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Synthesis and crystal structure of photoluminescent copper(I)-phosphine complexes with oxygen and nitrogen donor ligands

Dan Li^{a,*}, Rong-Zhen Li^a, Zheng Ni^a, Zhi-Yu Qi^a, Xiao-Long Feng^b, Ji-Wen Cai^b

^a Department of Chemistry, Shantou University, Shantou, Guangdong 515063, PR China

^b Instrumentation Analysis and Research Center & School of Chemistry and Chemical Engineering, Sun Yat-Sen (Zhongsan) University, Guangzhou 510275, PR China

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Abstract

Two mononuclear copper(I) complexes, $[Cu(PPh_3)_2(oxine)](BF_4)$ (1) and $[Cu(PPh_3)_2(Quin)](BF_4)$ (2), have been prepared and their structures determined by X-ray crystallography. In complex 1, the copper(I) is coordinated by two PPh₃ groups and one neutral bidentate oxine (8-hydroxyquinoline) in a distorted tetrahedral geometry. The copper(I) atom in complex 2 is surrounded by two PPh₃ and one quinoline (quin) to complete a three-coordinate environment. At room temperature in the solid state both complexes exhibit photoluminescence originated from the intraligand (oxine or quinoline) triplet enhanced by copper coordination. This may provide a new entry to develop new kinds of photoemissive materials. © 2003 Elsevier Science B.V. All rights reserved.

Keywords: Copper(I) complex; Crystal structure; Oxine; Quinoline; Triphenylphosphine; Photoluminescence

1. Introduction

The synthesis and structure of Cu(I) complexes have been widely explored for the versatility of their coordination geometries [1]. Such studies have covered different areas and have been related, for example, with structural problems in copper complexes, catalytic activities, biochemical systems and functional materials [2,3]. Structural studies of mononuclear Cu(I) complexes with N-donor and P-donor ligands have shown that three-coordinate copper(I) is relatively rare whereas four-coordinate geometry is the norm [4]. Some of the Cu(I) complexes have been found to be photoluminescent [5]. As Cu(I) is an unstable oxidation state, only a few complexes with O-donor ligands were synthesized and structurally characterized [6].

Following our interest on coordination and photoluminescence properties of Cu(I) with N-donor heterocycles [7], we describe in this paper the synthesis and characterization of a new photoluminescent Cu(I) complex containing a N, O-donor ligand oxine, as well as a complex with N-donor heterocycle quinoline for comparison. Both complexes were rendered air stable by introducing the ancillary PPh₃ ligand to stabilize the copper +1 state. Being built in a simple fashion, the complexes may act potentially as photoluminescent materials.

2. Experimental

2.1. General

All the reactions were carried out under N₂ atmosphere. The chemicals and reagents were obtained commercially and used without further purification. The Cu(I) starting materials, $[Cu(MeCN)_2(PPh_3)_2](BF_4)$ [8], was prepared by addition of PPh₃ to fresh prepared $[Cu(MeCN)_4](BF_4)$ [9] in CH₂Cl₂.

Infrared spectra were recorded in the range of $4000-400 \text{ cm}^{-1}$ on a Nicolet Magna 750 spectrometer.

^{*} Corresponding author. Tel.: +86-754-290-3154; fax: +86-754-251-0505.

E-mail address: dli@stu.edu.cn (D. Li).

Elemental analyses were carried out using a Perkin–Elmer 240C instrument. Ultraviolet and photoluminescence analyses were performed on a UV-1100 spectrometer and a Perkin–Elmer LS 55 luminescence spectrometer, respectively.

2.2. Syntheses

2.2.1. $[Cu(PPh_3), (oxine)](BF_4)$ (1)

Oxine (8-hydroxyquinoline, 145 mg, 1 mmol) was added to a solution of $[Cu(MeCN)_2(PPh_3)_2](BF_4)$ (378 mg, 0.5 mmol) in CHCl₃ (15 ml) under N₂ to give a light yellow–green solution. The solution was heated and stirred for 24 h. After reduction in volume, diethyl ether was added to yield a yellow precipitate. The solid was filtered off, dried and dissolved in a minimum volume of CHCl₃. Diffusion of diethyl ether gave a crop of dark yellow rod-like crystals after 2 days. Anal. Calcd. for C₄₅H₃₇BCuF₄NOP₂: C, 65.91; H, 4.52; N, 1.71; Found: C, 65.74; H, 4.60; N, 1.75. IR (KBr pellets), ν/cm^{-1} : 516s, 694vs, 744vs, 1435vs, 1478s, (PPh₃); 1096vs (BF₄⁻); 1378m, 1518m (oxine). UV, $\lambda_{max}/nm(\varepsilon/ \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 241(6.02), 261(2.69).

2.2.2. $[Cu(PPh_3)_2(Quin)](BF_4)$ (2)

Quinoline (128 mg, 1 mmol) was added to a solution of $[Cu(MeCN)_2(PPh_3)_2](BF_4)$ (378 mg, 0.5 mmol) in CHCl₃ (15 ml) under N₂. The light yellow solution was stirred for 20 h. After reduction in volume, diethyl ether was added to yield a yellow precipitate. The solid was filtered off, dried and dissolved in a minimum volume of CHCl₃. Diffusion of diethyl ether gave a crop of light yellow block-like crystals after 3 days. Anal. Calcd. for C₄₅H₃₇BCuF₄NP₂: C, 67.22; H, 4.61; N, 1.74; Found: C, 67.54; H, 4.81; N, 1.62. IR (KBr pellets), ν/cm^{-1} : 518s, 696vs, 743vs, 1435vs, 1480s, (PPh₃); 1094vs (BF₄⁻); 1312m, 1507m (quin). UV, $\lambda_{max}/nm(\epsilon/ \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$: 265(2.54), 313(0.44).

2.3. X-ray data collection

Intensity measurements were collected on a Brucker SMART CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). All calculations were performed using the SHELXTL package. The structures were solved by direct methods and refined by full-matrix least squares. The detailed crystal data and structure refinement parameters are given in Table 1.

3. Results and discussion

3.1. Synthesis

By introducing the PPh_3 ligand to stabilize the copper(I) state, we obtained two air stable Cu(I) complexes.

Table 1					
Data collection	and structure	refinement	parameters	of 1	and 2

	1	2
Empirical formula	C45H37BCuF4NOP2	$C_{45}H_{37}BCuF_4NP_2$
Formula weight	820.05	804.05
Temperature (K)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	11.372(3)	19.445(5)
b (Å)	22.171(5)	11.878(3)
$c(\mathbf{A})$	16.038(4)	17.637(4)
β (°)	97.942(5)	94.009(4)
$V(\text{\AA}^3)$	4005.0(16)	4063.5(16)
Z	4	4
$D_{\rm calc}~({\rm g~cm^{-3}})$	1.360	1.314
F(000)	1688	1656
$\mu (\mathrm{mm}^{-1})$	0.680	0.667
θ range (°)	2.56-26.37	4.08-25.03
Crystal size (mm)	$0.43 \times 0.20 \times 0.10$	$0.43 \times 0.28 \times 0.23$
Reflections collected/	21908/8147 (0.0255)	19882/7138
unique (R_{int})		(0.0351)
GoF on F^2	1.020	1.041
Final R_1 ,	0.0387, 0.1035	0.0416, 0.1069
$wR_2[I > 2\sigma(I)]$		

Oxine is a bidentate ligand with O- and N-donor atoms for coordinating to metals. Direct reaction between oxine and $[Cu(MeCN)_2(PPh_3)_2](BF_4)$ in CHCl₃ yields 1, in which the oxine coordinates to Cu(I) as a neutral molecule while its hydroxyl group remains unchanged, as expected. Elemental analysis has confirmed that the existence of the BF_4^- anion to balance copper +1 state. The strong IR absorption peak at 1096 cm⁻¹ also indicates the presence of the BF_4^- anion [10]. This contrasts with the reported Cu(I) complex $[Cu(2Me-quin) (PPh_3)_2]$ (where 2Me-quin represented 2-methylquinolin-8-olate), in which the hydroxyl group has been deprotonated [11]. Another neutral complex with deprotoned oxine was found in $[Cu(oxine)(PPh_3)_2]$ which was synthesized by the reaction between $[Cu(acac) (PPh_3)_2]$ (acac = acetylacetonate) and oxine in dichloromethane and characterized by elemental analysis [8].

Addition of solid quinoline to a chloroform solution of $[Cu(MeCN)_4(PPh_3)_2](BF_4)$ afforded a light yellow solution complex **2**. The characteristic absorptions of ligands triphenylphosphine and quinoline as well as the anion BF_4^- have been observed in the IR spectrum.

3.2. Crystal structures

X-ray crystallography has established that the crystal structure of complex 1 consists of monomeric $[Cu(PPh_3)_2(oxine)]^+$ cation (Fig. 1). Selected bond distances and angles are listed in Table 2. The oxine ligand is chelated to the copper ion through its N-donor and O-donor sites forming a five-membered chelating ring. The distorted four-coordinate geometry of Cu(I) is completed by two triphenylphosphine ligands, which is



Fig. 1. A view of ionic moieties in the monomeric complex $[Cu(PPh_3)_2(oxine)](BF_4)$. The H atoms are not shown for clarity.

Table 2 Selected bond distances (Å) and angles (°) for 1

Cu(1)–N(1)	2.037(2)	Cu(1)–P(2)	2.2675(8)
Cu(1)–P(1)	2.2549(7)	Cu(1)–O(1)	2.273(2)
N(1)-Cu(1)-P(1)	120.83(6)	N(1)-Cu(1)-O(1)	76.14(8)
N(1)-Cu(1)-P(2)	109.39(6)	P(1)-Cu(1)-O(1)	116.07(5)
P(1)-Cu(1)-P(2)	122.76(2)	P(2)-Cu(1)-O(1)	100.34(5)

similar to that in [Cu(2Me-quin)(PPh₃)₂] [O-Cu- $N = 83.0(4)^{\circ}$ with the same CuP₂NO core [11]. The O-Cu-N angle in 1 is 76.14(8)°, but the P-Cu-P [122.76(2)°], P-Cu-N [120.83(6)° and 109.39(6)°] and P-Cu–O $[100.34(5)^{\circ}$ and $116.07(5)^{\circ}]$ bond angles are closer to the ideal tetrahedral geometry than the corresponding values in [Cu(2Me-quin)(PPh₃)₂] with P-Cu-P of 117.2(4)°, P-Cu-N of 128.8(2)° and 104.6(3)°, P-Cu-O of $97.4(2)^{\circ}$ and $117.2(4)^{\circ}$. This may be due to the extreme steric crowding of the methyl group in the Me-quin ligand in $[Cu(2Me-quin)(PPh_3)_2]$. The bond distances Cu-P [2.2549(7), 2.2675(8) Å] and Cu-N [2.037(2) Å] in 1 are similar to those in [Cu(2Me-quin)] $(PPh_3)_2$ [Cu–P 2.202(3) and 2.308(4) Å; Cu–N 2.071(9) A] and other Cu(I)-triphenylphosphine or Cu(I)-(heterocyclic N-donor ligand) complexes [12,13]. The Cu-O bond distance of 2.273(2) A in 1 is significantly longer than those in $[Cu(2Me-quin)(PPh_3)_2]$ [2.088(14) A] and in [Cu(PPh₃)₂(H-Norf)](ClO₄) [2.074(2) and 2.0763(18) A, H-Norf = norfloxacine] [14], due perhaps to the attachment of the proton in hydroxyl group of oxine.

The structure of complex 2 is shown in Fig. 2. Bond distances and angles are reported in Table 3. The center copper(I) ion assumes a trigonal coordination geometry



Fig. 2. A view of the ionic components of the monomeric complex $[Cu(PPh_3)_2(Quin)](BF_4)$. The H atoms are not shown for clarity.

Table 3					
Selected	bond	distances	(Å) and	angles	(°) of 2

Cu(1)–N(1) Cu(1)–P(2)	2.069(2) 2.260(1)	Cu(1)–P(1)	2.268(1)
N(1)-Cu(1)-P(2) N(1)-Cu(1)-P(1)	117.47(7) 110.15(7)	P(2)–Cu(1)–P(1)	128.50(3)

composed of two triphenylphosphine ligands and a N atom from quinoline with normal bond distances for Cu–N of 2.069(2) Å and Cu–P of 2.260(1) and 2.268(1) Å. The dihedral angel between the P(1)–Cu(1)–P(2) plane and the quinoline plane is 70.7°. The P–Cu–P angle of 128.50(3)° is relatively larger than the other two N–Cu–P angles of 117.47(7)° and 110.15(7)°, indicative of steric hindrance effects from two bulky triphenyl-phosphine ligands. For comparison, the P–Cu–P bond angle in the (PPh₃)₂CuO₂CH₂CO₂H derivative is 131.1° [15].

3.3. Photoluminescent properties

The emission spectra of complex 1 and 2 in the solid state at room temperature upon excitation at 330 nm are illustrated in Figs. 3 and 4, respectively. Both spectra show certain fine vibrational progression with maxima at 519 and 512 nm, respectively. Many monomeric Cu(I)-phosphine complexes display photoluminescence. One example is the $[Cu(phen)(PPh_3)_2]^+$ system, in which the emission originates from low-lying metal-to-ligand charge transfer (MLCT) excited state with emission maximum at 605 nm [16]. As triphenylphosphine is emissive at ~470 nm [16], we assign that the emission for both complexes are intraligand (oxine or quinoline) in



Fig. 3. Emission spectrum excited at 330 nm of **1** in the solid state at room temperature.



Fig. 4. Emission spectrum excited at 330 nm of $\mathbf{2}$ in the solid state at room temperature.

nature. Similar assignment appears in the Cu(I)–phosphine monomer $[Cu(PPh_3)_2(H-Norf)](ClO_4)$ [14]. Although both free ligands oxine and quinoline do not emit at room temperature, we believe that the coordination of copper perturbs greatly the properties of the ligands and results in the emission of the complex. The fact that the phosphorescence of intraligand organic triplet is greatly enhanced through coordination to metal has been reported [17,18]. The enhancement of emission of organic molecules may provide a new entry to the design of new advanced emissive materials.

Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre with the deposition numbers of CCDC 182721 and 182722 for complexes 1 and 2, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk) or from the corresponding author on request.

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