



# Synthesis, structures and fluorescent properties of metal complexes based on polyphosphine ligands



Ting-Hong Huang<sup>\*</sup>, Hu Yang, Sheng-Lan Zhu, Bin Zhao, Yan Yang

College of Materials and Chemical Engineering, Sichuan University of Science & Engineering, Zigong, 643000, China

## ARTICLE INFO

### Article history:

Received 27 March 2016

Received in revised form

16 July 2016

Accepted 18 July 2016

Available online 22 July 2016

### Keywords:

Cu<sup>+</sup>/Ag<sup>+</sup> complexes

Polyphosphine ligands

Crystal structure

Fluorescent properties

## ABSTRACT

Based on polyphosphine ligands, four complexes, [Cu<sub>2</sub>(pba)<sub>2</sub>(pipzdtc)]·2DMF (**1**), [Cu<sub>2</sub>(pbaa)(Et-dtc)<sub>2</sub>]·2DMF (**2**), [Cu<sub>2</sub>(pnaa)(Et-dtc)<sub>2</sub>] (**3**) and [Ag<sub>2</sub>(pnaa)(Et-dtc)<sub>2</sub>]·2CH<sub>3</sub>CN (**4**) (pba = N,N-bis((diphenylphosphino)methyl)benzenamine, pbaa = N,N,N',N'-tetrakis((di-phenylphosphino)methyl)benzene-1,4-diamine, pnaa = N,N,N',N'-tetrakis((diphenylphosphino)-methyl)naphthalene-1,5-diamine, Et-dtc = N-ethylthiocarbamate and pipzdtc = piperazine-1,4-dicarbodithiolate), have been synthesized and characterized by IR, ESI-MS and X-ray crystal structure analysis. The structural analysis shows that each Cu<sup>+</sup>/Ag<sup>+</sup> in complexes **1–4** is four coordinate P<sub>2</sub>S<sub>2</sub>, and adopts a distorted-tetrahedral geometry, and 1D infinite chain of complexes **2** and **4** is built by C–H···π interaction of phenyl rings from pbaa and pnaa. All these indicate that the change of polyphosphine ligands and metal ions might be the key of construction of 1D infinite chain. Moreover, the emission spectra of complexes **2–4** in DMF solvent are also observed.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

In recent years, the design and syntheses of transition metal complexes containing multi-phosphine ligands have raised the interest scientific research because of their applications in novel reactivity, catalytic and luminescence properties [1–8]. To the best of our knowledge, ligation of multi-phosphine ligands to transition metal ions, especially Cu<sup>+</sup> and Ag<sup>+</sup> [9–12], forming a diversity of structural variations with di- [13–17], tri- [18–20], tetra- [21–23] and multi- [24,25] phosphine ligands, shows a rich range of luminescence. Furthermore, much work has so far focused on the change of chelating or bridging ligands in the study of related metal complexes [26–28]. Some diverse dithiocarbamate ligands have been served as second ligands to construct varieties of structures with though self-assembly, such as mononuclear, dinuclear, trinuclear and polynuclear structures and search for highly efficient luminescent complexes [29–33]. Therefore, the change of multi-phosphine and dithiocarbamate ligands is a powerful and synthetically convenient way for the formation of mixed-ligand metal complexes. Mixed-ligand Cu<sup>+</sup>/Ag<sup>+</sup> complexes containing both multi-phosphine ligands and dithiocarbamate ligands have been

prepared as candidates [34–36].

Hence, our efforts have been devoted to synthesize a series of new multi-phosphine ligands to mediate structural topologies and photophysical properties of Cu<sup>+</sup>/Ag<sup>+</sup> dithiocarbamate complexes. we wish to report the synthesis, structures and fluorescent properties of four complexes, [Cu<sub>2</sub>(pba)<sub>2</sub>(pipzdtc)]·2DMF (**1**), [Cu<sub>2</sub>(pbaa)(Et-dtc)<sub>2</sub>]·2DMF (**2**), [Cu<sub>2</sub>(pnaa)(Et-dtc)<sub>2</sub>] (**3**) and [Ag<sub>2</sub>(pnaa)(Et-dtc)<sub>2</sub>]·2CH<sub>3</sub>CN (**4**) (pba = N,N-bis((diphenyl phosphino)methyl)benzenamine, pbaa = N,N,N',N'-tetrakis((di-phenylphosphino)methyl)benzene-1,4-diamine, pnaa = N,N,N',N'-tetrakis((diphenylphosphino)-methyl)naphthalene-1,5-diamine, Et-dtc = N-ethylthio carbamate and pipzdtc = piperazine-1,4-dicarbodithiolate). Among our research strategies for these complexes, bulky phosphine ligands are expected to construct varieties of structures with different types of the weak interactions.

## 2. Results and discussion

### 2.1. Crystal structures

#### 2.1.1. Crystal structure of [Cu<sub>2</sub>(pba)<sub>2</sub>(pipzdtc)]·2DMF (**1**)

X-ray diffraction analysis shows that the asymmetric unit of **1** contains half a pipzdtc<sup>−</sup>, one Cu<sup>+</sup>, one pba and one DMF molecule (Fig. 1). Ligand pipzdtc<sup>−</sup> adopts a *trans* coordination mode to bridge two copper atoms, while each of Cu (I) ion takes a distorted

<sup>\*</sup> Corresponding author.

E-mail address: [hth\\_chem@126.com](mailto:hth_chem@126.com) (T.-H. Huang).

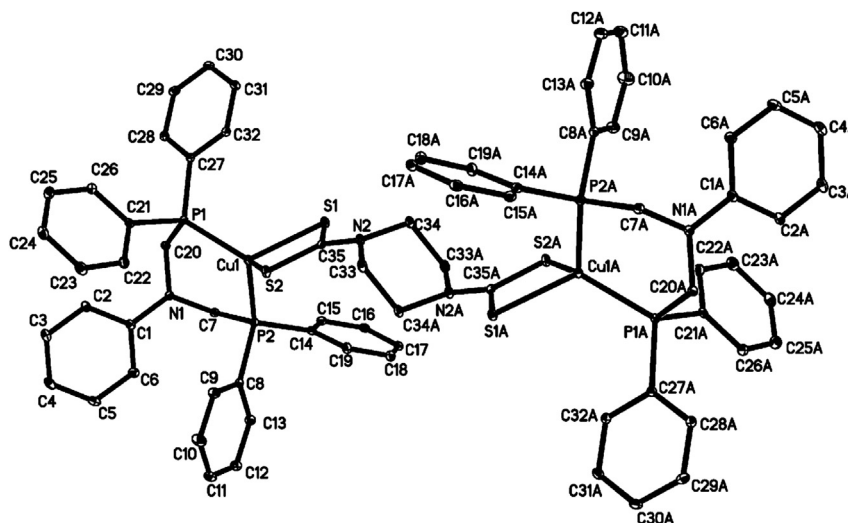


Fig. 1. Molecular structures of  $[\text{Cu}_2(\text{pba})_2(\text{pipzdtc})]$ . All hydrogen atoms are deleted for clarity.

tetrahedral geometry constructed by two S atoms from  $\text{pipzdtc}^-$ , two P atoms from pba, forming a S-shape conformation. The Cu–P bond lengths are in the range of 2.2293(10) to 2.2412(11) Å and the Cu–S bond lengths are 2.3543(11) and 2.3801(10) Å, comparable with those in similar copper(I) compounds [37]. Corresponding P–Cu–S bond angles vary from 110.40(4) to 122.53(4)°, P–Cu–P and S–Cu–S bond angles are 106.01(4) and 76.56(4)°, and the metal ions are separated by a Cu(I)⋯Cu(I) distance of 10.435 Å. Moreover, the packing structure of complex **1** also involves C–H⋯S hydrogen bonds ( $\text{H}\cdots\text{S} = 2.53$  and  $2.54$  Å,  $\text{C}\cdots\text{S} = 3.053$  and  $3.059$  Å).

### 2.1.2. Crystal structure of $[\text{Cu}_2(\text{pbaa})(\text{Et-dtc})_2]\cdot 2\text{DMF}$ (**2**)

For **2**, the overall structure formed is analogous to that of **1**. X-ray diffraction analysis shows that the asymmetric unit of **2** contains half a pbaa, one  $\text{Cu}^+$ , one N-ethylthiocarbamate anion (Et-dtc<sup>−</sup>) and one DMF molecule (Fig. 2). Ligand pbaa adopts a *trans* coordination mode to bridge two copper atoms, while is coordinated by two P atoms from half a pbaa, two S atoms from one N-ethylthiocarbamate anions, forming a distorted tetrahedral geometry. The Cu–P and Cu–S bond lengths are 2.2185(13)–2.2347(12) Å and 2.3564(13)–2.4107(14) Å within the normal ranges [38]. Corresponding P–Cu–P and S–Cu–S bond angles are 103.13(4) and

75.59(4)°, while the P–Cu–S bond angle ranges from 108.40(5) to 126.93(5)°. The Cu⋯Cu separation of 12.752 Å is also longer than the corresponding values in compound **1**. Moreover, intermolecular C–H⋯ $\pi$  interactions are also observed with the centroid-to-centroid distances from 5.075 to 5.079 Å, dihedral angles from 76.28 to 81.23°, and  $\text{H}\cdots\pi_{\text{centroid}}$  distances from 2.94 to 2.98 Å, which leads to the formation of 1D infinite chain along the *a* axis in complex **2** (Fig. 3). In the packing structure, there are the weak interactions of C–H⋯O hydrogen bonds between DMF and the cations ( $\text{H}\cdots\text{O} = 2.11$  and  $2.48$  Å,  $\text{C}\cdots\text{O} = 2.58$  and  $3.43$  Å).

### 2.1.3. Synthesis of $[\text{Cu}_2(\text{pnaa})(\text{Et-dtc})_2]$ (**3**)

For **3**, the overall structure formed is analogous to that of complex **1** and **2**. X-ray diffraction analysis shows that the asymmetric unit of **3** contains half a pnaa, one  $\text{Cu}^+$  and one N-ethylthiocarbamate anion (Et-dtc<sup>−</sup>) (Fig. 4). Ligand pnaa adopts a *trans* coordination mode to bridge two copper atoms, while each of Cu(I) ion takes a distorted tetrahedral geometry constructed by two P atoms from half a pnaa, two S atoms from one N-ethylthiocarbamate anions, forming a S-shape conformation. The Cu–P and Cu–S bond lengths are 2.2185(13)–2.2347(12) Å and 2.6116(11)–2.6145(10) Å within the normal ranges [39]. Corresponding P–Cu–P and S–Cu–S bond angles are 98.96(4) and

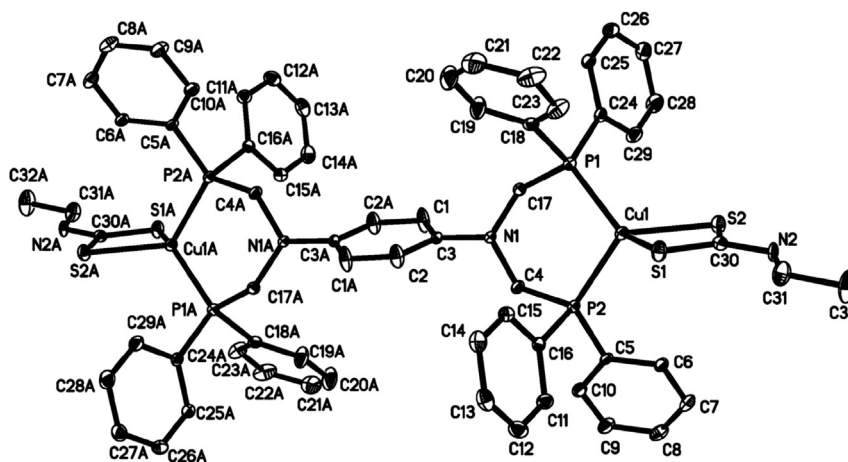


Fig. 2. Molecular structures of  $[\text{Cu}_2(\text{pbaa})(\text{Et-dtc})_2]$ . All hydrogen atoms are deleted for clarity.

Download English Version:

<https://daneshyari.com/en/article/1407516>

Download Persian Version:

<https://daneshyari.com/article/1407516>

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