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# Synthesis, structure and electronic spectra of new three-coordinated copper(I) complexes with tricyclohexylphosphine and diimine ligands

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# ABSTRACT

Three new copper(I) complexes with tricyclohexylphosphine (PCy<sub>3</sub>) and different diimine ligands, [Cu(phen)(PCy<sub>3</sub>)]BF<sub>4</sub> (**1**) (phen = 1,10'-phennanthroline), [Cu(bpy)(PCy<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub> (**2**) (bpy = 2,2'-bipyridine) and [Cu(MeO-CNN)(PCy<sub>3</sub>)]BF<sub>4</sub> (**3**) (MeO-CNN = 6-(4-methoxyl)phenyl-2,2'-bipyridine), have been synthesized and characterized. X-ray structure reveals that complexes **1** and **3** are three-coordinated with trigonal geometry, while complex **2** adopts distorted tetrahedron geometry. Complexes **1** and **3** exhibit ligand redistribution reactions in chloromethane solution by addition of excess amount of PCy<sub>3</sub>, in which three-coordinated **1** changes into four-coordinated [Cu(phen)(PCy<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, and **3** leads to form [Cu(P-Cy<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub> and CNN-OMe. All the three complexes display yellow <sup>3</sup>MLCT emissions in solid state at room temperature with  $\lambda_{max}$  at 558, 564 and 582 nm for **1**, **2** and **3**, respectively, and red-shift to 605, 628 and 643 nm at 77 K in dichloromethane solution.

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# 1. Introduction

Copper(I) complexes with diimine chelate ligands have attracted much attention for their low-lying charge-transfer (CT) excited states, and potential applications in electrochemical devices and in solar energy conversion schemes [1–6]. However, these complexes often show weak and short-lived excited states for geometric relaxation as well as solvent attack. Incorporating of ancillary sterical phosphine ligands may solve these problems. For this reason, a series of mixed-ligand copper(I) complexes containing diimine and phosphine ligands have been synthesized [7–14]. Some of these complexes show strong and ling-lived excited state [10], and are used as electrophosphorescent materials in organic light-emitting diodes (OLEDs) [11–12]. But until now most of the ancillary ligands are limited in phenyl-substituted phosphines. Related studies on bulky cyclohexyl-substituted phosphine ligands such as tricyclohexylphosphine (PCy<sub>3</sub>) are rare. Because of its bulky steric effect, copper(I) complexes containing PCy<sub>3</sub> often have lower co-ordination numbers as compared with those of PPh<sub>3</sub> [15–16]. Their photophysical properties are also different correspondingly. Herein, we successfully designed and obtained three new mixedligand copper(I) complexes with PCy<sub>3</sub> and different diimine ligands, [Cu(phen)(PCy<sub>3</sub>)]BF<sub>4</sub> (1), [Cu(bpy)(PCy<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub> (2),  $[Cu(MeO-CNN)(PCy_3)]BF_4$  (3). Their structures and spectroscopic properties were also investigated.

# 2. Experimental

# 2.1. Materials and reagents

All reactions were performed under a dinitrogen atmosphere. Solvents were distilled by standard techniques and saturated with dinitrogen before use.  $[Cu(CH_3CN)_4]BF_4$  and ligand MeO-CNN were prepared by literature method [17–18].

# 2.2. Synthesis

# 2.2.1. Synthesis of $[Cu(phen)(PCy_3)]BF_4(1)$

A mixture of  $[Cu(CH_3CN)_4]BF_4$  (100 mg, 0.32 mmol) and phen (58 mg, 0.32 mmol) in dichloromethane (20 mL) was stirred under nitrogen atmosphere at room temperature for 2 h. Then PCy<sub>3</sub> (179 mg, 0.64 mmol) was added kept stirring for 2 h. The solvents were removed and the solid residue was afforded. Yellow single crystals suitable for X-ray diffraction were obtained from the solution of dichloromethane by vapor diffusion with diethyl ether. Yield: 183 mg (82%). *Anal.* Calc. for C<sub>31</sub>H<sub>43</sub>BCl<sub>2</sub>CuF<sub>4</sub>N<sub>2</sub>P (1·CH<sub>2</sub>Cl<sub>2</sub>, 695.90): C, 53.50; H, 6.23; N, 4.03. Found: C, 52.12; H, 56.69; N, 4.28%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 8.70 (m, 2H), 8.55 (m, 2H), 8.02 (s, 2H), 7.75 (m, 2H), 5.27 (s, 2H), 1.46–1.70 (m, 17H), 1.18 (s, 16H).



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#### 2.2.2. Synthesis of $[Cu(bpy)(PCy_3)_2]BF_4(2)$

Complex **2** was prepared in a similar way to complex **1** except that bpy was used in place of phen. The yellow crystals were obtained suitable for X-ray diffraction. Yield: 78%. *Anal.* Calc. for C<sub>46</sub>H<sub>74</sub>BCuF<sub>4</sub>N<sub>2</sub>P<sub>2</sub> (867.36): C, 63.70; H, 8.60; N, 3.23. Found: C, 63.98; H, 8.21; N, 3.61%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.50 (d, *J* = 9.0 Hz, 2H), 8.26 (d, *J* = 5.4 Hz, 2H), 8.11 (m, 2H), 7.30 (m, 2H), 1.50~1.72 (m, 34H), 1.20 (s, 32H).

# 2.2.3. Synthesis of $[Cu(MeO-CNN)(PCy_3)_2]BF_4$ (3)

Complex **3** was prepared in a similar way to complex **1** except that MeO-CNN was used in place of phen. The yellow crystals were obtained suitable for X-ray diffraction. Yield: 84%. *Anal.* Calc. for C<sub>46</sub>H<sub>74</sub>BCuF<sub>4</sub>N<sub>2</sub>P<sub>2</sub> (867.36): C, 63.70; H, 8.60; N, 3.23. Found: C, 63.98; H, 8.21; N, 3.61%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.50 (d, *J* = 9.0 Hz, 2H), 8.26 (d, *J* = 5.4 Hz, 2H), 8.11 (m, 2H), 7.30 (m, 2H), 1.50~1.72 (m, 34H), 1.20 (s, 32H).

# 2.3. Photophysical measurements

UV–Vis absorption spectra were recorded using Hitachi U-3010 spectrophotometer. Emission spectra were performed with Hitachi F-4500 fluorescence spectrometer. <sup>1</sup>H NMR spectra were obtained on a Bruker Avance DPX-400 MHz.

# 2.4. X-ray crystallography

Crystals of complexes **1–3** were obtained by vapor diffusion of diethyl ether into  $CH_2Cl_2$  solution. Crystal data and details of data collection as well as refinement are summarized in Table 1. Diffraction data were collected at room temperature with graphitemono-chromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) on a Bruker SMART CCD area detector. Diffracted data were corrected for absorption correction using sADABS [19] program. The structures were solved by direct methods using the program SHELXS 97 [20] and refined

Crystallographic data for complexes **1–3**.

Complexes	$1 \cdot CH_2Cl_2$	2	3
Formula Formula weight	C <sub>31</sub> H <sub>43</sub> BCl <sub>2</sub> CuF <sub>4</sub> N <sub>2</sub> P 695.9	C <sub>46</sub> H <sub>74</sub> BCuF <sub>4</sub> N <sub>2</sub> P <sub>2</sub> 867.36	C <sub>35</sub> H <sub>47</sub> BCuF <sub>4</sub> N <sub>2</sub> OP 693.07
Crystal system	orthorhombic	triclinic	monoclinic
Space group	Pbca	ΡĪ	Pn
Color	yellow	yellow	yellow
Crystal size (mm)	$0.49 \times 0.40 \times 0.38$	$0.50 \times 0.48 \times 0.36$	$0.33\times0.27\times0.25$
a (Å)	9.8734(11)	11.585(1)	11.466(2)
b (Å)	19.548(2)	11.874(1)	11.836(2)
c (Å)	34.497(3)	19.190(2)	12.548(3)
α (°)	90	80.407(2)	90
β (°)	90	78.382(1)	92.597(4)
γ (°)	90	61.905(1)	90
$V(Å^3)$	6658.3(12)	2273.1(4)	1701.1(6)
Ζ	8	2	2
$Dc ({\rm Mg}{\rm m}^{-3})$	1.688	1.267	1.353
T (K)	298	298(2)	293(2)
Number of reflections	5812	7869	4475
$\theta$ Range (°)	2.17-25.01	2.15-25.38	2.20-27.48
$\mu$ (mm <sup>-1</sup> )	0.928	0.601	0.741
F(000)	3496	928	728
$R_1, wR_2$ $[I > 2\sigma(I)]$	0.0639, 0.1432	0.0638, 0.1629	0.0437, 0.1029
Goodness of fit (GOF) on F <sup>2</sup>	1.053	1.092	0.966

by full-matrix least squares on  $F^2$  using the SHELXL 97 [21] program package. The non-hydrogen atoms were refined anisotropically.

# 3. Result and discussion

#### 3.1. Synthesis and crystal structures

Copper complexes were prepared by reaction different diimine ligands with  $[Cu(CH_3CN)_4]BF_4$  and  $PCy_3$  in dry dichloromethane under N<sub>2</sub> atmosphere in a 1:1:2 stoichiometry. The reaction resulted in the formation of  $[Cu(phen)(PCy_3)]BF_4$ ,  $[Cu(bpy)(PCy_3)_2]$ -BF<sub>4</sub>, and  $[Cu(MeO-CNN)(PCy_3)]BF_4$  for complexes **1–3**, where the ligand stoichiometry were confirmed by <sup>1</sup>H NMR, elemental analysis and X-ray diffraction. All three complexes are yellow solid and soluble in most organic solvents such as dichloromethane, chloroform and acetonitrile. They are stable in air and moisture.

The molecular structures of complexes of 1-3 have been characterized by X-ray analysis. The copper(I) center adopts different coordinated geometry according to the diimine ligands. For complex **1** (see Fig. 1 and Table 2), the Cu(I) center adopts trigonal geometry with the N1-Cu1-N2, N1-Cu1-P1 and N2-Cu1-P1 angles 82.21(19), 142.39(14) and 132.52(14)°, respectively. Its Cu-N (2.029(5) and 2.070(5)Å) and Cu1–P1 (2.1714(15)Å) distances are shorter than those of tetrahedron copper(I) complexes  $[Cu(phen)(PPh_3)_2]^+$  [8,22]. However, the Cu(I) center in complex **2** (see Fig. 2 and Table 2) adopts distorted tetrahedron geometry with N1-Cu1-N2 and P1-Cu1-P2 angles 77.17(2) and 130.30(5)°, respectively. The average Cu-N and Cu-P distances are 2.166 and 2.295 Å, respectively, which are comparable to those observed in  $[Cu(phen)(PPh_3)_2]^+$  and  $[Cu(bpy)(PPh_3)_2]^+$  [9,23]. In addition, the bpy ligand in **2** is not coplanar, with a dihedral angle 27.5(3)° between the two pyridyl moieties. This value is larger than that  $(17.0(2)^{\circ})$  in  $[Cu(bpy)(PPh_3)_2]^+$ , which is reasonable since larger steric effect in PCy<sub>3</sub> than that in PPh<sub>3</sub>.

The coordinate geometry of **3** (see Fig. 3 and Table 2) is similar to that of **1**, and the copper center adopts trigonal configuration with N1–Cu1–N2, N1–Cu1–P1 and N2–Cu1–P1 angles 80.79(17), 127.65(13) and 148.80(12)°, respectively. The Cu–N (2.054(4) and 2.036(4) Å) and Cu–P (2.1732(13) distances are comparable to those in **1**, but shorter than those in  $[Cu_2(\mu\text{-diimine})(\text{MeO-CNN})_2(\text{PCy}_3)_2](\text{BF}_4)_2$  [17]. The two pyridyl rings of MeO-CNN ligand



Fig. 1. Molecular structure of  $1 \cdot CH_2Cl_2$  at the 30% probability displacement ellipsoids. The counter ion, dichloromethane molecules and hydrogen atoms are omitted for clarity.

Table 2	
Selected bond lengths (Å) and angles (°) for $\textbf{1-3}.$	

Complex <b>2</b>			
Cu1-N1	2.029(5)	Cu1-N2	2.070(5)
Cu1-P1	2.1714(15)		
N1-Cu1-N2	82.21(19)	N1-Cu1-P1	142.39(14)
N2-Cu1-P1	132.52(14)		
Complex <b>2</b>			
Cu1-N2	2.147(4)	Cu1-P1	2.289(7)
Cu1-N1	2.195(4)	Cu1-P2	2.301(0)
N2-Cu1-N1	77.17(2)	N2-Cu1-P2	113.88(1)
N2- Cu1- P1	104.62(1)	N1-Cu1-P2	101.37(1)
N1- Cu1- P1	117.31(1)	P1-Cu1-P2	130.30(5)
Complex <b>3</b>			
Cu1-N1	2.054(4)	Cu1-P1	2.1732(13)
Cu1-N2	2.036(4)		
N2-Cu1-N1	80.79(17)	N1-Cu1-P1	127.65(13)
N2-Cu1-P1	148.80(12)		



**Fig. 2.** Molecular structure of **2** at the 30% probability displacement ellipsoids. Hydrogen atoms and the counter ion are omitted for clarity.

are almost coplanar with a dihedral angle of  $6.0(3)^\circ$ , and the pendant aromatic rings are twist with the adjacent pyridine fragments with torsion angle of  $43.2(3)^\circ$ .

# 3.2. Electronic spectra properties

The UV-Vis spectra of complexes 1 and 3 (see Fig. 4) are dominated by intense intraligand transitions with  $\lambda_{max}$  in 271 nm for  $\boldsymbol{1}$ and 274 and 332 nm for **3**, given the low-energy  $\pi$ - $\pi$ \* absorption of the free diimine ligands phen (263 nm in dichloromethane) and MeO-CNN (273 nm and 312 nm (sh) in dichloromethane). The weak low-energy transitions at  $\lambda > 350 \text{ nm}$  (tails about 450 nm) can be assigned to MLCT (metal-to-ligand charge-transfer) transitions involving the diimine ligand and the Cu(I) ion. In contrast, complex 2 shows intense high-energy intraligand transitions at  $\lambda_{max}$  = 293 nm, and moderate low-energy MLCT transitions in the 350-450 nm region, which resembles that observed in  $[Cu(Phen)(PPh_3)_2]^+$  and  $[Cu(bpy)(PPh_3)_2]^+$  [8–9]. The MLCT of **2** shifts toward shorter wavelength in the polar solvent, which is consistent with the behavior of  $[Cu(Phen)(PPh_3)_2]^+$ . However, the MLCT of complexes 1 and 3 show positive solvatochromism effect (Fig. 4), which implies that both complexes have a larger dipole moment in the excited state than the ground state.



**Fig. 3.** Molecular structure of **3** at the 30% probability displacement ellipsoids. All hydrogen atoms and dichloromethane molecules are omitted for clarity.



**Fig. 4.** Room temperature absorption spectra of **1–3** measured in dichloromethane. The insert shows the absorption spectra of **3** in different solvents (a:  $CH_2Cl_2$ , b:  $CH_3OH$ ), recorded using the same concentration.

It was reported that copper (I) complexes containing diimine and diphosphine ligands often undergo solvent-dependent, ligand redistribution reactions [8-10], and their coordinated geometry in solution may be also different from that in solid. Therefore, we investigated how addition of excess PCy<sub>3</sub> alters the UV-Vis spectra of all complexes in dichloromethane solution. The absorption spectra of 2 are almost not affected when excess PCy<sub>3</sub> is added to the solution, which indicates that no ligand redistribution reactions happen in solution. However, the absorption spectra of 1 and 3 vary greatly when excess PCy<sub>3</sub> is added to the solution (Fig. 5). When excess PCy<sub>3</sub> is added to the solution of 1, new broad band in the 350-450 nm region is observed. It increases while the absorption at 271 nm decreases, and shows an isosbestic point at 320 nm. The spectra no longer change when 5 to 10-fold excess of PCy<sub>3</sub> was added. Since the broad band in the 350–450 nm region is very similar to MLCT transition of 2, we envision that new fourcoordinated species  $[Cu(phen)(PCy_3)_2]^+$  forms as shown in Eq. (1). Attempts to obtain pure [Cu(phen)(PCy<sub>3</sub>)<sub>2</sub>]<sup>+</sup> in solid by addition excess amount of PCy<sub>3</sub> to 1 is failure, and only 1 and colorless unreacted PCy<sub>3</sub> are obtained by slow diffusion diethyl ether into the dichloromethane solution.



**Fig. 5.** UV-Vis spectral of **1** (0.2 mM) in dichloromethane solution upon addition of 0, 0.2, 0.4 and 1.0 mM. The insert shows the absorption spectra of **3** (0.2 mM) in dichloromethane solution upon addition of 0, 0.2, 0.6 and 1.0 mM.



Fig. 6. Room temperature emission spectra of 1–3 measured in solid. ( $\lambda_{ex}$  = 355 nm).

$$[Cu(phen)(PCy_3)]^+ + PCy_3 \rightleftharpoons [Cu(phen)(PCy_3)_2]^+$$
(1)  
$$[Cu(CNN-OMe)(PCy_3)]^+ + PCy_3 \rightleftharpoons [Cu(PCy_3)_2]^+ + CNN-OMe$$
(2)

The absorption changes of **3** upon gradual titration with PCy<sub>3</sub> are different from those of **1**. As the PCy<sub>3</sub> concentration increase, the band at 327 nm gradually decreases and then vanishes, while band at 274 nm gradually increases. Since the absorption after adding excess amount of PCy<sub>3</sub> are very similar to that of the free ligand CNN-OMe, we deduce that ligand redistribution reactions as shown in Eq. (2) may happen in solution. Indeed, when we add excess amount of PCy<sub>3</sub> to **3**, the yellow color disappears, and colorless green luminescence crystals of [Cu(PCy<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub> [15b] and blue luminescence crystals of CNN-OMe are formed by slow diffusion diethyl ether into the dichloromethane solution. The formation of four-coordinated species for **1** while not for **3** in solution may be due to the steric hindrance of the pendant aromatic rings in CNN-OMe ligand, and the crystal lattice energy of **1** may lead to the dissociation of [Cu(phen)(PCy<sub>3</sub>)<sub>2</sub>]<sup>+</sup> in solid state.

Upon excitation at 370 nm, complexes **1–3** exhibit intense photoluminescence with  $\lambda_{max}$  at 558, 564 and 582 nm in the solid state at room temperature, respectively (Fig. 6). Since the emission energies are comparable to those of some reported mixed-ligand copper(I) complexes containing diimine and diphosphine ligands [13–14], the yellow emissions are assigned to the <sup>3</sup>MLCT state. The three complexes do not display any detectable emission in solution at room temperature, but display strong luminescence at 77 K in dichloromethane. The emission energies at 77 K in dichloromethane appears to follow the same trend as those in solid state with the  $\lambda_{max}$  at 605, 628 and 643 nm for **1**, **2** and **3**, respectively.

# 4. Conclusions

In this work, we have synthesized and structurally characterized three new copper(I) complexes with tricyclohexylphosphine and different diimine ligands. X-ray structure shows that the copper(I) atom adopts three- or four-coordinated geometry according to the diimine ligand. The three-coordinated **1** can change into  $[Cu(phen)(PCy_3)_2]^*$  in chloromethane solution by addition excess amount of PCy<sub>3</sub>, while **3** leads to  $[Cu(PCy_3)_2]BF_4$  and CNN-OMe. All the three complexes display yellow <sup>3</sup>MLCT emissions in solid state or 77 K in solution.

### Supplementary material

CCDC 724743, 724744 and 724745 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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