

Synthesis, Characterization And Spectral Behavior of Some Mixed-Ligand Copper (II) Complexes Involving 3,4-Pyridinedicarboxylic Acid and Diimines

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Abstract

Six mixed-ligand complexes of copper(II) $[Cu_3(pdc)_2(bipy)].2BF_4$ (1), $[Cu_4(pdc)_2(4,4'-Me_2bipy)_2(dm f)_2].4BF_4$ (2), $[Cu_4(pdc)_2(5,5'-Me_2bipy)_2(dm f)_2].4BF_4$ (3), $[Cu_4(pdc)_2(phen)(dm f)_2].4BF_4$ (4), $[Cu_3(pdc)_2(dmp)_2(dm f)_2].2BF_4$ (5) and $[Cu_3(pdc)(bathophen)(dm f)_4].4BF_4$ (6) have been synthesized by solvothermal method in 3:1:1 metal-to-ligand molar ratio. The synthesized complexes have been characterized by elemental analyses (C, H, N), IR-spectra and electron paramagnetic resonance (EPR) spectra.

Keywords: Mixed-ligand Cu (II) complexes, 3,4- pyridinedicarboxylic acid, diimines, EPR-Spectra.

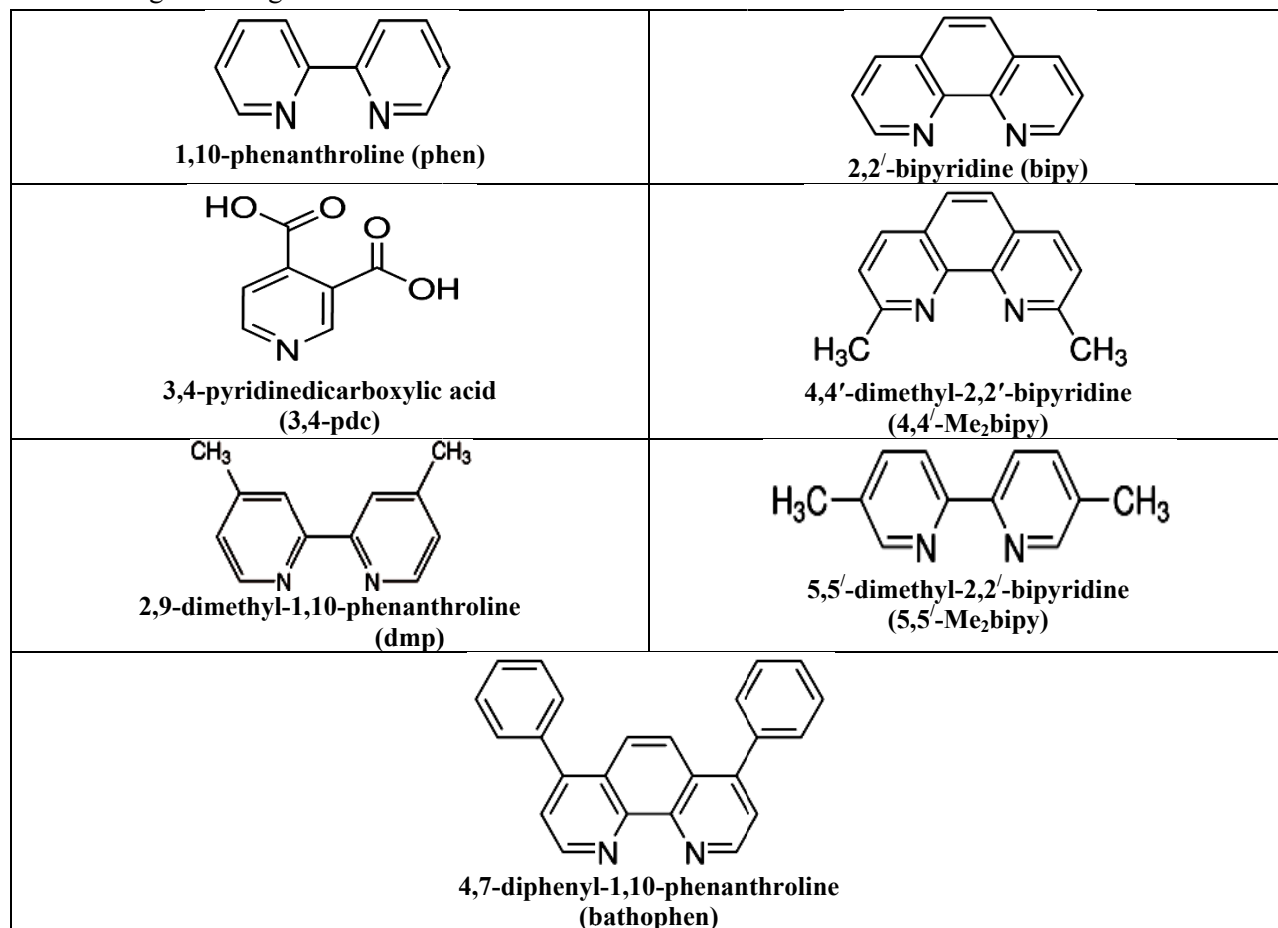
Introduction

Solid engineering is of interest for both structural and topological innovations of organic–inorganic frameworks due to their potential applications in material science as catalytic, conductive, luminescent, magnetic, nonlinear optical or porous devices [1–5]. Coordination polymer design depends not only on the chosen metals and organic linkers but also on the reaction conditions like temperature, solvents, and counter ions. Polycarboxylate ligands have been often used as good building blocks to construct transition metal or lanthanide coordination polymers [6–16]. In this ligand class, positional isomers of pyridinedicarboxylate anions, such as 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, and 3,5-pdc²⁻ are representative of hybrid spacers (N,O-donors), frequently applied to achieve varied coordination polymers or metal–organic frameworks within supramolecular arrangements [17]. The presence of both pyridine and carboxylate functionalities gives these ligands versatile coordination modes toward different metal ions [8, 18–21]. Especially, the multifunctional ligand 3,4-pyridinedicarboxylic acid (3,4-h₂pdc), also known as cinchomeric acid, an asymmetric molecule containing five coordination sites, is an excellent building block and, therefore, it has been extensively employed in the construction of metal–organic frameworks [15]. The two carboxyl groups are considerably flexible so as to connect metal ions in different orientations. Therefore, it can adopt rich accessible coordination modes to construct a variety of polymers [22]. Due to steric hindrance between the carboxylic groups in the 3- and 4-positions, the participation of only one carboxylic group in coordination to the metal center is expected. However, the rotational freedom of the carboxylic groups makes them flexible enough to participate in the coordination environment at the same time, as reported [14, 20].

The d⁹ configuration of Cu (II) in an octahedral field leads to a significant Jahn-Teller distortion that usually manifests itself as an axial elongation, consistent with the lability and geometric flexibility of Cu (II) complexes [23]. Ternary complexes of oxygen-donor ligands and heteroaromatic N-bases have attracted much interest as they can display exceptionally high stability [24-26]. Metal complexes containing diimine ligands such as 1,10 – phenanthroline and bipyridine have gained importance because

of their versatile roles as binding blocks for the synthesis of metallo – dendrimers and as molecular scaffolding for supramolecular assemblies, and in analytical chemistry, catalysis, electrochemistry, ring opening metathesis polymerization and biochemistry [27]. The medicinal application of metal complexes has also been a subject of great interest recently [28]. For instance, to name among others, phen and its copper complexes have been reported to exert a range of biological activities, such as antitumour, anti-candida [29]. Antimycobacteria [30] and antimicrobial effects [31]. Nitrogen containing chiral ligands has found wide applications in chemotherapy and asymmetric catalysis. Among them, bipyridines and 1, 10 – phenanthrolines are particularly attractive for their ability to coordinate several metal ions, and thus to generate different catalytic species involved in a great variety of reactions [32]. The ligands (1, 10 – phenanthroline and 2, 2' – bipyridine) are strong field bidentate ligands that form very stable chelates with many first row transition metals [33].

2,9-dimethyl-1,10-phenanthroline, often called neocuproin, is useful as an analytical reagent for the estimation of copper (I), due, in large measure to its formation of the brilliant red copper complex [19], bis(phenanthroline)copper(I) complex have received much attention for their being less expensive and environment friendly, interesting photochemical and photophysical properties [19-25] suitable for practical applications such as light harvesting for photovoltaic cells and as molecular sensors [20-24]. In this work, we report the synthesis, characterization and spectral behavior of some mixed-ligand copper (II) complexes involving 3,4-pyridinedicarboxylic acid and diimines. The structures of 3,4-pdc and diimines ligands are given below :



Experimental

Materials and methods

All organic solvents and chemicals used for the synthesis were purchased commercially and used without further purification. Elemental analyses (C, H, N) were performed on a EURO VECTOR EA 3000 ELEMENTAL ANALYSER. FTIR Spectrum was recorded in the range 450-4000 cm^{-1} on a Agilent Cary 630 FTIR Spectrometer using a KBr pellet. X-band EPR Spectra was recorded at a room temperature on JES-FA200 ESR Spectrometer Model JEOL.

Synthesis of complexes 1 to 6

Six mixed-ligand complexes of copper (II) with 3,4-pyridinedicarboxylic acid (3,4-PDC) and diimines, where diimines= bipy (**1**), 4,4'-Me₂bipy (**2**), 5,5'-Me₂bipy (**3**), phen (**4**), dmp (**5**) and bathophen (**6**) have been synthesized conventionally by refluxing the reaction mixture of Cu(BF₄)₂.H₂O (3 mM, 711.5 mg) dissolved in 20 cc DMF, 3,4-pdc (1 mM, 167.12 mg) dissolved in 20 cc DMF and diimines (2,2'-bipy 1 mM, 156.19 mg, 4,4'-Me₂bipy, 1 mM, 184 mg, 5,5'-Me₂bipy, 1 mM, 184 mg, Phen, 1 mM, 198 mg, dmp, 1 mM, 217.27 mg and bathophen, 1 mM, 332 mg) dissolved in 20 cc DMF. Added the solution of 3,4-pdc in copper tetrafluoroborate solution and after that the solution of diimines was added in the above mixed solution in a round bottom flask and refluxed this solution mixture on water bath for 72 hours. Filtered the precipitate, washed it with alcohol and dried at room temperature, blue color powder of complexes **1**, **2**, **3** and **4** were obtained in 17%, 27.7%, 18.3% and 16.25% yield, respectively, green color powder of complex **5** and **6** were obtained in 28.2% and 16.68% yield.

Result and discussion

Elemental analysis

Complexes	C%	H%	N%
[Cu ₃ (pdc) ₂ (bipy)].2BF ₄ (1)	Calculated : 34.48% Found: 34.44%	Calculated : 2.02% Found: 2.06%	Calculated : 7.09% Found: 6.96%
[Cu ₄ (pdc) ₂ (4,4'-Me ₂ bipy) ₂ (dmf) ₂].4BF ₄ (2)	Calculated : 32.96% Found: 33.01%	Calculated : 3.21% Found: 3.09%	Calculated : 7.69% Found: 7.28%
[Cu ₄ (pdc) ₂ (5,5'-Me ₂ bipy) ₂ (dmf) ₂].4BF ₄ (3)	Calculated : 36.79% Found: 36.00%	Calculated : 2.58% Found: 2.80%	Calculated : 6.77% Found: 6.45%
[Cu ₄ (pdc) ₂ (phen)(dmf) ₂].4BF ₄ (4)	Calculated : 33.07% Found: 32.62%	Calculated : 2.91% Found: 2.85%	Calculated : 7.71% Found: 7.12%
[Cu ₃ (pdc) ₂ (dmp) ₂ (dmf) ₂].2BF ₄ (5)	Calculated : 41.31% Found: 40.62%	Calculated : 3.44% Found: 3.31%	Calculated : 8.50% Found: 8.69%
[Cu ₃ (pdc)(bathophen)(dmf) ₄].4BF ₄ (6)	Calculated : 43.78% Found: 43.54%	Calculated : 4.07% Found: 3.96%	Calculated : 8.31% Found: 8.10%

IR Spectra

The FTIR spectra of complexes **1-6** indicated the characteristic bands due to coordinated carboxylate anion. A broad band in the region of 3200-3600 cm^{-1} can be attributed to the presence hydroxyl ν_{OH} ion. The carboxylate stretching vibration (ν_{COOH}) for free H₂pdc is observed at 1717 cm^{-1} . But the band for ν_{COOH} disappeared when pdc is coordinated to Cu(II) ion. An anti-symmetric carboxylate stretching frequencies ($\Delta = \nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$) is often used to correlate the carboxylate

coordination mode [34, 35]. The $\Delta\nu$ for all the complexes is greater than 200 cm^{-1} suggesting the monodentate coordination of carboxylate in the dianion.

In addition, band at 668 cm^{-1} attributed to pyridyl vibration and band at 3019 cm^{-1} assigned to aromatic ν_{CH} . The presence of BF_4^- group is declared by two bands at around 1057 cm^{-1} and 760 cm^{-1} which are attributed to the anti-symmetric stretching and anti-symmetric bending vibration modes, respectively [36]. DMF shows characteristic absorption bands [37] at 1655 and 655 cm^{-1} . When DMF binds, the band at 1655 cm^{-1} shifts to 1645 cm^{-1} due to the weakening of the double-bond nature of the carbonyl bond and the band at 655 cm^{-1} shifts to 700 cm^{-1} , possibly due to the increase in the order of the amide C-N bond [38, 39].

The appearance of a lower shifted peak at 1645 cm^{-1} , a higher shifted peak at 700 cm^{-1} indicate that the complexes **2**, **3**, **4**, **5** and **6** coordinates to an oxygen atom in the C=O bond but not to the nitrogen atom of DMF.

Electron Paramagnetic Resonance Spectra

X-band EPR Spectra of polycrystalline powdered copper (II) mixed –ligand complexes were studied at room temperature (298 K). The EPR spectra of Cu (II) mixed ligand complexes are shown in **Figure 1(a, b)**. The relevant EPR spectral parameters are given in **Table 1**.

The Cu^{2+} ion has $3d^9$ electronic configuration with one unpaired electron and $S=1/2$ with nuclear spins: ^{63}Cu , $I=3/2$ (69%) and ^{65}Cu , $I=3/2$ (31%) gives characteristics hyperfine splitting, resulting in 4-lines.

Lohr and Lipscomb [40] have shown that in a compressed tetrahedron d_{xy} is the ground state, d_{xz} and d_{yz} are degenerate and $d_{x^2-y^2}$ and d_{z^2} are also nearly degenerate and lie somewhat higher than the d_{xz} and d_{yz} orbitals until the complex is nearly square planar.

The EPR spectra of tetrahedral complexes **1**, **2**, **3** and **4** show only one signal which may be due to strong dipole-dipole interaction (Figure 1(a)) with characteristic g values 2.167, 2.224, 2.175 and 2.174 respectively. On the other hand complexes **5** and **6** however, show similar spectra (Figure 1(b)) but with sharp peaks in the parallel and perpendicular region.

Table 1 EPR data for polycrystalline powdered Cu (II) complexes at 298 K

Complexes	g_{\parallel}	g_{\perp}	g_{av}
$[\text{Cu}_3(\text{pdc})_2(\text{bipy})].2\text{BF}_4$ (1)	-	-	2.167
$[\text{Cu}_4(\text{pdc})_2(4,4'\text{-Me}_2\text{bipy})_2(\text{dmf})_2].4\text{BF}_4$ (2)	-	-	2.224
$[\text{Cu}_4(\text{pdc})_2(5,5'\text{Me}_2\text{bipy})_2(\text{dmf})_2].4\text{BF}_4$ (3)	-	-	2.175
$[\text{Cu}_4(\text{pdc})_2(\text{phen})(\text{dmf})_2].4\text{BF}_4$ (4)	-	-	2.174
$[\text{Cu}_3(\text{pdc})_2(\text{dmp})_2(\text{dmf})_2].2\text{BF}_4$ (5)	2.373	2.148	2.223
$[\text{Cu}_3(\text{pdc})(\text{bathophen})(\text{dmf})_4].4\text{BF}_4$ (6)	2.389	2.142	2.225

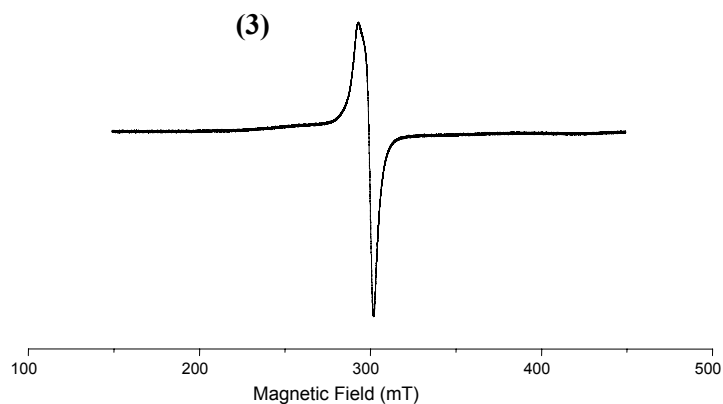


Figure 1(a). X-band EPR spectra of polycrystalline powdered Cu (II) complex $[\text{Cu}_4(\text{pdc})_2(5,5'\text{Me}_2\text{bipy})_2(\text{dmf})_2] \cdot 4\text{BF}_4$ (3) formed in 3:1:1 metal to ligand molar ratio at 298 K.

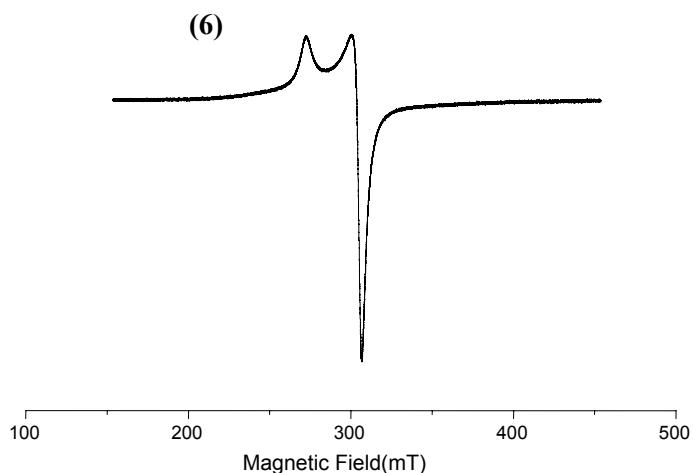
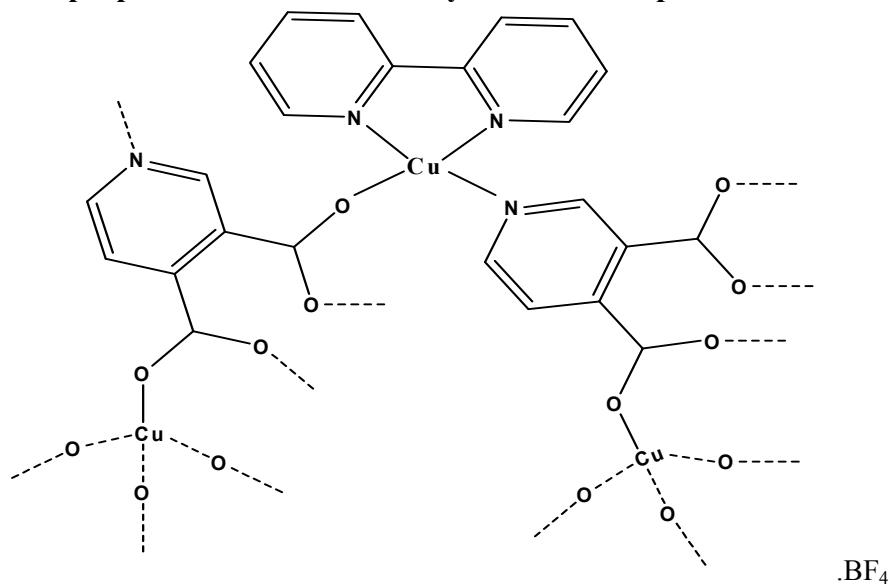
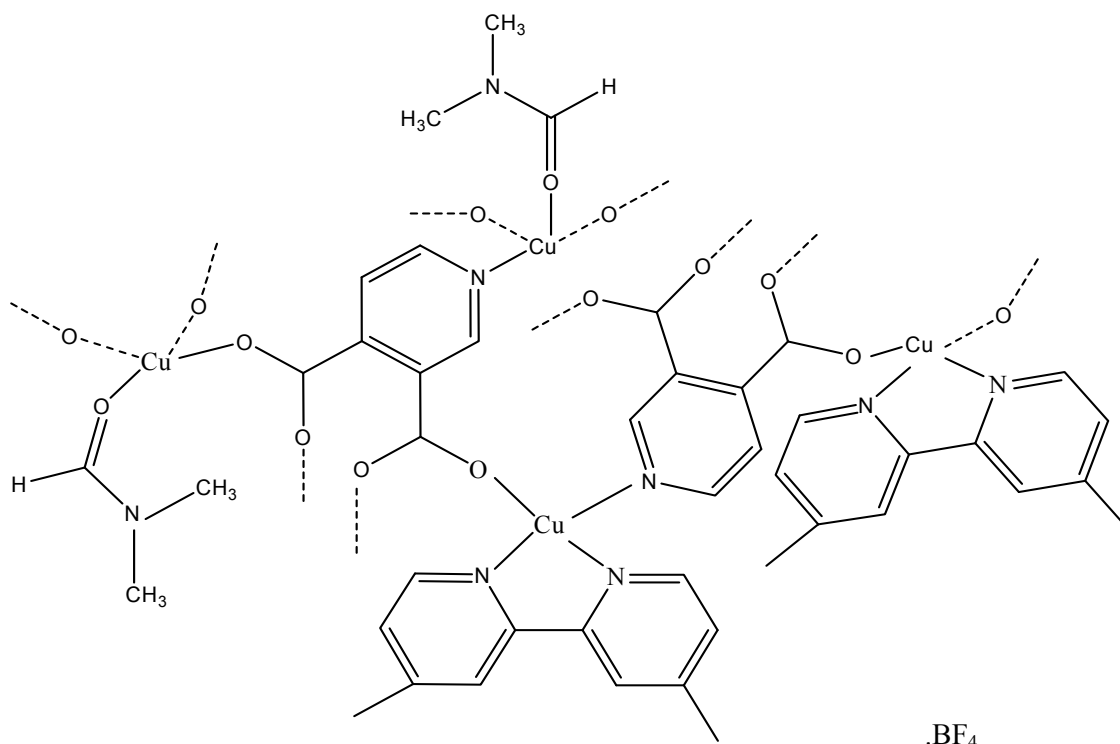


Figure1(b). X-band EPR spectra of polycrystalline powdered Cu (II) complex $[\text{Cu}_3(\text{pdc})(\text{bathophen})(\text{dmf})_4] \cdot 4\text{BF}_4$ (6) formed in 3:1:1 metal to ligand molar ratio at 298 K.

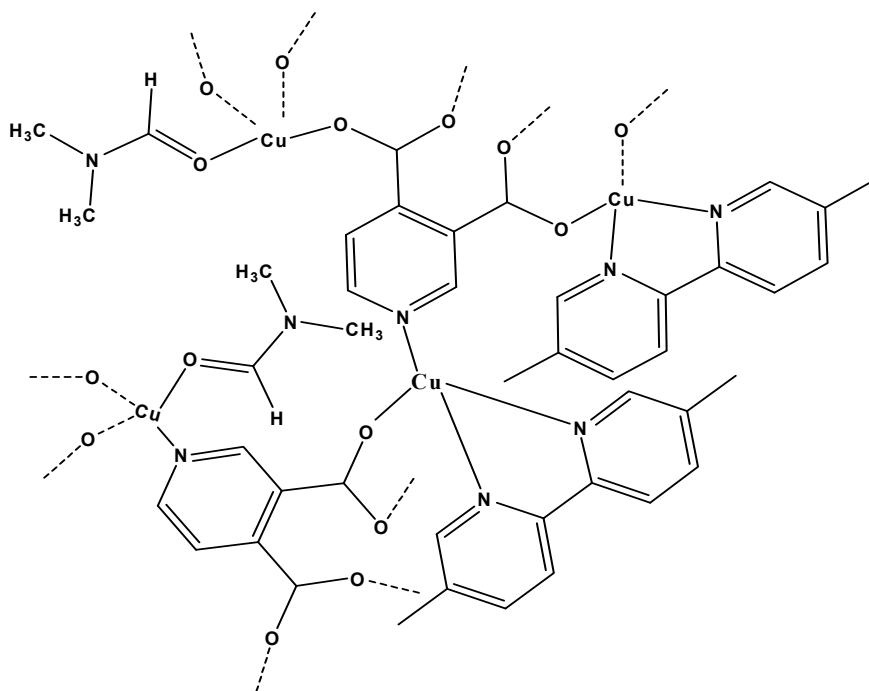
The proposed structures of the synthesized complexes are:



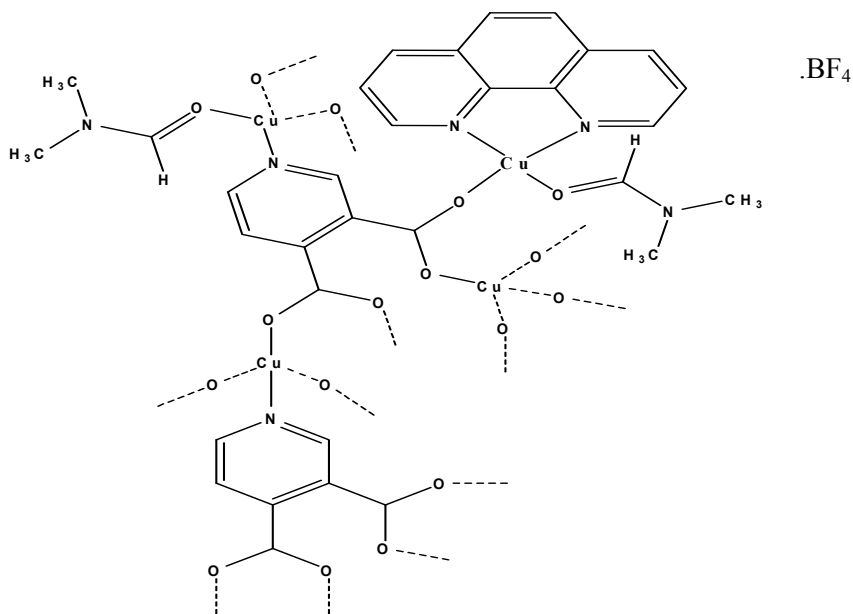
Complex 1



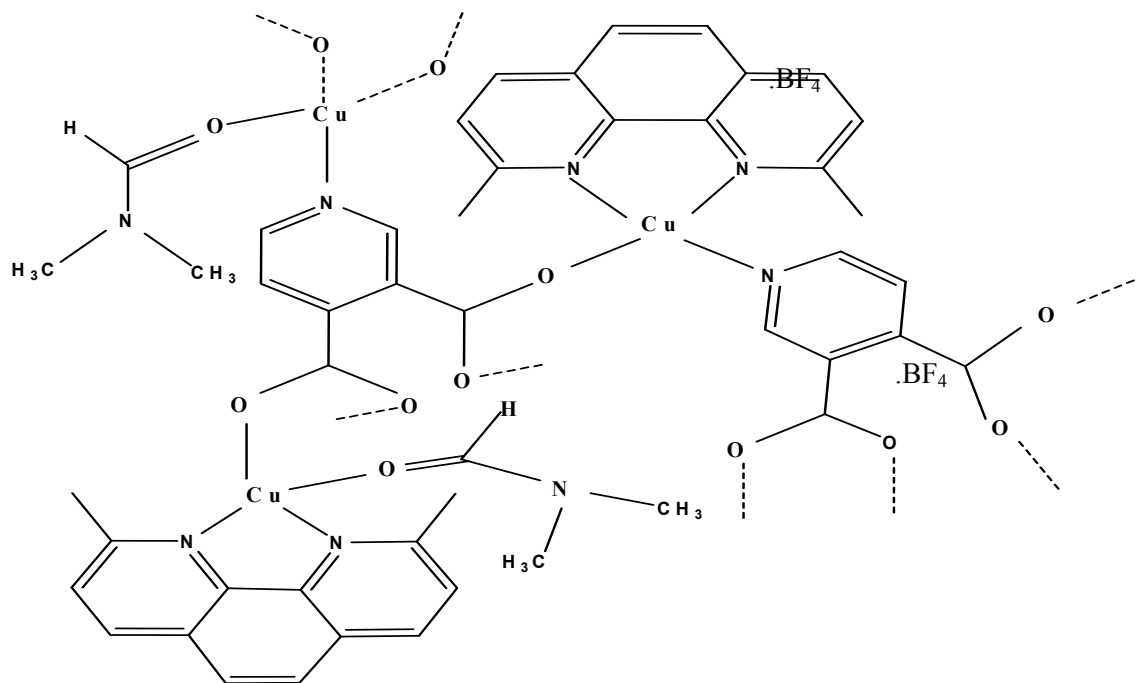
Complex 2



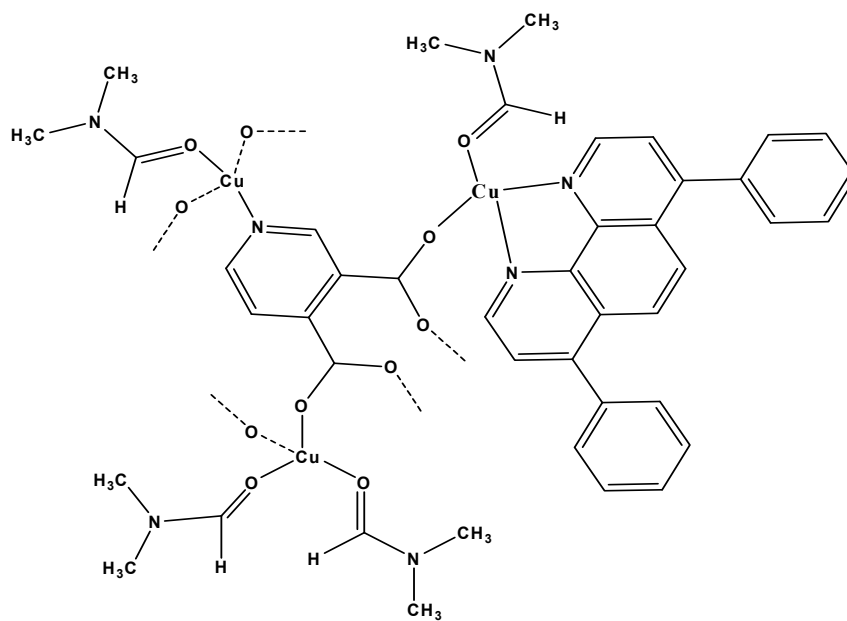
Complex 3



Complex



Complex 5



Complex

Conclusions

In the present work, synthesis, characterization and spectral studies of mixed-ligand Cu (II) complexes of 3,4-pyridinedicarboxylic acid with aromatic diimines have been performed. Elemental analyses, FT-IR spectra and room temperature Electron paramagnetic resonance spectra have been used for structural characterization of these complexes (**1-6**). Infrared spectra suggested that the starting acid H₂pdc was completely deprotonated and coordinated to the metal centers through carboxylate O in monodentate fashion and one nitrogen from the pyridine ring and the appearance of a lower shifted peak at 1645 cm⁻¹, a higher shifted peak at 700 cm⁻¹ indicate that the complexes **2, 3, 4, 5** and **6** coordinates to an oxygen atom in the C=O bond but not to the nitrogen atom of DMF. On the basis of EPR spectra, tetrahedral geometries have been proposed in all the mixed-ligand copper (II) complexes without any magnetic coupling between metal sites.

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