

Synthesis and structural characterization of five copper(I) complexes of [2,3-f]-pyrazino-[1,10]phenanthroline-2,3-dicarbonitrile and triphenylphosphine

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ABSTRACT

Five new copper(I) complexes containing PPh₃ and C₁₆H₆N₆, [Cu(PPh₃)(C₁₆H₆N₆)Cl]·H₂O (**1**), [Cu(PPh₃)(C₁₆H₆N₆)Br]·CH₃CN (**2**), [Cu(PPh₃)(C₁₆H₆N₆)I]·CH₃CN (**3**), [Cu(PPh₃)(C₁₆H₆N₆)(CN)]·0.5 CH₂Cl₂ (**4**) and Cu(PPh₃)(C₁₆H₆N₆)(SCN) (**5**) {PPh₃ = triphenylphosphine, C₁₆H₆N₆ = [2,3-f]-pyrazino-[1,10] phenanthroline-2,3-dicarbonitrile} have been synthesized for the first time. These complexes are obtained by the reactions of CuX (X = Cl, Br, I, CN, SCN) with the bidentate ligand C₁₆H₆N₆ and the monodentate ligand PPh₃ in the molar ratio of 1:1:1 in the mixed solvent of CH₂Cl₂ and CH₃CN (5 ml/5 ml). They are characterized by X-ray crystallography, luminescence, IR, ¹H NMR and ³¹P NMR. In solid state the complexes **1–5** are mononuclear with similar structures, but in solution they have different structures according to their different ¹H NMR signals. All the complexes exhibit intense luminescence in solid state at room temperature.

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Copper(I) complexes of functionalized phosphines have drawn much attention in recent years for their special structures, novel reactivity performances, catalytic and luminescent properties [1–7]. Especially some mixed-ligand complexes with phosphines and 1,10-phenanthroline (phen) or its derivatives exhibit efficient electroluminescence and thus are suitable for organic lightemitting diode applications [8,9].

The ligand (C₁₆H₆N₆) has an extensive conjugated system and multiple coordination groups including strong chelating phen ring, bridging pyrazine ring and cyanite groups, so it is a good candidate in synthesizing luminescent complexes containing multifunctional ligand. Neutral heteroleptic complexes of the form [CuX(NN)P], where X = halide or pseudohalide, P = phosphine and NN = [2,3-f]-pyrazino-[1,10] phenanthroline-2,3-dicarbonitrile (C₁₆H₆N₆), haven't been studied.

In this work, the following five new Cu(I) complexes of PPh₃ and C₁₆H₆N₆ are prepared: [Cu(PPh₃)(C₁₆H₆N₆)Cl]·H₂O (**1**), [Cu(PPh₃)(C₁₆H₆N₆)Br]·CH₃CN (**2**), [Cu(PPh₃)(C₁₆H₆N₆)I]·CH₃CN (**3**), [Cu(PPh₃)(C₁₆H₆N₆)(CN)]·0.5CH₂Cl₂ (**4**) and Cu(PPh₃)(C₁₆H₆N₆)(SCN) (**5**). They are characterized by X-ray crystallography, luminescence, IR, ¹H NMR and ³¹P NMR.

The compounds **1–5** are obtained by the reactions of copper (I) salt with PPh₃ and C₁₆H₆N₆ in the mixed solvent of dichloromethane and acetonitrile [10]. Complexes **1–5** are all insoluble in diethyl ether but soluble in ethanol, methanol, acetonitrile and DMF. The molar ratio of Cu:P:N in the product [Cu(PPh₃)(C₁₆H₆N₆)X] (X = Cl, Br, I, CN and SCN) agrees with that of the starting materials (CuX: PPh₃: C₁₆H₆N₆ = 1:1:1).

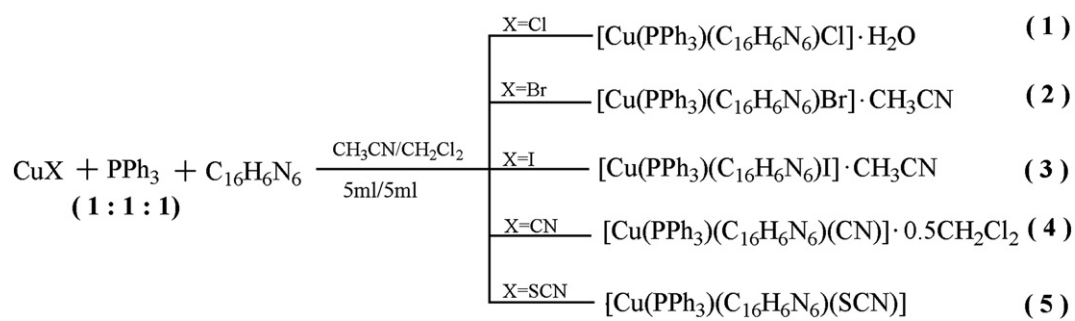
The choice of solvent plays an important role in the synthesis of complexes. The title complexes **1–5** were successfully prepared by the reactions of MX with PPh₃ and C₁₆H₆N₆ in mixed solvent of CH₂Cl₂ and CH₃CN. If the mixed solvent of CH₂Cl₂/CH₃OH or CH₂Cl₂/DMF is chosen in above reactions, no crystal was obtained.

In addition, the reaction time is very important for the generation of compounds **1–5**. If the starting materials in the mixed solvent were stirred longer than 3 h, the deep red solution began to turn green, which indicates that copper(I) began to be oxidized to copper(II). The synthesis of compounds **1–5** is shown in Scheme 1.

The perspective view of **1** is shown in Fig. 1A. The asymmetry unit of **1** contains one molecule of Cu(PPh₃)(C₁₆H₆N₆)Cl and one isolated molecule of water [11]. In the basic unit, the metal center is bonded to the two N atoms from C₁₆H₆N₆ ligand, one P atom from PPh₃ and one Cl atom to form the tetrahedral geometry. Similar to the corresponding angles in the compound [Cu(phen)(PPh₃)Cl]₂·H₂O (79.8°–121.62°)[12], the angles around Cu are obviously distorted from the ideal angles, which can be attributed to the need to accommodate bidentated ligand C₁₆H₆N₆. The bond distance of Cu–P is shorter

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Scheme 1. The routine of synthesis for complexes 1–5.

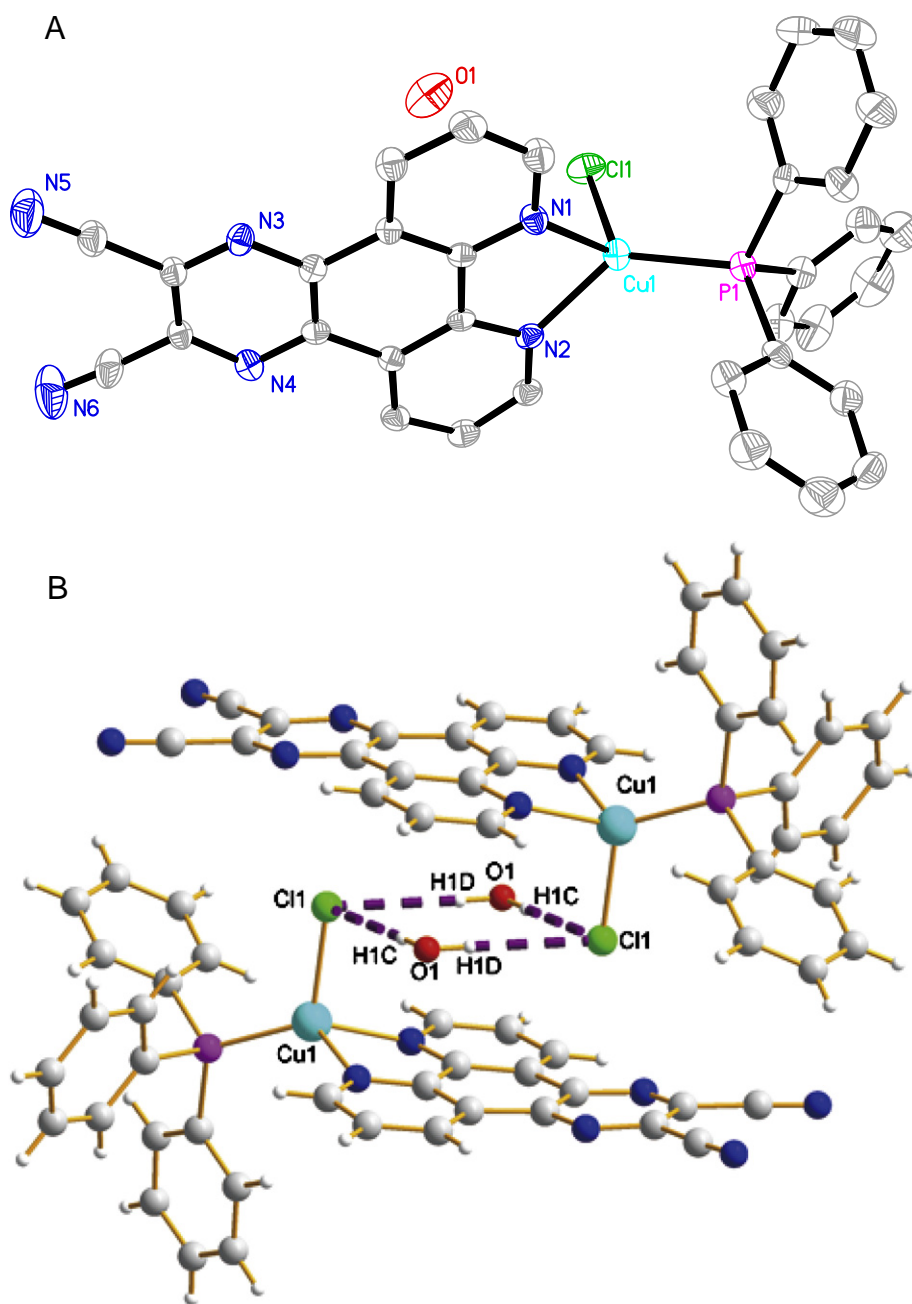


Fig. 1. A. Perspective view of crystal structure of complex 1. All the hydrogen atoms are omitted for clarity. B. The hydrogen bonds in complex 1.

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