

Syntheses and structures of neutral dicopper(I) halide complexes with bispyridylpyrrole ligand

Ya-Ping Wang^a, Jing-Jing Xiao^a, Xiao-Hui Hu^a, Xiao-Yi Yi^{a,b,*}

^a School of Chemistry and Chemical Engineering, Central South University, Changsha, Hunan 410083, PR China

^b State Key Laboratory of Medicinal Chemical Biology, Nankai University, Tianjin 300071, PR China

ARTICLE INFO

Article history:

Received 26 April 2015

Received in revised form 18 June 2015

Accepted 19 June 2015

Available online 3 July 2015

Keywords:

Dicopper complexes

Bispyridylpyrrole

Photoluminescence

X-ray crystal structures

ABSTRACT

A new class of neutral dicopper(I)–halide complexes with $\{\text{Cu}_2(\mu\text{-X})\}$ ($\text{X} = \text{Cl}, \text{Br}$ and I) core supported by bispyridylpyrrole ligand have been synthesized and characterized. Replacements of chloride ligand in $[\text{Cu}_2(\mu\text{-X})_2(\text{PPh}_3)_3]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) by the anionic PDP_H^- ($\text{PDP}_\text{H}^- = 2,5\text{-bis}(2'\text{-pyridyl})\text{pyrrole}$) or PDP_Br^- ($\text{PDP}_\text{Br}^- = 2,5\text{-bis}(6'\text{-bromo-}2'\text{-pyridyl})\text{-pyrrole}$) ligand gives complexes **1–6**. They are $[(\text{PDP}_\text{H})\text{Cu}_2(\mu\text{-X})(\text{PPh}_3)_2]$ ($\text{X} = \text{Cl}$ (**1**); Br (**2**); I (**3**)) and $[(\text{PDP}_\text{Br})\text{Cu}_2(\mu\text{-X})(\text{PPh}_3)_2]$ ($\text{X} = \text{Cl}$ (**4**); Br (**5**); I (**6**)). The X-ray crystallographic studies reveal these complexes are isostructural. Two phosphine–copper(I) units are linked by one halogen atom and one nitrogen atom from bridging bispyridylpyrrole ligand to form 4-membered Cu_2XN core. Each copper atom is located in the center of distorted tetrahedral geometry. The PDP_H^- and PDP_Br^- ligands display $\mu_2\text{-}\kappa_2(\text{N}, \text{N}')$, $\kappa_2(\text{N}', \text{N}'')$ bonding mode. The separation of $\text{Cu}\cdots\text{Cu}$ in **1–6** is in the range of 2.6708(15)–2.7959(6) Å. The photophysical properties of **1–6** are described.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Copper complexes are widely used as catalysts [1], oxygen sensors [2], supramolecular assemblies and protein probes [3]. Currently, copper(I) halide complexes have attracted increasing interest in organic light-emitting diodes due to abundance and cost-efficiency [4]. Halide not only acts as terminal or bridging ligand coordinating Cu(I) to form mononuclear, multi-nuclear copper complexes, but also tunes the emission properties of copper complexes. A lot of dicopper(I) halide complexes, as shown in Scheme 1 I–III, containing N, and N^N ligands (such as substituted piperazine, pyridine, bipyridine, N-heteroaromatic hydrocarbon), P and P^P ligands (such as phosphine, diphosphine) and N^P ligands (such as substituted phosphinopyridine) are reported, and their luminescent properties have been detailedly discussed [5–10]. The structural feature of these complexes is that two copper are linked by double bridging halide ligands with ratio of Cu and X 1:1. The analogous complexes with and ratio of Cu and X 2:1, such as these presented in this work (Scheme 1 IV), are less common in

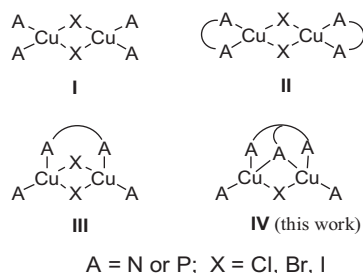
the literatures. Only tridentate terpyridine [11], phenylamino-bis(phosphonite) [12], triphospholyl [13], bis(μ -thiolato) [14] and pybox (such as Ph-pybox donated as 2,6-bis[4'-(R)-phenyloxazolin-2'-yl]pyridine) [15] ligands were reported to generate IV type copper complexes. To our knowledge, the luminescent behaviors of these complexes were not discussed.

Thus, we herein focus on synthesis of type IV dicopper(I) complexes containing bispyridylpyrrole ligand and study of their photoluminescent properties. To select bispyridylpyrrole (PDP^-) as ligand in this work is based on its versatile coordination capability and electronic effects. PDP^- ligand has versatile coordination mode. The central pyrrolate N atom can behave as π -donor or acceptor corresponding to the metal site π -bonding properties [16]. It was proved in our previous works, PDP^- ligand can aggregate Ag(I), Cu(I) to form di- or tri-nuclear metal complexes [17]. Furthermore, aromatic structure of PDP^- ligand containing a large conjugated backbone is a favorable factor to obtain luminescent complex.

A series of luminescent neutral dicopper(I) halide complexes based on the bridging bispyridylpyrrolide ligand, namely $[(\text{PDP}_\text{H})\text{Cu}_2(\mu\text{-X})(\text{PPh}_3)_2]$ (where $\text{PDP}_\text{H}^- = 2,5\text{-bis}(2'\text{-pyridyl})\text{pyrrole}$, $\text{X} = \text{Cl}$ (**1**); Br (**2**); I (**3**)) and $[(\text{PDP}_\text{Br})\text{Cu}_2(\mu\text{-X})(\text{PPh}_3)_2]$ (where $\text{PDP}_\text{Br}^- = 2,5\text{-bis}(6'\text{-bromo-}2'\text{-pyridyl})\text{-pyrrole}$, $\text{X} = \text{Cl}$ (**4**); Br (**5**); I (**6**)) are described in the paper.

* Corresponding author at: School of Chemistry and Chemical Engineering, Central South University, Changsha, Hunan 410083, PR China. Tel./fax: +86 731 88879616.

E-mail address: xyyi@csu.edu.cn (X.-Y. Yi).



Scheme 1. Backbone of dicopper halide complex.

2. Experimental section

2.1. General considerations

All manipulations were carried out under nitrogen by standard Schlenk techniques unless otherwise stated. Solvents were purified, distilled and degassed prior to use. ^1H NMR spectra were recorded on a Bruker AV 400 spectrometer operating at 400 MHz, and chemical shifts (δ , ppm) were reported with reference to SiMe_4 . Infrared spectra (KBr) were recorded on a AVATR360 FT-IR spectrophotometer. UV–Vis spectra were recorded on UV759S machine. Fluorescence lifetime (τ) measurements were carried out with a time correlated single photon counting (TCSPC) nanosecond fluorescence spectrometer (Edinburgh FLS920) at ambient temperature (298 K). For **1–6**, data analysis was carried out by simple tail fit method and was fitted with a monoexponential decay function. The goodness of fit was estimated by using χ^2 values (between 1.0 and 1.2). All the computational analysis in this work was carried out using GAUSSIAN 09 software package and ChemBioOffice2014. The initial molecular structure of complex **1** was preliminarily optimized by MM2 (a modified version of Allinger's MM2 force field) and PM3 (Parameterized Model Revision 3) methods. The molecular geometry obtained was further analyzed and optimized employing DFT method at the B3LYP/6-311G (d) level. The atomic charge values were determined using Mulliken population analysis (MPA) to describe the reactivity of complex **1**. The starting 2,5-bis(2'-pyridyl)pyrrolide (HPDPH) [18], 2,5-bis(6'-bromo-2'-pyridyl)pyrrolide (HPDPBr) [19], $[\text{Cu}_2(\mu\text{-Cl})_2(\text{PPh}_3)_3]$, $[\text{Cu}_2(\mu\text{-Br})_2(\text{PPh}_3)_3]$ and $[\text{Cu}_2(\mu\text{-I})_2(\text{PPh}_3)_3]$ [20] were prepared according to literature methods. All of other chemicals were obtained from J&K Scientific Ltd.

2.2. Preparation of $[(\text{PDPH})\text{Cu}_2(\mu\text{-Cl})(\text{PPh}_3)_2]$ (**1**)

A mixture of HPDPH (46.3 mg, 0.209 mmol) and 60% NaH (5.0 mg, 0.125 mmol) in THF (10 mL) was stirred for about ten minutes. To the resulting yellow solution was added $[\text{Cu}_2(\mu\text{-Cl})_2(\text{PPh}_3)_3]$ (203.7 mg, 0.209 mmol). The reaction mixture was stirred for 48 h. The precipitate was filtered off. The yellow filtrate was layered with hexane to give yellow crystals of **1** and colorless large block crystals of starting $[\text{Cu}_2(\mu\text{-Cl})_2(\text{PPh}_3)_3]$, which were separated by picking. Isolated yield of **1** is 92.2 mg (48.5%). ^1H NMR (CDCl_3): δ 8.339 (s, 2H), 7.692–7.446 (m, 20H), 7.211 (s, 14H), 6.857 (s, 2H), 6.744 (s, 2H); ^{31}P NMR (CDCl_3): δ -2.96 (s, PPh_3). IR (KBr, cm^{-1}): 3050(m), 1595(s), 1511(m), 1480(w), 1381(w), 1324(m), 1151(w), 1095(w), 747(m), 695(m), 523(w). Anal. Calc. for $\text{C}_{50}\text{H}_{40}\text{N}_3\text{Cu}_2\text{P}_2\text{Cl}$: C, 66.18; H, 4.44; N, 4.63. Found: C, 66.19; H, 4.36; N, 4.47%.

The exactly same procedure was operated to prepare complexes **2–6**, only using $[\text{Cu}_2(\mu\text{-Br})_2(\text{PPh}_3)_3]$, $[\text{Cu}_2(\mu\text{-I})_2(\text{PPh}_3)_3]$ instead of $[\text{Cu}_2(\mu\text{-Cl})_2(\text{PPh}_3)_3]$, or HPDPBr in place of HPDPH.

2.3. $[(\text{PDPH})\text{Cu}_2(\mu\text{-Br})(\text{PPh}_3)_2]$ (**2**)

2 was isolated in yield of 40.9%. ^1H NMR (CDCl_3): δ 8.381 (s, 2H), 7.695–7.396 (m, 20H), 7.055 (s, 14H), 6.891–6.881 (m, 2H), 6.736 (s, 2H); ^{31}P NMR (CDCl_3): δ -2.28 (s, PPh_3). IR (KBr, cm^{-1}): 3050(m), 1627(w), 1594(s), 1512(m), 1478(w), 1432(s), 1376(w), 1324(m), 1260(w), 1151(w), 1094(w), 1044(w), 785(w), 747(m), 695(m), 523(w), 501(w). Anal. Calc. for $\text{C}_{50}\text{H}_{40}\text{N}_3\text{Cu}_2\text{P}_2\text{Br}\cdot 2\text{THF}\cdot 2\text{H}_2\text{O}$: C, 62.99; H, 4.56; N, 3.80. Found: C, 62.81; H, 4.49; N, 3.74%.

2.4. $[(\text{PDPH})\text{Cu}_2(\mu\text{-I})(\text{PPh}_3)_2]$ (**3**)

3 was isolated in yield of 46.7%. ^1H NMR (CDCl_3): δ 8.420 (d, $J = 3.1$ Hz, 2H), 7.392–7.347 (m, 4H), 7.197 (d, $J = 5.0$ Hz, 10H), 7.093–7.063 (m, 10H), 7.006–7.004 (m, 10H), 6.891–6.859 (m, 2H), 6.738 (s, 2H); ^{31}P NMR (CDCl_3): δ -2.08 (s, PPh_3). IR (KBr, cm^{-1}): 3049(m), 1639(w), 1594(s), 1510(m), 1478(w), 1323(m), 1149(w), 1093(w), 745(m), 694(m), 499(w). Anal. Calc. for $\text{C}_{50}\text{H}_{40}\text{N}_3\text{Cu}_2\text{P}_2\text{I}\cdot 0.5\text{THF}\cdot \text{H}_2\text{O}$: C, 59.43; H, 4.22; N, 3.99. Found: C, 59.17; H, 4.32; N, 3.80%.

2.5. $[(\text{PDPBr})\text{Cu}_2(\mu\text{-Cl})(\text{PPh}_3)_2]$ (**4**)

4 was isolated in yield of 51.1%. ^1H NMR (CDCl_3): δ 7.222–7.095 (m, 32H), 7.11 (s, 2H), 7.094 (s, 2H), 7.012 (d, $J = 4.7$ Hz, 2H), 6.643 (s, 2H); ^{31}P NMR (CDCl_3): δ -2.42 (s, PPh_3). IR (KBr, cm^{-1}): 3049(m), 1582(s), 1541(w), 1504(w), 1434(m), 1417(s), 1322(m), 1164(m), 1101(w), 1045(w), 995(w), 790(w), 747(m), 695(m), 522(w). Anal. Calc. for $\text{C}_{50}\text{H}_{38}\text{N}_3\text{Cu}_2\text{P}_2\text{Br}_2\text{Cl}\cdot 2\text{THF}$: C, 57.99; H, 3.86; N, 3.50. Found: C, 57.95; H, 4.08; N, 3.27%.

2.6. $[(\text{PDPBr})\text{Cu}_2(\mu\text{-Br})(\text{PPh}_3)_2]$ (**5**)

5 was isolated in yield of 40.8%. ^1H NMR (CDCl_3): δ 7.196–7.068 (m, 34H), 7.020 (d, $J = 3.8$ Hz, 2H), 6.645 (s, 2H); ^{31}P NMR (CDCl_3): δ -3.80 (s, PPh_3). IR (KBr, cm^{-1}): 3049(w), 1582(s), 1542(w), 1505(w), 1434(m), 1417(s), 1323(m), 1165(m), 1102(w), 1046(w), 996(w), 791(w), 748(m), 696(m), 523(w), 499(w). Anal. Calc. for $\text{C}_{50}\text{H}_{38}\text{N}_3\text{Cu}_2\text{P}_2\text{Br}_3$: C, 54.12; H, 3.45; N, 3.79. Found: C, 54.14; H, 3.80; N, 3.79%.

2.7. $[(\text{PDPBr})\text{Cu}_2(\mu\text{-I})(\text{PPh}_3)_2]$ (**6**)

6 was isolated in yield of 35.0%. ^1H NMR (CDCl_3): δ 7.181–7.094 (m, 34H), 7.025 (d, $J = 3.8$ Hz, 2H), 6.624 (s, 2H); ^{31}P NMR (CDCl_3): δ -4.20 (s, PPh_3). IR (KBr, cm^{-1}): 3048(w), 1583(s), 1542(w), 1505(w), 1496(w), 1434(m), 1417(s), 1324(m), 1165(m), 1102(w), 1047(w), 996(w), 790(w), 747(m), 695(m), 522(w), 499(w). Anal. Calc. for $\text{C}_{50}\text{H}_{38}\text{N}_3\text{Cu}_2\text{P}_2\text{Br}_2\text{I}\cdot 0.5\text{THF}\cdot \text{H}_2\text{O}$: C, 51.67; H, 3.50; N, 3.48. Found: C, 51.65; H, 3.60; N, 3.51%.

2.8. X-ray crystallography

Diffraction data of **1–6** were recorded on a Bruker CCD diffractometer with monochromatized Mo K α radiation ($\lambda = 0.71073$ Å). The collected frames were processed with the software SAINT. The absorption correction was treated with SADABS [21]. Structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [22]. Atomic positions of non-hydrogen atoms were refined with anisotropic parameters. All hydrogen atoms were introduced at their geometric positions and refined as riding atoms. In complex **4**, the unit cell includes a large region of disordered solvent molecules, which

Download English Version:

<https://daneshyari.com/en/article/1308948>

Download Persian Version:

<https://daneshyari.com/article/1308948>

[Daneshyari.com](https://daneshyari.com)