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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_3) and different diimine ligands, $[Cu(phen)(PCy_3)]BF_4$ (**1**) (phen = 1,10′-phennanthroline), $[Cu(bpy)(PCy_3)_2]BF_4$ (**2**) (bpy = 2,2′-bipyridine) and $[Cu(MeO\text{-}CNN)(PCy_3)]BF_4$ (**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_3, in which three-coordinated **1** changes into four-coordinated $[Cu(phen)(PCy_3)_2]^+$, and **3** leads to form $[Cu(PCy_3)_2]BF_4$ and CNN-OMe. All the three complexes display yellow ^{3}MLCT emissions in solid state at room temperature with λ_{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.

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_3) are rare. Because of its bulky steric effect, copper(I) complexes containing PCy_3 often have lower co-ordination numbers as compared with those of PPh_3 [15–16]. Their photophysical properties are also different correspondingly. Herein, we successfully designed and obtained three new mixed-ligand copper(I) complexes with PCy_3 and different diimine ligands, $[Cu(phen)(PCy_3)]BF_4$ (**1**), $[Cu(bpy)(PCy_3)_2]BF_4$ (**2**), $[Cu(MeO\text{-}CNN)(PCy_3)]BF_4$ (**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_3 (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 $C_{31}H_{43}BCl_2CuF_4N_2P$ (**1**·CH_2Cl_2, 695.90): C, 53.50; H, 6.23; N, 4.03. Found: C, 52.12; H, 56.69; N, 4.28%. ^{1}H NMR (400 MHz, $CDCl_3$): 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 $C_{46}H_{74}BCuF_4N_2P_2$ (867.36): C, 63.70; H, 8.60; N, 3.23. Found: C, 63.98; H, 8.21; N, 3.61%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 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 $C_{46}H_{74}BCuF_4N_2P_2$ (867.36): C, 63.70; H, 8.60; N, 3.23. Found: C, 63.98; H, 8.21; N, 3.61%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 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. ^{1}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 graphitemonochromatized Mo Kα radiation (λ = 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 by full-matrix least squares on F^2 using the SHELXL 97 [21] program package. The non-hydrogen atoms were refined anisotropically.

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

Complexes	**1**·CH_2Cl_2	**2**	**3**
Formula	$C_{31}H_{43}BCl_2CuF_4N_2P$	$C_{46}H_{74}BCuF_4N_2P_2$	$C_{35}H_{47}BCuF_4N_2OP$
Formula weight	695.9	867.36	693.07
Crystal system	orthorhombic	triclinic	monoclinic
Space group	*Pbca*	*P*$\bar{1}$	*Pn*
Color	yellow	yellow	yellow
Crystal size (mm)	0.49 × 0.40 × 0.38	0.50 × 0.48 × 0.36	0.33 × 0.27 × 0.25
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)
Z	8	2	2
Dc (Mg m^{-3})	1.688	1.267	1.353
T (K)	298	298(2)	293(2)
Number of reflections	5812	7869	4475
θ Range (°)	2.17–25.01	2.15–25.38	2.20–27.48
μ (mm^{-1})	0.928	0.601	0.741
F(0 0 0)	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^2	1.053	1.092	0.966

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_2 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_4, and [Cu(MeO-CNN)(PCy_3)]BF_4 for complexes **1–3**, where the ligand stoichiometry were confirmed by ^{1}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)°) in [Cu(bpy)(PPh_3)$_2$]$^+$, which is reasonable since larger steric effect in PCy_3 than that in PPh_3.

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$_2$(μ-diimine)(MeO-CNN)$_2$(PCy_3)$_2$](BF_4)$_2$ [17]. The two pyridyl rings of MeO-CNN ligand

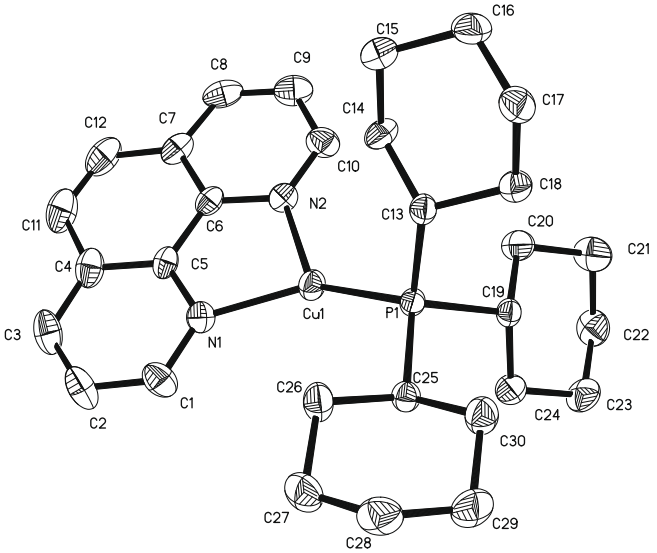

Fig. 1. Molecular structure of **1**·CH_2Cl_2 at the 30% probability displacement ellipsoids. The counter ion, dichloromethane molecules and hydrogen atoms are omitted for clarity.