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# Cu[(PPh<sub>3</sub>)<sub>2</sub>O](acac): Cu<sup>+</sup> charge-compensated by a coordinating acac<sup>-</sup> anion

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#### Abstract

A complex  $Cu[(PPh_3)_2O](acac)[(PPh_3)_2O = Bis(2-diphenyl-phosphinophenyl) ether; acac = acetylacetone] was obtained by solution reactions and structurally characterized. The title complex is characterized by an isolated structure. X-ray structure analysis of the title complex shows that acac and <math>(PPh_3)_2O$  behave as chelating ligands. Photoluminescent investigation reveals that the title complex displays a strong blue-light emission.

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Copper(I) complexes containing phosphine ligands have been the focus of much investigation in the last few years because of the novel structural and reactive features of these complexes. In light of this growing interest [1], many examples of complexes containing phosphine ligands are known with a variety of metals in different oxidation states and stereochemistry [2]. Among these complexes, copper(I) complexes are relatively rare [3] and copper(I) complexes containing mixed phosphine and acac ligands have not been documented thus far. To our best knowledge, among the known copper(I) complexes containing acac ligand, the charge of the Cu<sup>+</sup> center is usually compensated by an isolated anionic moiety, such as ClO<sub>4</sub><sup>-</sup>, F<sub>6</sub>P<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and Br<sup>-</sup>, which does not coordinate to the  $Cu^+$  center [4] and the examples of the Cu<sup>+</sup> center charge-compensated by a coordinating anionic moiety are very rare [5]. Herein we describe the synthesis, structure and photoluminescence of a complex  $Cu[(PPh_3)_2O](acac)$ , which is the first example of copper(I) complexes containing mixed phosphine and acac ligands. Furthermore, in the title complex, the charge

\* Corresponding author. E-mail address: xym8790@yahoo.com.cn (Y.-M. Xie). of the Cu<sup>+</sup> center is compensated by a coordinating anionic moiety, i.e. acac<sup>-</sup>.

The title complex was obtained from the reaction of copper powder, bis(2-diphenyl-phosphinophenyl) ether and acac by solution reactions [6]. X-ray diffraction analysis [7] reveals that the structure of the title complex consists of discrete molecules. A view of the molecule, with the numbering scheme, is depicted in Fig. 1. In the title complex the copper(I) ion is tetrahedrally coordinated by two phosphorus atoms from one (PPh<sub>3</sub>)<sub>2</sub>O ligand and two oxygen atoms from one acac moiety. The Cu-P distances in  $Cu[(PPh_3)_2O](acac)$  are 2.2426(8) and 2.2666(8) Å, with a mean value of 2.2546(8) Å, comparable with the average value of 2.2312(8) Å found in [Cu(PPh<sub>3</sub>)<sub>2</sub>(NO<sub>3</sub>)] [8]. The observed Cu-Oacac distances of 2.056(2) and 2.044(2) Å are longer than those Cu-O<sub>acac</sub> distances found in the copper(I) complexes containing acac ligands, in which the copper metals are coordinated by acac and other ligands, such as acetic acid, phen, Me<sub>2</sub>bipy, NCS, and so on. [9]. This may be caused by the fact that the coordination of (PPh<sub>3</sub>)<sub>2</sub>O 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 1.357(5) to 1.405(4) Å, with the average value of 1.3794(7) Å. In acac

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Fig. 1. ORTEP drawing of the title complex with 25% thermal ellipsoids. Hydrogen atoms were omitted for clarity.

moiety, the bond lengths of C(38)-C(39) and C(39)-C(40)being 1.389(5) and 1.394(5) Å are shorter than those of single bonds C(37)-C(38) and C(40)-C(41) being 1.525(5) and 1.522(5) Å, but close to the average value of 1.3794(7) Å of the C–C bonds in the phenyl rings, indicating C(38), C(39)and C(40) atoms form a conjugated system. The formation of this conjugated system may be interpreted by the following mechanism: before coordinating to the copper center, the acac ligand rearranges as an enol-form and then coordinates to the copper center with the formation of the conjugated system, as shown in the Scheme 1. For the title complex, there are weak intermolecular  $\pi \cdots \pi$ stacking interactions between the rings composed of atoms C25–C30. The distance between the ring centroids is ca. 3.74 Å. There is no hydrogen bonding among the isolated molecules. The weak intermolecular  $\pi \cdots \pi$  stacking interactions and the van de Waals' force should contribute to the stability of the crystal packing (Fig. 2).

Structural studies involving phosphine species of other transition metals (Mn [10], Mo [11]) are less common



Scheme 1. The formation of the conjugated system.



Fig. 2. Packing diagram of the title complex with hydrogen atoms were omitted for clarity. The dashed lines represent  $\pi \cdots \pi$  stacking interactions.

but, in general, reveal linear P–M–P fragments and planar  $M_2P_4$  skeletal units. For d<sup>10</sup> complexes, however, the P–M–P units are distinctly non-linear [12]. X-ray structural characterization of the title complex, clearly reveals that the P–M–P angle [114.08(3)°] in the complex is not restricted by steric crowding of (PPh<sub>3</sub>)<sub>2</sub>O phenyl rings, as the cases found in the Refs. [3c,3d].

To date, few copper(I) complexes containing acac ligand have been reported. Moreover, in these complexes the charge of the  $Cu^+$  center in one isolated moiety is usually compensated by another isolated anionic moiety, such as  $ClO_4^-$ ,  $F_6P^-$ ,  $NO_3^-$  and  $Br^-$ , which does not coordinate to the  $Cu^+$  center [4] and, to our best knowledge, only one complex in which the  $Cu^+$  center is charge-compensated by a coordinating anionic moiety has been documented [5]. In the title complex, however, the charge of the  $Cu^+$ center is compensated by a coordinating anionic moiety – acac<sup>-</sup>. Therefore, the title complex is the first example of which the  $Cu^+$  center is charge-compensated by a coordinating acac<sup>-</sup> anion.

The solid-state emission spectrum of the title complex is investigated at room temperature. The emission spectrum of the title complex is given in Fig. 3. The photoluminescence spectrum study shows that the title complex exhibits a broad and strong blue-light emission band with a maximum wavelength of 461 nm upon photo-excitation at 357 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 brief, by using solution reactions of copper powder,  $(PPh_3)_2O$  and acac, a new complex was obtained, which is the first example in the complexes the Cu<sup>+</sup> center being charge-compensated by a coordinating acac<sup>-</sup> anion. This complex exhibits a broad and strong photoluminescent emission band, and it is a candidate of blue-light materials. It is believed that more and more copper(I) complexes with



Fig. 3. Solid-state emission and excitation spectra of the title complex at room temperature. Red solid line: emission spectrum; green dashed line: excitation spectrum.

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

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## Appendix A. Supplementary material

CCDC No. 648740 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007.09.027.

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- [6] Synthesis of the title complex: The acac (1 mmol, 0.100 g) was added to a mixture of metallic copper powder (1 mmol, 0.064 g) and bis(2diphenyl-phosphinophenyl) ether (1 mmol, 0.538 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. The crystals are stable in air. Yield: 86% (based on copper powder).
- [7] (a) *Crystal data*: C<sub>41</sub>H<sub>35</sub>CuO<sub>3</sub>P<sub>2</sub>, M = 701.17, triclinic,  $P\bar{1}$  (No. 2), a = 9.764(2), b = 11.031(3), c = 18.137(5) Å,  $\alpha = 103.635(8)$ ,  $\beta = 102.774(15)$ ,  $\gamma = 101.700(11)^\circ$ , V = 1783.3(7) Å<sup>3</sup>, Z = 2,  $\mu$ (Mo K $\alpha$ ) = 0.739 mm<sup>-1</sup>, T = 293(2) K,  $R_1 = 0.0500$ ,  $wR_2 = 0.1271$ . X-ray diffraction data were collected on Rigaku Mercury CCD X-ray

diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) using a  $\omega$  scan technique. CrystalClear software was used for data reduction and empirical absorption correction. The structure was solved by the direct methods using the Siemens SHELXTL<sup>TM</sup> 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; (b) Rigaku, CrystalClear Version 1.35, Rigaku Corporation, 2002; (c) Siemens, SHELXTL<sup>TM</sup> Version 5 Reference Manual, Siemens Energy & Automation, Inc., Madison, Wisconsin, USA, 1994.

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