



# Copper(I)/silver(I)-phosphine-*N*-{(2-pyridyl)methylidene}-6-coumarin complexes: Syntheses, structures, redox interconversion, photophysical properties and DFT computation

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## ABSTRACT

Mixed ligand complexes of Cu(I) and Ag(I) with bis(diphenylphosphino)methane (dppm)/1,2-bis(diphenylphosphino)ethane (dppe) and *N*-{(2-pyridyl)methylidene}-6-coumarin (L) have been synthesized and characterized by elemental analyses, conductivity, <sup>1</sup>H NMR, UV–Vis and fluorescence spectral data. The coordination of dppm to M(I) forms a binuclear metallacycle, [(L)M(μ-dppm)<sub>2</sub>M(L)](X)<sub>2</sub> (X = NO<sub>3</sub> or ClO<sub>4</sub>), and one of the complexes has been characterized by single crystal X-ray structure analysis. The dppe ligand is a bidentate chelator, which is supported by the X-ray structure of [Cu(dppe)(L)]ClO<sub>4</sub>. In the Ag(I) complex, dppe is serving as a bridging agent to form the binuclear complex [(L)Ag(μ-dppe)Ag(L)](NO<sub>3</sub>)<sub>2</sub>, and NO<sub>3</sub><sup>−</sup> asymmetrically chelates Ag(I), which exhibits solvent polarity dependent coordination. In a coordinating polar solvent, like MeCN, the nitrate group dissociates and shows conductivity, while in nitrobenzene the complex is non-conducting and supports no dissociation. The complexes are more fluorescent than free L. Cyclic voltammetry shows a Cu(II)/Cu(I) quasireversible couple, while the Ag(I) complexes exhibit deposition of Ag(0) on the electrode surface. The coulometric and Cl<sub>2</sub> oxidation of the Cu(I) complexes have isolated Cu(II) complexes that are established by spectroscopic and magnetic data. The electronic configuration of the complexes is assessed by DFT computation, and the spectral and redox properties are explained.

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## 1. Introduction

Use of natural products as synthetic precursors to design new molecules with various interests has been of long standing demand [1]. Coumarin, a natural product found in many plants, such as Tonka bean, lavender, sweet clover grass, licorice, strawberries, apricots, cherries, cinnamon, etc., has been used by many researchers to synthesize new derivatives [2–9]. Some of the coumarin derivatives and their metal complexes exhibit anticancer activity [10–14]. The Schiff bases of coumarin are well known for their fluorescent properties and usefulness as laser dyes [15]. This has inspired us to synthesize coumarinyl-azo (–N=N–) and imine (–C=N–) derivatives. We have synthesized *N*-{(2-pyridyl)methylidene}-6-coumarin (L) and have used it to synthesize copper(I) and silver(I) complexes [16]. In this article, we use dppm (bis-(diphenylphosphino)methane) and dppe (1,2-bis-(diphenylphosphino)ethane) as co-ligands to synthesize mixed ligand Cu(I) and Ag(I) complexes of L to examine the luminescence activity of the coumarin Schiff base in the presence of diphosphino ligands.

Bis-(diphenylphosphino)methane (dppm) is a versatile ligand used to construct rigid M<sub>2</sub>P<sub>4</sub> frameworks (M = Cu(I), Ag(I)) in the design of clusters [17]. 1,2-Bis(diphenylphosphino)ethane (dppe) chelates to constitute mononuclear MP<sub>2</sub> complexes and also bridges to generate a binuclear M<sub>2</sub>P<sub>4</sub> framework [18]. Mixed ligand complexes of Cu(I) and Ag(I)-{*N*-{(2-pyridyl)methylidene}-6-coumarin (L)} and dppm/dppe are reported in this work. All these compounds are characterized by spectroscopic data. The structures of [(L)Cu(μ-dppm)<sub>2</sub>Cu(L)](ClO<sub>4</sub>)<sub>2</sub> (**1**), [(L)Ag(μ-dppe)Ag(L)](NO<sub>3</sub>)<sub>2</sub> (**4**) and [Cu(dppe)(L)]ClO<sub>4</sub> (**5**) have been confirmed by X-ray crystallography. Quantum chemical calculations using density functional theory (DFT) have been carried out to explain the electronic configuration, spectral and redox properties of the compounds.

## 2. Results and discussion

### 2.1. Synthesis and formulation

*N*-{(2-Pyridyl)methylidene}-6-coumarin (L) was synthesized by the condensation of pyridine-2-carboxaldehyde with 6-amino-coumarin. The condensation is supported by the elimination of ν(NH<sub>2</sub>) (3329 and 3409 cm<sup>−1</sup>) of 6-aminocoumarin, a new band

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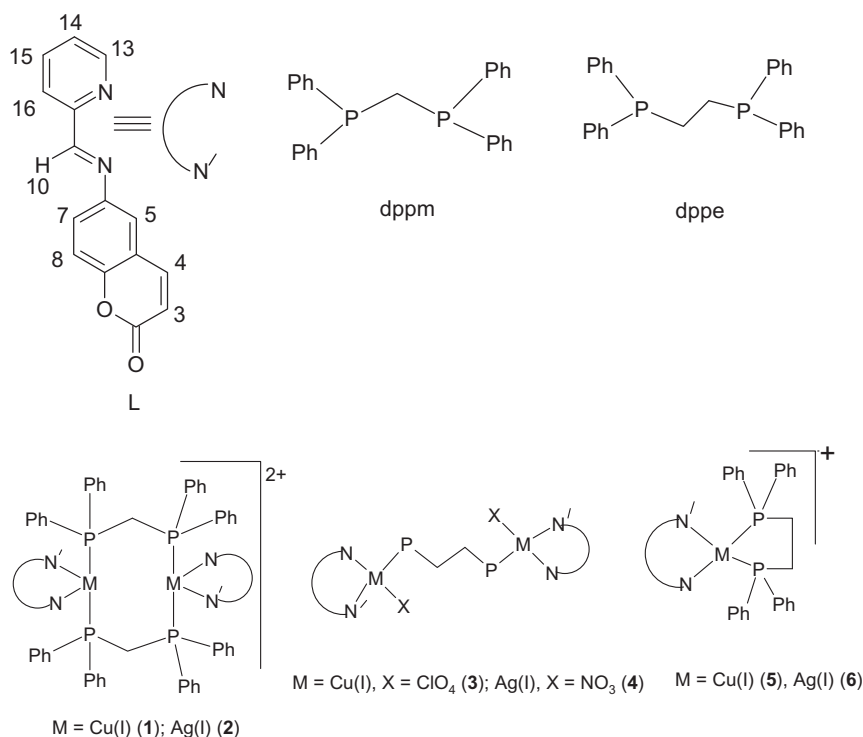
at  $1565\text{ cm}^{-1}$  (assigned to  $\nu(\text{C}=\text{N})$ ) and lactone  $\nu(\text{COO})$  at  $1716\text{ cm}^{-1}$ . The electronic absorption spectrum of L in acetonitrile gives two intense bands at 325 and 278 nm, which are assigned to  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions. The  $^1\text{H}$  NMR spectrum shows a singlet signal at 8.63 ppm for  $\text{CH}=\text{N}$ , the pyridyl protons appear at  $\delta$  7.8–8.7 ppm and the coumarin protons appear at  $\delta$  6.5 to 7.7 ppm [16].

The reaction of L, dppm and  $[\text{Cu}(\text{MeCN})_4]\text{ClO}_4$  (1:1:1 M ratio, respectively) in dry methanol under a  $\text{N}_2$  environment for 2 h isolated a yellow precipitate of  $[(\text{L})\text{Cu}(\mu\text{-dppm})_2\text{Cu}(\text{L})](\text{ClO}_4)_2$  (**1**) (Scheme 1). A similar reaction using  $\text{AgNO}_3$  under identical conditions separated  $[(\text{L})\text{Ag}(\mu\text{-dppm})_2\text{Ag}(\text{L})](\text{NO}_3)_2$  (**2**). The reaction product of dppe with L and  $[\text{Cu}(\text{MeCN})_4]\text{ClO}_4/\text{AgNO}_3$  is dependent on the composition of reactants; for the reaction with L:M:dppe (M refers to the metal salts used in the reaction) of 1:1:0.5 mol proportions, the products are  $[(\text{L})\text{Cu}(\mu\text{-dppe})\text{Cu}(\text{L})](\text{ClO}_4)_2$  (**3**) and  $[(\text{L})\text{Ag}(\mu\text{-dppe})\text{Ag}(\text{L})](\text{NO}_3)_2$  (**4**), while equimolar proportions (1:1:1 M ratio) of L:M:dppe has isolated products of the compositions  $[\text{Cu}(\text{dppe})(\text{L})]\text{ClO}_4$  (**5**) and  $[\text{Ag}(\text{dppe})(\text{L})]\text{NO}_3$  (**6**). The complexes were crystallized by slow diffusion of hexane into a dichloromethane solution of the complexes.

The molar conductance was measured in the polar solvent MeCN and the non-polar solvent nitrobenzene. The molar conductance ( $\Lambda_{\text{M}}$ ) data of **1** and **2** in  $\text{CH}_3\text{CN}$  are 117 and  $130\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$  and in nitrobenzene 24 and  $28\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ , respectively. The  $\Lambda_{\text{M}}$  values support 1:1 electrolyte character. Complexes **5** and **6** also support 1:1 conductivity ( $\Lambda_{\text{M}}$ : 108 (MeCN) and 27 (nitrobenzene) for **5**; 126 (MeCN) and 33 (nitrobenzene) for **6**). A remarkable observation is that compounds **3** and **4** are non-conducting in nitrobenzene ( $\Lambda_{\text{M}} < 5\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ ) while they are 1:1 electrolytes in acetonitrile solution ( $\Lambda_{\text{M}}$ : 122 and  $138\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$  for **3** and **4**, respectively). This result signifies dissociation of the complex in a polar coordinating solvent whilst in a non-polar medium  $\text{ClO}_4^-$  or  $\text{NO}_3^-$  remains coordinated to metal ion center.

## 2.2. Molecular structures

The molecular structures of **1**, **4** and **5** are shown in Fig. 1a–c. The bond parameters are listed in Table 1. The structures of **1** (Fig. 1a) and **4** (Fig. 1b) consist of binuclear  $\text{M}_2\text{N}_4\text{P}_4$  and  $\text{M}_2\text{N}_4\text{P}_2\text{O}_2$  coordination types, respectively, while the structure of **5** (Fig. 1c) has an  $\text{MN}_2\text{P}_2$  coordination. M(I) is present at the center of a distorted tetrahedron. The charges of the cationic complexes  $[(\text{L})\text{Cu}(\mu\text{-dppm})_2\text{Cu}(\text{L})]^{2+}$  (**1**) and  $[\text{Cu}(\text{dppe})(\text{L})]^+$  (**5**) are satisfied by  $\text{ClO}_4^-$ , and in complex **4** (Fig. 1b) the charge is balanced by  $\text{NO}_3^-$ . The ligand L acts as an  $\text{N,N}'$ -chelator (N refers to N(pyridine) and N' refers to N(imine)) end capping agent. The pendant coumarinyl ring makes dihedral angles of  $10.1(4)^\circ$  (**1**),  $12.1(5)^\circ$  (**4**) and  $34.6(12)^\circ$  (**5**) with chelated diimine ring,  $-(\text{M}-\text{N}=\text{C}-\text{C}=\text{N}-)$ , and may assist in the distortion from an ideal tetrahedral geometry. The chelate angles,  $\text{M}(\text{N}, \text{N}')$ , of  $78.7(3)^\circ$  (**1**),  $71.2(3)^\circ$  (**4**) and  $80.55(10)^\circ$  (**5**) are extended by L on coordination to M(I) and they are comparable with reported results in the series of chelated Cu(I) and Ag(I) complexes [19]. The small chelate angle may be one of the reasons for the geometrical distortion. The  $\text{P}(1)-\text{M}(1)-\text{P}(2)$  angle is  $133.67(8)^\circ$  for **1**, which supports this structural deviation from an ideal tetrahedral geometry. The distortion may be due to steric demand of the pendant coumarinyl group of the chelating  $\text{N,N}'$ -unit. The  $\text{M}-\text{N}(\text{pyridine})$  distances ( $2.133(7)$  (**1**),  $2.320(8)$  (**4**) and  $2.054(2)$  (**5**) Å) are shorter than the  $\text{M}(\text{I})-\text{N}(\text{imine})$  distances ( $2.215(6)$  (**1**),  $2.405(8)$  (**4**) and  $2.082(2)$  Å (**5**)), which reflects the preferentially stronger interaction of M(I) with N(pyridine) compared to exocyclic N(imine) of L. The  $\text{M}-\text{P}$  distances ( $\text{M}(1)-\text{P}(1)$ :  $2.282(2)$  (**1**),  $2.361(3)$  (**4**),  $2.266(9)$  Å (**5**);  $\text{M}(1)-\text{P}(2)$ :  $2.344(2)$  (**1**),  $2.340(3)$  (**4**),  $2.271(9)$  Å (**5**)) are comparable with the reported results [20]. In **4**,  $\text{NO}_3^-$  acts as a weakly chelating agent and the unsymmetrical binding is estimated from the unequal Ag–O bond lengths:  $\text{Ag}(1)-\text{O}(5)$ , 2.631 and  $\text{Ag}(1)-\text{O}(6)$ , 2.803 Å, which are



Scheme 1. The ligands and the complexes.

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