

## **Synthesis, Structure and Photoluminescence of [Cu(acac)(dppe)]<sub>n</sub> with Novel 1D Zigzag Chain-Like Motif**

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A novel complex [Cu(acac)(dppe)]<sub>n</sub> (**1**) [acac = acetylacetonate; dppe = 1,2-bis(diphenylphosphino)ethane] was obtained by solution reactions and structurally characterized by X-ray diffraction. The crystal structure analysis indicates that the title complex is characteristic of a polymeric chain formed by the dppe ligands bridging neighboring copper centers. The copper atom is in a distorted tetrahedral geometry. Photoluminescent investigation reveals that the title complex displays a strong emission in blue-light region.

**Keywords:** Copper complex, Crystal structure, Hydrothermal reaction, Photoluminescence

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### **INTRODUCTION**

Copper(I) is an important metal ion with soft Lewis acid character. It has a strong tendency to form covalent bonds with soft ligands (such as P and S donor atoms) and make close Cu...Cu contacts. These characteristics of copper(I) have resulted in the formation of oligomers and polymers with diverse coordination networks. Studies of inorganic-organic coordination networks over the past decade have helped to develop new materials that exhibit photoluminescent, catalytic, conducting, magnetic exchange characteristics, and so forth [1-5].

Metal complexes of phosphines and functionalized phosphines have drawn much attention in the recent past [6-8]. In light of this growing interest, many complexes containing phosphine ligands are known with a variety of metals in different oxidation states and stereochemistry [9-11]. Among these complexes, however, copper(I) complexes are relatively

rare and copper(I) complexes containing mixed dppe and acac ligands have not been documented thus far. Herein we describe the synthesis, structure and photoluminescence of a novel complex [Cu(acac)(dppe)]<sub>n</sub> (**1**) [acac = acetylacetonate; dppe = 1,2-bis(diphenylphosphino)ethane], which is the first example of copper(I) complexes containing mixed dppe and acac ligands. Furthermore, among the metal complexes with both dppe and acac ligands, the title complex has an unprecedented one-dimensional zigzag chain-like structure, although three other metal (Ni, Co or Ru) complex containing both bis-phosphines and acac ligands with isolated motifs have been reported [12,13].

### **EXPERIMENTAL**

#### **Instrumentation**

All reactants of A.R. grade were obtained commercially and used without further purification.

X-ray diffraction data were collected on Rigaku Mercury CCD X-ray diffractometer with graphite monochromated Mo-

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$K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) using a  $\omega$  scan technique. The crystal clear software was used for data reduction and empirical absorption correction. The structure was solved by the direct methods using the Siemens SHELXTL™ Version 5 package of crystallographic software. The difference Fourier maps based on the atomic positions yield all non-hydrogen atoms. The structure was refined using a full-matrix least-squares refinement on  $F^2$ . All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were generated theoretically, allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but not refined.

### Synthesis

$[\text{Cu}(\text{acac})(\text{dppe})]_n$  (**1**). The acac (1 mmol, 0.100 g) was

added to a mixture of metallic copper powder (1 mmol, 0.064 g) and 2,2-bis(diphenylphosphino)ethane (1 mmol, 0.398 g) in 20 ml acetone. The mixture was stirred at room temperature for 48 h giving a white precipitate. The product was collected by filtration and washed with acetone. Colorless crystals were obtained by recrystallization of the product from methanol and ether.

## RESULTS AND DISCUSSION

Complex **1** was obtained from the reaction of copper powder, dppe and acac by solution reactions. X-ray diffraction analysis reveals that complex **1** features a zigzag chain-like structure. The summary of crystallographic data and structure analysis is given in Table 1. The selected bond lengths and

**Table 1.** Crystal Data of  $[\text{Cu}(\text{acac})(\text{dppe})]_n$

Empirical formula	$\text{C}_{31}\text{H}_{31}\text{CuO}_2\text{P}_2$
Formula weight	561.04
X-rays	$\text{MoK}\alpha$
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 10.732(5) \text{ \AA}$ $b = 11.903(5) \text{ \AA}$ $c = 11.912(5) \text{ \AA}$ $\alpha = 111.236(5)^\circ$ $\beta = 95.319(3)^\circ$ $\gamma = 102.150(3)^\circ$
$Z$	2
$V$	$1363(1) \text{ \AA}^3$
$D_x$	$1.368 \text{ mg m}^{-3}$
Absorption coefficient	$0.945 \text{ mm}^{-1}$
Crystal size	$0.12 \times 0.10 \times 0.04 \text{ mm}$
No. of reflections collected/unique	10669/6114 [ $R_{(\text{int})} = 0.0271$ ]
Refinement	Full matrix least squares on $F^2$
Goodness-of-fit on $F^2$	0.983
Final $R$ indices	$R_1 = 0.0474$ , $wR_2 = 0.1373$
R indices (all data)	$R_1 = 0.0693$ , $wR_2 = 0.1640$
Index ranges	$-12 \leq h \leq 13$ , $-15 \leq k \leq 14$ , $-14 \leq l \leq 15$
Measurement	Rigaku Mercury CCD diffractometer
Monochromator	Graphite
Structure determination	Siemens SHELXTL
$(\Delta/\sigma)_{\text{max}}$	0

**Table 2.** Selected Bond Lengths and Bond Angles of **1**

Bond lengths (Å)		Bond lengths (Å)	
Cu(1)-O(1)	2.072(2)	C(16)-C(17)	1.378(5)
Cu(1)-O(2)	2.100(2)	C(17)-C(18)	1.363(6)
Cu(1)-P(1)	2.271(1)	C(18)-C(19)	1.362(6)
Cu(1)-P(2)	2.279(1)	C(19)-C(20)	1.376(5)
O(1)-C(28)	1.245(4)	C(21)-C(22)	1.392(5)
O(2)-C(30)	1.253(4)	C(21)-C(26)	1.392(5)
C(1)-C(6)	1.385(4)	C(22)-C(23)	1.377(5)
C(1)-C(2)	1.390(4)	C(23)-C(24)	1.374(7)
C(2)-C(3)	1.382(5)	C(24)-C(25)	1.362(7)
C(3)-C(4)	1.363(7)	C(25)-C(26)	1.373(5)
C(4)-C(5)	1.373(7)	C(27)-C(28)	1.529(5)
C(5)-C(6)	1.374(5)	C(28)-C(29)	1.393(5)
C(7)-C(8)	1.384(5)	C(29)-C(30)	1.413(5)
C(7)-C(12)	1.388(5)	C(30)-C(31)	1.515(5)
C(8)-C(9)	1.373(5)		
C(9)-C(10)	1.379(6)	Bond angles (°)	
C(10)-C(11)	1.347(6)	O(1)-Cu(1)-O(2)	89.79(10)
C(11)-C(12)	1.381(5)	O(1)-Cu(1)-P(1)	108.00(8)
C(13)-C(13)#1	1.522(6)	O(2)-Cu(1)-P(1)	107.66(8)
C(14)-C(14)#2	1.522(6)	O(1)-Cu(1)-P(2)	115.53(8)
C(15)-C(16)	1.389(4)	O(2)-Cu(1)-P(2)	102.50(8)
C(15)-C(20)	1.404(4)	P(1)-Cu(1)-P(2)	126.31(4)

Symmetry code: #1 -x, -y, -z+1; #2 -x+1, -y+1, -z+1.

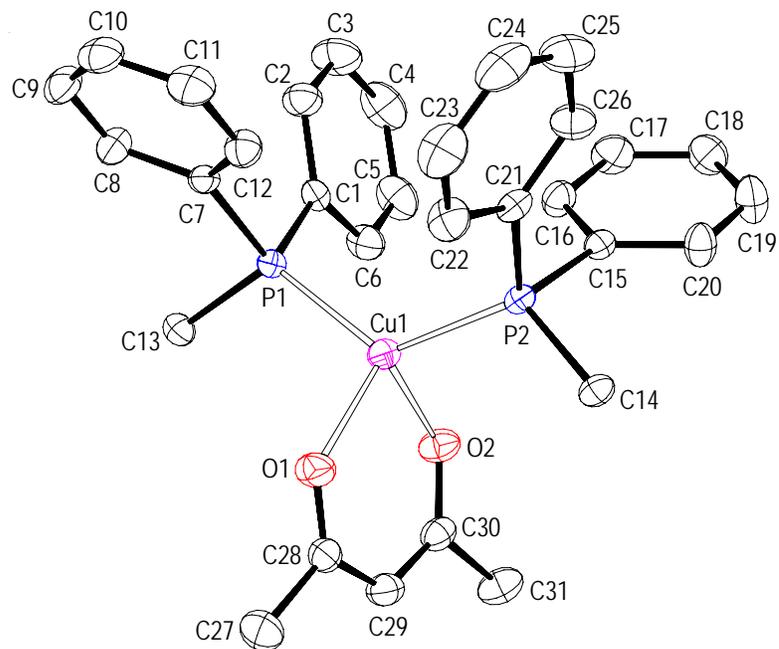
bond angles are listed in Table 2.

A view of the molecule, along with the numbering Scheme, is depicted in Fig. 1. The copper(I) ion is tetrahedrally coordinated by two phosphorus atoms from two dppe ligands and two oxygen atoms from one acac moiety. The Cu-P distances in **1** are 2.271(1) and 2.279(1) Å, with a mean value of 2.275(1) Å, comparable with those reported in the references [14,15]. The observed Cu-O<sub>acac</sub> distances of 2.072(2) and 2.100(2) Å are longer than those Cu-O<sub>acac</sub> distances (<2.0 Å) found in other copper(I) complexes containing acac ligands, in which the copper metals are coordinated by acac and non-dppe ligands [16-20]. This may be caused by the fact that the coordination of dppe ligand to Cu lead to the weakening and lengthening of the Cu-O<sub>acac</sub> bond. The bond lengths of the C-C bonds in the phenyl rings are range from 1.347(6) to 1.404(4)

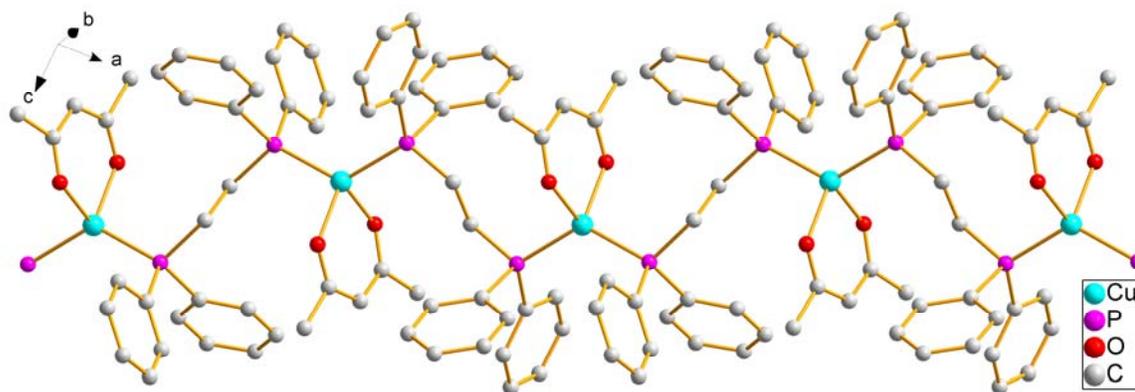
Å, with the average value of 1.377(7) Å. In acac moiety, the bond lengths of C(28)-C(29) and C(29)-C(30) being 1.393(5) and 1.413(5) Å are obviously shorter than those of single bonds C(27)-C(28) and C(30)-C(31) being 1.529(5) and 1.515(5) Å, but close to the average value of 1.377(7) Å of the C-C bonds in the phenyl rings, indicating C(28), C(29) and C(30) atoms form a conjugated system.

The neighboring copper metals are bridged by dppe ligands to form a zigzag polymeric chain extending along [1,1,0] direction, as shown in Fig. 2. For **1**, there are no  $\pi \dots \pi$  stacking interactions and hydrogen bonding among the polymeric chains, therefore, the van de Waals' force should be the only contribution to the stability of the crystal packing (Fig. 3).

The solid-state emission spectrum of the title complex was



**Fig. 1.** ORTEP drawing of **1** with 30% thermal ellipsoids and hydrogen atoms being omitted for clarity.

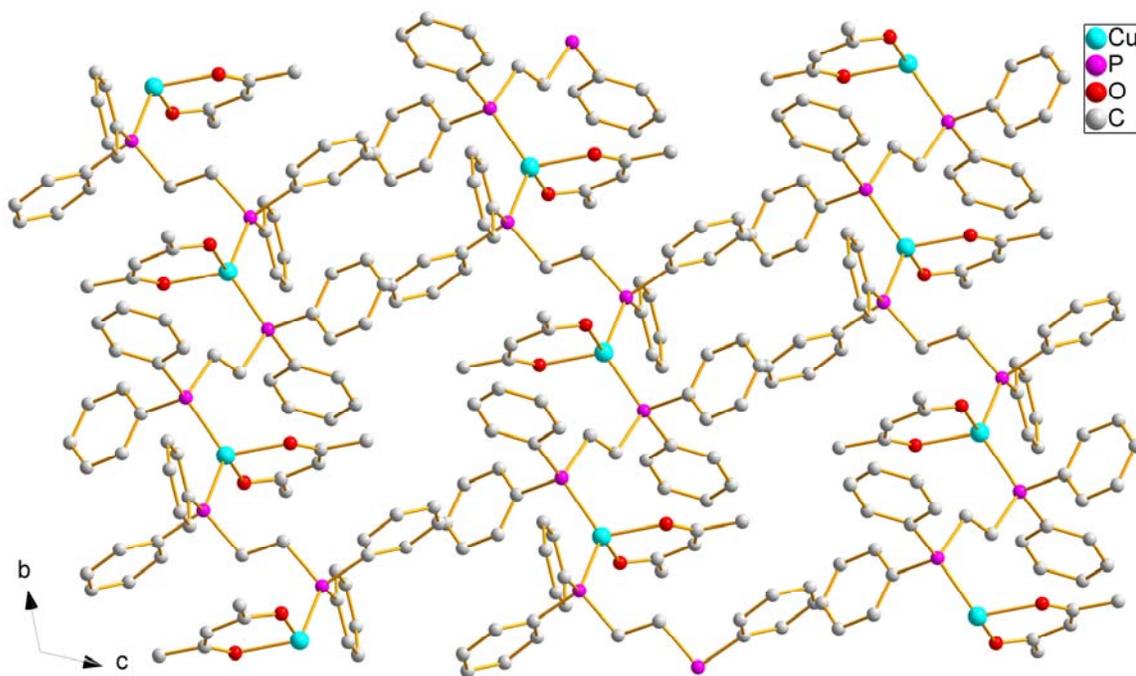


**Fig. 2.** One-dimensional zigzag polymeric chain of **1**.

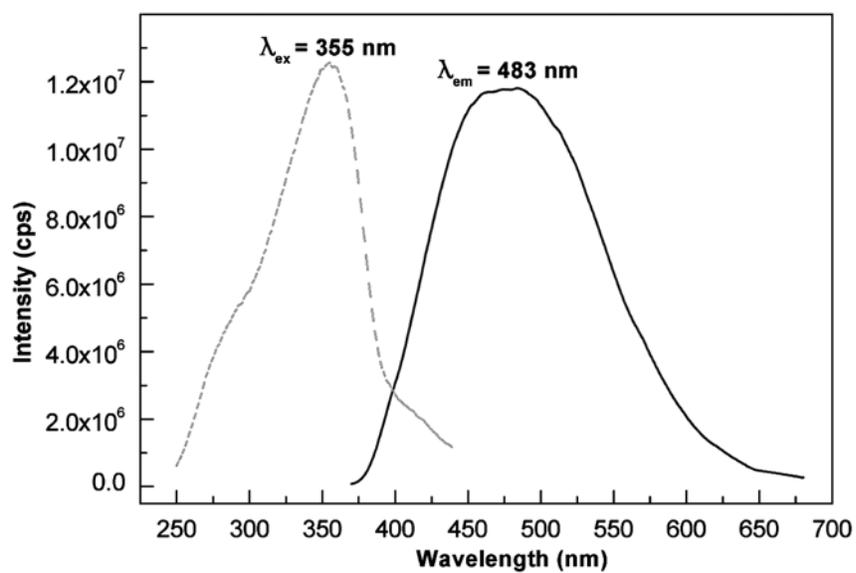
investigated at room temperature. The emission spectrum of the title complex is given in Fig. 4. The photoluminescence spectrum study shows that the title complex exhibits a strong blue-light emission band with a maximum wavelength of 483 nm upon photo-excitation at 355 nm. The emission should probably be assigned to metal-to-ligand charge transfers (MLCT). Thus, this complex may be a candidate in blue-light

luminescent materials.

In summary, by using solution reactions of copper powder, dppe and acac, a new complex was obtained, which is the first example of copper(I) complexes containing both dppe and acac ligands. This complex exhibit a strong photoluminescent emission band, and it probably can be used as a blue-light material. It is believed that many copper(I) complexes with



**Fig. 3.** Packing diagram of **1** with hydrogen atoms being omitted for clarity.



**Fig. 4.** Solid-state emission and excitation spectra of **1** at room temperature. Red solid lines: emission spectra; Green dashed lines: excitation spectra.

good photoluminescent property can be developed. Future investigations in this field are in progress in our laboratory.

## SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 666155. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CBZ 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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