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Structures and luminescence properties of two copper(I) halide complexes featuring 2-(2-benzimidazolyl)-6-methylpyridine

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Abstract

Two new copper(I) halide complexes bearing 2-(2-benzimidazolyl)-6-methylpyridine (Hbmp) and PPh₃ ligands, Cu(Hbmp)(PPh₃)X (X = Br (1); I (2)), have been synthesized and characterized. Single-crystal X-ray structure analysis reveals that the halide ligand has a significant impact on the Cu–N_{pyridyl} bond lengths. Complexes 1 and 2 show the solid-state emissions at ambient temperature, varying with the halide bound to the {Cu(Hbmp)(PPh₃)} motif, which are perhaps best attributed to the metal-to-ligand charge-transfer (Cu(I) \rightarrow Hbmp) transition mixed with some ligand-to-ligand charge-transfer (X and PPh₃ \rightarrow Hbmp) character. © 2012 Jing Lin Chen. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

Keywords: Copper(I) complex; 2-(2-Benzimidazolyl)-6-methylpyridine; Crystal structure; Photoluminescence

Copper(I) complexes have been widely studied in view of their intriguing photophysical properties and promising applications in, for instance, organic light-emitting devices, dye-sensitized solar cells, and luminescence sensors [1]. The structural and electronic properties of the ligands have a great impact on the photophysical properties of the resulting cuprous compounds [2]. For example, $[Cu(1,10-phenanthroline)_2]^+$ is non-emissive in solution, whereas its derivatives with two bulky substituents at the 2,9-positions show luminescence behavior. Thus the appropriate choice of the ligand is very important in modifying the emissive properties of the Cu(I) complexes.

Recently, we have initiated the study on photoactive copper(I) complexes of multidentate *N*-heterocyclic chelating ligands [3]. It is shown that both *N*-heterocycle chelate and the ancillary ligand such as halide and phosphine have an important influence on the photophysical properties of the Cu(I) systems. Similar to 1,10-phenanthroline, 2-(2-benzimidazoly)-6-methylpyridine (Hbmp) can coordinate with the Cu(I) atom as a neutral chelate using its two sp^2 N atoms from the pyridyl and benzimidazole moieties. In addition, it is possible that the N–H group of the benzimidazole may have some effects on the luminescence properties of the Cu(I) species. Herein, we report crystal structures and luminescence properties of two new Cu(I) halide complexes with Hbmp, Cu(Hbmp)(PPh₃)X (X = Br (1); I (2)). It is

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	Complex 1	Complex 2		Complex 1	Complex 2
Empirical formula	C ₃₁ H ₂₆ BrCuN ₃	$C_{31}H_{26}ICuN_3P{\cdot}1.5H_2O$	α [°]	87.685(4)	90
Formula mass	689.09	688.98	<i>β</i> [°]	69.758(3)	115.80(3)
Temperature [K]	296(2)	293(2)	ν[°]	85.061(4)	90
Wavelength [Å]	0.71073	0.71073	V [Å ³]	1669.3(8)	5868(2)
Crystal system	Triclinic	Monoclinic	Reflections collected/unique	10077/5426	12291/5928
Space group	ΡĪ	<i>C</i> 2/c	Data/restraints/ parameters	5426/5/379	5928/0/352
a [Å]	10.984(3)	34.999(7)	Good-of-fit on F^2	1.045	1.171
<i>b</i> [Å]	11.315(3)	9.3376(19)	$R_1 [I > 2\sigma(I)]$	0.0435	0.0823
c [Å]	14.370(4)	19.943(4)	wR_2	0.1019	0.1951

Table 1 Crystallographic data for **1** and **2**.

demonstrated that 1 and 2 are all emissive in the solid state, and the halide coordinated to the $\{Cu(Hbmp)(PPh_3)\}$ unit has a notable effect on the emissive properties of the corresponding Cu(I) complexes.

1. Experimental

Hbmp was synthesized according to a literature method [4]. Elemental analyses were conducted on a Perkin-Elmer model 240C elemental analyzer. Infrared spectra were recorded on a Nicolet 5700 FT-IR spectrometer. Solid-state emission spectra were determined on a Perkin-Elmer LS55 luminescence spectrometer. Single-crystal X-ray diffraction data of 1 (CCDC 873457) and 2 (CCDC 873458) were measured on a Bruker SMART CCD diffractometer, and the crystallographic data of 1 and 2 were given in Table 1. All calculations (see Supporting Information) were carried out by TD-DFT method at the PBE1PBE level with the help of Gaussian 03 program [5].

1.1. Synthesis of Cu(Hbmp)(PPh₃)Br (1)

A mixture of PPh₃ (52.5 mg, 0.200 mmol) and CuBr (14.3 mg, 0.100 mmol) in CH₂Cl₂ (20 mL) was stirred for 3 h at room temperature. To the resulting colorless solution was added with stirring Hbmp (20.9 mg, 0.100 mmol). The admixture was stirred for another 4 h, and then the solvent was removed at reduced pressure to give a yellow residue. Yellow crystals were obtained by slow diffusion of Et₂O into a 3:1 mixture of CH₂Cl₂ and CH₃CN in several days. Yield: 38.2 mg, 0.062 mmol, 62%. Anal. Calcd. for C₃₁H₂₆BrCuN₃P: C, 60.5; H, 4.3; N, 6.8. Found: C, 60.8; H, 4.5; N, 6.5%. Selected IR (KBr, cm⁻¹): 1435vs, 1096s, 743vs, 695vs, 524s, 507m, 490m (PPh₃); 3437m (N–H), 1604m, 1574w, 1467s, 1398m, 1319m, 801w (Hbmp).

1.2. Synthesis of $Cu(Hbmp)(PPh_3)I(2)$

A similar procedure to **1** was adopted except that CuBr was displaced with CuI. Orange-yellow crystals were afforded by slow diffusion of Et₂O into a 3:1 mixture of CH₂Cl₂ and CH₃CN in a few days. Yield: 70%. Anal. Calcd. for C₃₁H₂₆CuIN₃P: C, 56.2; H, 4.0; N, 6.4. Found: C, 56.4; H, 4.3; N, 6.2%. Selected IR (KBr, cm⁻¹): 1434vs, 1096s, 743vs, 695vs, 524s, 505m, 493m (PPh₃); 3432m (N–H), 1605m, 1574w, 1467s, 1397w, 1318m, 806w (Hbmp).



Scheme 1. Synthetic route of complexes 1 and 2.



Fig. 1. ORTEP drawings of 1 (a) and 2 (b); pairwise stacking views of 1 (c) and 2 (d).

2. Results and discussion

Mono-copper(I) halide complexes of Hbmp, Cu(Hbmp)(PPh₃)X (X = Br (1); I (2)), are obtained by treatment of cuprous halide with two equivalents of PPh₃ in CH₂Cl₂, followed by addition of one equivalent of Hbmp (Scheme 1). In the above reaction, the non-isolated intermediate is actually a dicopper(I) cluster (PPh₃)₂Cu(μ -X)₂Cu(PPh₃) [3b].

In 1 and 2, each four-coordinated Cu(I) ion is surrounded by two sp^2 N atoms from one pyridyl and one imidazolyl, one P atom of PPh₃, and one halide to generate an N₂PX distorted tetrahedral arrangement (Fig. 1a and b, Table S2). The Cu–N_{imidazolyl} lengths (2.064 and 2.065 Å) are shorter than the Cu–N_{pyridyl} distances (2.162 and 2.147 Å) for 1 and 2, implying that the imidazolyl-N donor has a stronger bonding with the Cu(I) ion, consistent with other Cu(I) complexes bearing the benzimidazolyl [6]. It is interesting to note that only the Cu–N_{pyridyl} length depends on the halide, whereas the Cu–N_{imidazolyl} length is basically identical in 1 and 2, suggesting that the halide only has a significant impact on the pyridyl of Hbmp. Moreover, it is observed that the Cu–N_{pyridyl} distance (2.162 Å) in 1 is longer than that (2.147 Å) of 2, consistent with the calculated higher Mayer bond order (0.566) of the Cu–N_{pyridyl} bond in 2 relative to that (0.538) of 1, which is most likely due to the different electron-donating nature of the halide (Br⁻ < I⁻). Further support is given by the natural population analysis that I⁻ (-0.7982e) which donates more electrons holds less negative charge than Br⁻ (-0.8094e). The Cu–N, Cu–P, and Cu–X lengths in 1 and 2 are comparable to those observed in other tetrahedral Cu(I) halide complexes with one PPh₃ [7]. It is observed that the Hbmp ligands of two adjacent enantiomeric molecules in 1 and 2 are largely parallel and exhibit a pairwise π -m stacking (Fig. 1c and d). The interplanar separations are in the range of 3.2–3.5 Å for 1 and 2, indicating the existence of a weak intermolecular π -m interaction between two neighboring Hbmp ligands [8].

The free Hbmp emits a purple color with $\lambda_{max} = 373$ nm in the solid state at room temperature, originating from ligand-centered $\pi \to \pi^*$ transition. Complexes 1 and 2 exhibit a solid-state emission with the maximum at 569 and 531 nm at ambient temperature, respectively (Fig. 2). From the orbital plots and partial molecular orbital compositions calculated via TD-DFT method (Fig. 2 and Table 2), it is seen that the highest occupied molecular orbitals (HOMO) of 1 and 2 are basically composed of Cu(I), halide, and PPh₃, while the lowest unoccupied molecular orbitals (LUMO) largely focus on Hbmp with $\geq 94\%$ contribution. The conclusions on the orbital compositions of 1 and 2 are consistent with the related work [6a,9]. Thus, the emissive excited states of 1 and 2 are probably best regarded as the metal-to-ligand charge-transfer (Cu(I) \rightarrow Hbmp) transition with some mixing of the ligand-to-ligand charge-transfer (X and PPh₃ \rightarrow Hbmp) character. Moreover, the solid-state emission ($\lambda_{max} = 569$ nm) of 1 has a red-shifting of around 38 nm



Fig. 2. HOMO and LUMO plots of 1 (left) and 2 (right) calculated by TD-DFT method at the PBE1PBE level; solid-state emission spectra of 1 and 2 at ambient temperature (middle).

	Molecular orbital	Molecular orbital contribution (%)				
		Cu	Х	PPh ₃	Hbmp	
Complex 1	LUMO	1.68	0.98	1.52	95.81	
	НОМО	44.92	24.45	22.90	7.73	
Complex 2	LUMO	2.06	1.34	1.71	94.88	
	НОМО	38.87	31.94	22.76	6.43	

Partial molecular orbital compositions (%) of 1 and 2 calculated by TD-DFT method at the PBE1PBE level.

relative to that ($\lambda_{max} = 531 \text{ nm}$) of **2**, consistent with the order of ligand field strength of the halide (I⁻ < Br⁻) [10]. Therefore, it is believed that the emissive properties of **1** and **2** are related to the electronic nature of the halide, further supported via the variation of the Cu–N_{pyridyl} bond length of **1** and **2**.

3. Conclusion

In summary, two new luminescent Cu(I) halide complexes of 2-(2-benzimidazoly)-6-methylpyridine (Hbmp) have been synthesized and characterized. It is demonstrated that the halide introduced to the $\{Cu(Hbmp)(PPh_3)\}$ motif plays a major role in influencing the molecular structures and luminescence properties of Cu(I)–Hbmp complexes. Further study on luminescent copper(I) halide complexes of N-heterocyclic chelating ligands is underway.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cclet.2012.07.014.

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