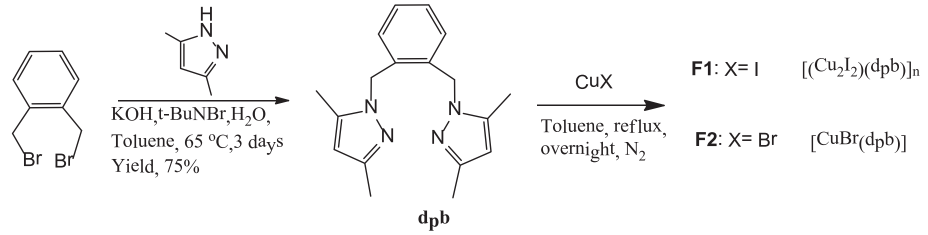
http://dx.doi.org/10.1016/j.inoche.2015.06.014



Scheme 1. The synthetic routes for the Cu(I) halide complexes.

days' air exposure in solution. The ligand and Cu(I) complexes were characterized by ^{1}H NMR, elemental analysis and MALDI-TOF spectroscopy.

The single 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 Figs. 1 and 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 μ_2-iodide ions each occupy the opposite corners of the distorted square plane (Cu_2I_2), 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 that 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_4I_4 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 π–π* transitions inside the dipyrazole ligand [1]. 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 π* 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 (π–π*), metal-to-ligand charge transfer (MLCT), halogen-to-ligand charge transfer (XLCT) and cluster-centered (CC).

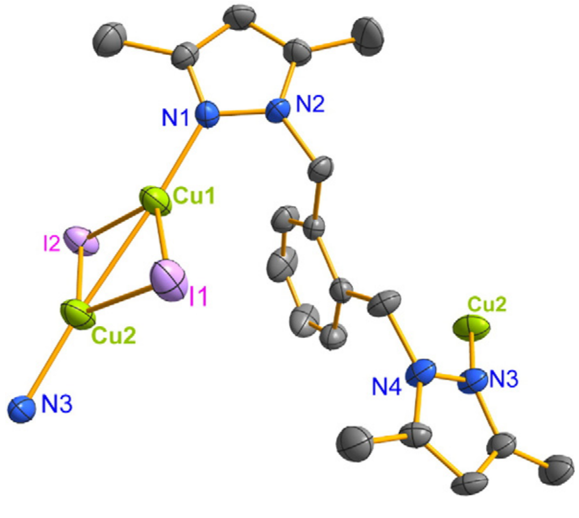


Fig. 1. Perspective view of the structure of F1. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Cu1–N1 1.975(3), Cu1–Cu2 2.5659(7), Cu1–I1 2.5687(6), Cu2–I1 2.6233(6), N1–Cu1–Cu2 175.90(9), N1–Cu1–I1 121.68(9),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

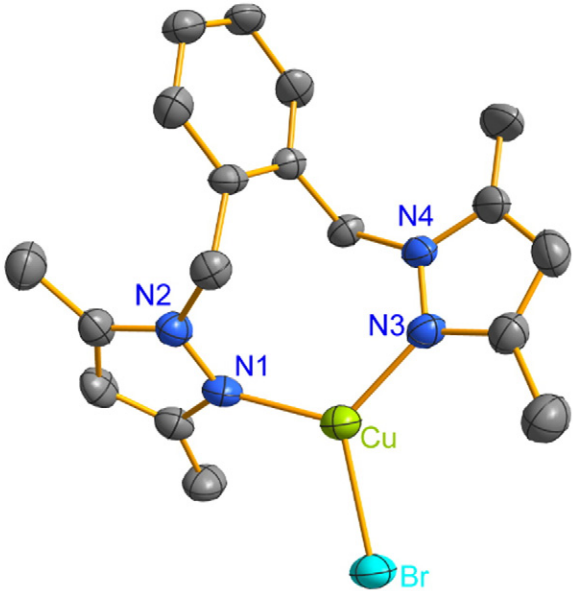


Fig. 2. Perspective view of the structure of F2. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Cu–N1 2.007(3), Cu–N3 1.973(4), Cu–Br 2.3472(12), N3–Cu–N1 119.94(13), N3–Cu–Br 124.57(10), N1–Cu–Br 115.47(9), N2–N1–Cu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