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Synthesis and Studies on Copper(II) Complexes of NO Donor Schiff Base

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Abstract

A series of copper(II) complexes ligated by 2,3-Dimethyl-4-formyl-[2'-(aminomethyl)pyridine]-1-phenyl-3-pyrazolin-5-one (DFAPP), [Cu(DFAPP)$_2$Cl$_2$](**1**), [Cu(DFAPP)$_2$Br$_2$](**2**),[Cu(DFAPP)$_2$](NO$_3$)$_2$(**3**) and [Cu(DFAPP)$_2$](ClO$_4$)$_2$(**4**) has been synthesized and characterized with the help of elemental analysis, molar conductance magnetic moments and IR, UV and EPR spectroscopic data. The Schiff base is found to act as bidentate ligand using NO donor set of atoms leading to an octahedral geometry around central metal ion in the complexes **1** and **2** and a square planar geometry in **3** and **4**.

Keywords: Copper(II) complexes, Schiff base, Spectra, Magnetic Susceptibility

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Introduction

Transition metal complexes with Schiff base as ligands have been amongst the widely studied coordination compounds in the past few years, since they are found to be widely applicable in biochemical, analytical and antimicrobial fields [1-3]. The metal ions present in complexes can accelerate the drug action and efficacy of the organic therapeutic agents [4]. Transition metal complexes are currently being used to bind and react at specific sequences of DNA in a search for novel chemotherapeutic agents and better anticancer drugs [5]. Herein, we have synthesized and characterized a series of novel copper(II) complexes of Schiff base ligand 2,3-Dimethyl-4-formyl-[2'-(aminomethyl)pyridine]-1-phenyl-3-pyrazolin-5-one. Cu(II) complexes of antipyrine systems, primarily exhibiting square planar or distorted octahedral geometries, lack anion responsiveness. In contrast, the studied complexes demonstrate anion-dependent switching in geometry, enabling tunable reactivity.

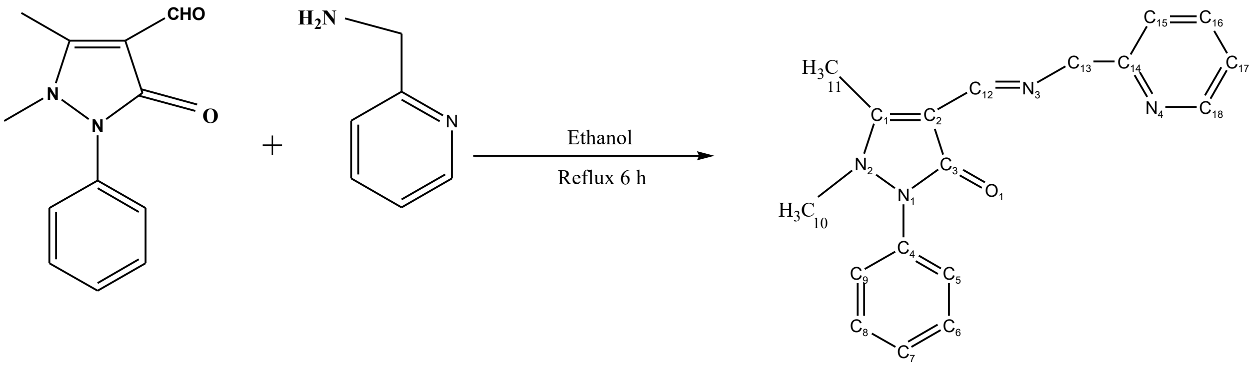
Materials and Methods

High purity 4-antipyrine carboxaldehyde, 2-amino methylpyridine, copper(II) chloride hexahydrate, copper(II) nitrate trihydrate, *Tris*-HCl (E.Merck,India) was purchased from respective concerns and used as such. Bromide and perchlorate of copper(II) were prepared by dissolving Analar copper carbonate in the respective 50% acids and crystallizing the salts after concentrating the resulting solutions on a steam bath. All other chemicals and solvents were of AR grade.

The C, H and N contents in the complexes were determined on a perkin–Elmer 240 CHN analyser. All the complexes were analyzed for their metal, halide and perchlorate contents by standard methods [6, 7]. Molar conductivities were measured using freshly prepared 10^{-3} M solutions dimethyl formamide, acetonitrile, nitrobenzene and methanol at room temperature using a Thoshniwal conductivity bridge with dip type conductance cell (cell constant 0.9741) which was calibrated with 0.01M KCl solution. The infrared spectra were recorded in the range 4000-100 cm^{-1} on a Schimadzu IR 470 spectometermeter.^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrophotometer using acetone-d$_6$ as solvent. Solid state electronic spectra in the range 1100-200 nm were recorded using Schimadzu UV-VIS-2450 spectrometer. The X-band EPR spectrum of copper(II) complexes were recorded in a varian E-112 EPR Spectrophotometer at liquid nitrogen temperature using DPPH free radical as 'g' marker. In all the spectra, the field set is 3000 Gauss and the scan range is 2000 Gauss. Magnetic susceptibility measurements were performed on pulverized samples at room temperature on a Sherwood Magwy MSB MK1 balance. The diamagnetic corrections were calculated using pascal's constants.

Synthesis of 2,3-Dimethyl-4-formyl-[2'-(aminomethyl)pyridine]-1-phenyl-3-pyrazolin-5-one

The ligand, DFAPP, was prepared by the condensation of antipyrine-4-carboxaldehyde and 2-(aminomethyl)pyridine in ethanolic medium. To a boiling solution of 10 mmol (1.0815 g) 2-(aminomethyl)pyridine in ethanol (20 ml), 10 mmol (2.1624 g) antipyrine-4-carboxaldehyde in ethanol (30 ml) was added and refluxed on a steam bath for about 6 h. The light brown crystals that obtained after cooling the resulting solution were filtered out and washed with cold ethanol to remove the unreacted reactants if any. It was then recrystallised from ethyl acetate and dried over phosphorus(V)oxide under vacuum. DFAPP is light yellow in colour, its molecular formula is $C_{18}H_{18}N_4O$, molecular mass is 306.37.



Scheme 1 2,3-dimethyl-4-formyl-[2′-(aminomethyl)pyridine]-1-phenyl-3-pyrazoline-5-one (DFAPP)

The yield: 85%. m.p.148°C. Anal. Cal. for $C_{18}H_{18}N_4O$ (306.37) C, 70.57; H, 5.92; N, 18.29. Found: C, 70.47; H, 5.87; N, 18.26%. IR(cm^{-1}): 1660 (-C=O), 1562 (-CH=N-), 1460, 698 (Pyridyl N). ^{1}H NMR(δ): 8.42 (s,1H, -CH=N-), 7.23-7.67 (m, -Ph), 7.14-8.67 (m, py. ring), 3.71 (s,2H, $-N-CH_2-$), 3.34(s,3H, $-N-CH_3$), 2.55 (s,3H, $=C-CH_3$). ^{13}C NMR (δ):166.71 (C12). UV-VIS ($\lambda_{Max/nm}$): 335 (n - π*), 247 (π- π*).

Synthesis of complexes

*[Cu(DFAPP)Cl_2] (**1**)*

A solution of $CuCl_2.6H_2O$ in acetone (1 mmol, 10 mL) was added to a hot solution of DFAPP in ethyl acetate (2 mmol, 30 mL) and the mixture was refluxed for about 3 hours on a water bath. The precipitated bright green complex was filtered, washed repeatedly with ethyl acetate and dried under vacuum. Yield 85%, m.p. 164 ^{0}C : Anal. Cal. for $C_{36}H_{36}N_8O_2Cl_2Cu$ (747.18): C, 58.87; H, 4.85; N, 14.99; Cl, 9.48; Cu, 8.50. Found: C, 57.79; H, 4.76; N, 14.88; Cl, 9.40; Cu, 8.58%. IR (cm^{-1}): 1643 [νC=O], 1589 [ν-CH=N], 443 [νCu-N], 563 [νCu─O], 279 [Cu-Cl]. ($\lambda_M/\Omega^{-1}cm^2mol^{-1}$): 49 (in DMF), 20 (in MeOH), 15 (in $Ph-NO_2$), 100 (in CH_3-CN). UV-VIS ($\lambda_{Max/nm}$): 342 (n - π*), 240 (π- π*), 500 (d-d transition), 390 (C-T transition). μ_{eff} = 1.81 BM

*[Cu(DFAPP)Br_2] (**2**)*

A solution of $CuBr_2.4H_2O$ in acetone (1 mmol, 10 mL) was added to a hot solution of DFAPP in ethyl acetate (2 mmol, 30 mL) and the mixture was refluxed for about 3 hours on a water bath. The precipitated pale green complex was filtered, washed repeatedly with ethyl acetate and dried under vacuum. Yield 75%, m.p. 154 ^{0}C : Anal. Cal. for $C_{36}H_{36}N_8O_2Br_2Cu$ (836.07): C, 51.71; H, 4.34; N, 13.40; Br, 19.11; Cu, 7.60. Found: C, 51.64; H, 4.25; N, 13.32; Br, 19.18; Cu, 6.52%. IR (cm^{-1}): 1650 [νC=O], 1578 [ν-CH=N], 450 [νCu-N], 567 [νCu─O], 280 [Cu-Cl]. ($\lambda_M/\Omega^{-1}cm^2mol^{-1}$): 45 (in DMF), 44 (in MeOH), 12 (in $Ph-NO_2$), 101 (in CH_3-CN). UV-VIS ($\lambda_{Max/nm}$): 341 (n - π*), 236 (π- π*), 476 (d-d transition), 392 (C-T transition). μ_{eff} = 1.79 BM

*[Cu(DFAPP)] $(ClO_4)_2$ (**3**)*

A solution of $Cu(ClO_4)_2.6H_2O$ in acetone (1 mmol, 10 mL) was added to a hot solution of DFAPP in ethyl acetate (2 mmol, 30 mL) and the mixture was refluxed for about 3 hours on a water bath. The precipitated green complex was filtered, washed repeatedly with ethyl acetate and dried under vacuum. Yield 75%, m.p. 225 ^{0}C : Anal. Cal. for $C_{36}H_{36}N_8O_{10}Cl_2Cu$ (875.18): C, 49.40; H, 4.14; N, 12.80; ClO_4, 7.26; Cu, 12.80. Found: C, 49.31; H, 4.07; N, 12.71; ClO_4, 11.53; Cu, 7.18%. IR (cm^{-1}): 1650 [νC=O], 1570 [ν-CH=N], 462 [νCu-N], 549 [νCu─O]. ($\lambda_M/\Omega^{-1}cm^2mol^{-1}$): 149 (in DMF), 178 (in MeOH), 55 (in $Ph-NO_2$), 231 (in CH_3-CN). UV-VIS ($\lambda_{Max/nm}$): 339 (n - π*), 231 (π- π*), 728 (d-d transitions), 321 (C-T transition). μ_{eff} = 1.78 BM

*[Cu(DFAPP)] $(NO_3)_2$ (**4**)*

A solution of $Cu(NO_3)_3.3H_2O$ in acetone (1 mmol, 10 mL) was added to a hot solution of DFAPP in ethyl acetate (2 mmol, 30 mL) and the mixture was refluxed for about 3 hours on a water bath. The precipitated green complex was filtered, washed repeatedly with ethyl acetate and dried under vacuum. Yield 78%, m.p. 167 ^{0}C : Anal. Cal. for $C_{36}H_{36}N_{10}O_8Cu$ (800.29): C, 54.02; H, 4.42; N, 15.99; Cu, 7.94. Found: C, 53.91; H, 4.53; N, 15.86; Cu, 7.85%. IR (cm^{-1}): 1650 [νC=O], 1575 [ν-CH=N], 450 [νCu-N], 565 [νCu─O]. ($\lambda_M/\Omega^{-1}cm^2mol^{-1}$): 145 (in DMF), 171 (in MeOH), 271 (in CH_3-CN). UV-VIS ($\lambda_{Max/nm}$): 342 (n - π*), 233 (π- π*), 730 (d-d transition), 390 (C-T transition). μ_{eff} = 1.85 BM

Results and Discussion

Physical characterization

The metal, chloride, bromide [6], perchlorate [7], carbon, hydrogen and nitrogen content in the complexes were determined. The elemental analysis data of the Cu(II) complexes are presented in the **Table 1**. The data suggest that the complexes **1- 4** may be formulated as $Cu(DFAPP)_2X_2$ (where X = Cl^-, Br^-, NO_3^- or ClO_4^-). The molar conductance values of the complexes **1-2** in dimethylformamide is in the range 42-45 $Ohm^{-1}cm^2mol^{-1}$ behave as non-electrolytes and that of **3-4** are in the range 145-149 $Ohm^{-1}cm^2mol^{-1}$ behave as 1:2 elecrolytes [8]. All the complexes except **4** were soluble in acetonitrile, dimethylformamide, methanol and nitrobenzene while **4** was insoluble in nitrobenzene. All of them are insoluble in acetone, toluene, benzene, carbon tetrachloride, ethyl acetate, and chloroform.

Table 1 EPR bonding parameters of copper(II) complexes

Complex	$g_{\|}$	$g_{\perp}$	$A_{\|}$	$A_{\perp}$	g_{iso}	α^2
$[Cu(DFAPP)_2Cl_2]$ (**1**)	2.28	2.04	150	66.66	2.04	0.76
$[Cu(DFAPP)_2Br_2]$ (**2**)	2.28	2.040	160	76.66	2.12	0.77
$[Cu(DFAPP)_2](ClO_4)_2$ (**3**)	2.28	2.05	140	73.33	2.12	0.75
$[Cu(DFAPP)_2\ ](NO_3)_2$ (**4**)	2.25	2.03	170	83.33	2.10	0.78

Infrared spectral studies

The infrared spectrum of the ligand exhibits a strong absorption at 1660 cm^{-1} corresponding to stretching vibrations of the pyrazolone ring carbonyl oxygen. The band observed at 1562 cm^{-1} is attributable to –C=N stretching vibrations [9]. The absorptions at 1460 and 698 cm^{-1} in the ligand are assigned respectively to ring stretching and out of plane deformation modes of pyridine moiety of DFAPP.

In the complexes, the band at 1660 cm^{-1} is shifted to 1643-1650 cm^{-1} indicating coordination of carbonyl oxygen. At the same time strong band at 1562 cm^{-1} is shifted to the region 1575-1589 cm^{-1}suggesting coordination of imine nitrogen [10]. The bands at 1460 and 698 cm^{-1} remain unaltered indicating non participation of pyridyl nitrogen in coordination [9]. Thus DFAPP acts as a neutral bidentate ligand coordinating through carbonyl oxygen and imine nitrogen.

The nitrate complex exhibits the vibrational frequencies characteristic of uncoordinated nitrate ions. A very strong band at 1384 cm^{-1} and a medium band at 825 cm^{-1} are attributable to ν_3 and ν_2 vibrations of uncoordinated nitrate ion of D_{3h} symmetry [11].

In perchlorate complex, the very strong band at 1087 cm^{-1} is attributable to the ν_3 vibration of uncoordinated perchlorate ion of T_d symmetry. The band at 624 cm^{-1} due to ν_4 vibration of uncoordinated perchlorate (T_d) ion also supports the existence of uncoordinated perchlorate ion in the complex [12].

The low frequency skeletal vibrations in the range 549-565 cm^{-1} and 443-462 cm^{-1} are due to M-O and M-N stretching respectively provides direct evidence for complexation [13].

In the infrared spectra of the halide complexes **1** and **2** the bands at 279 and 280 cm^{-1} and were due to the ν(Cu-Cl) and ν(Cu-Br) vibrations which was absent in the ligand spectrum [14].

Electronic spectra and Magnetism

The electronic spectrum of DFAPP exhibits two main peaks at about 335 and 247 nm which are assignable to the n-π* and π-π* transitions respectively. In the complexes **1-4**, the n-π* band is red shifted to 339-342 region and π-π* band is blue shifted to 231-240 nm compared to DFAPP.

The broad bands in the region 728-730 nm in complexes **3** and **4** are consistent with $^2B_{1g} \rightarrow {}^2A_{1g}$ transition in square planar copper(II) complexes. The broadness of the band can be taken as an indication of distortion from perfect planar geometry [15]. The magnetic moments of the complexes **3** and **4** are 1.78 BM and 1.85 BM respectively which is as expected for square planar complexes of copper(II) [16].

In complexes **1** and **2** copper(II) has a d^9 configuration having an absorption band in the region 476-500 nm which may be assigned to $^2B_{1g} \rightarrow {}^2E_{2g}$ transition corresponding to octahedral geometry around copper(II) ion [17, 18]. The μ_{eff} values of **1** and **2** are 1.81 BM and 1.79 BM respectively, which confirms octahedral geometry around central metal ion [19].

Furthermore, the complexes **1- 4** show an intense absorption band in the 371-392 nm region which may be due to charge transfer transition. The tentative structures of the complexes are given in **Figures 1** and **2**.

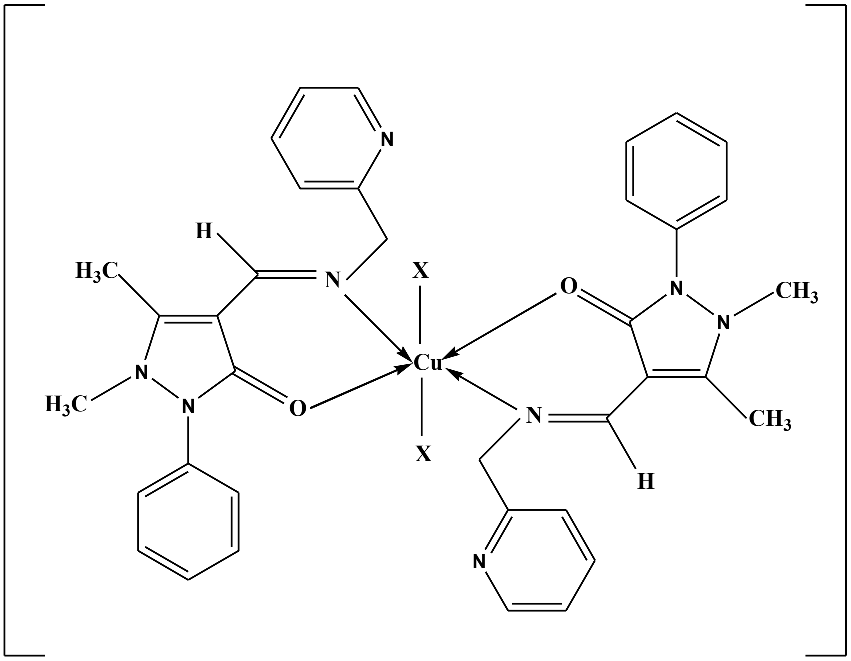


Figure 1 $[Cu(DFAPP)_2X_2]$ (where X = Br^- or Cl^-) (**1** and **2**)

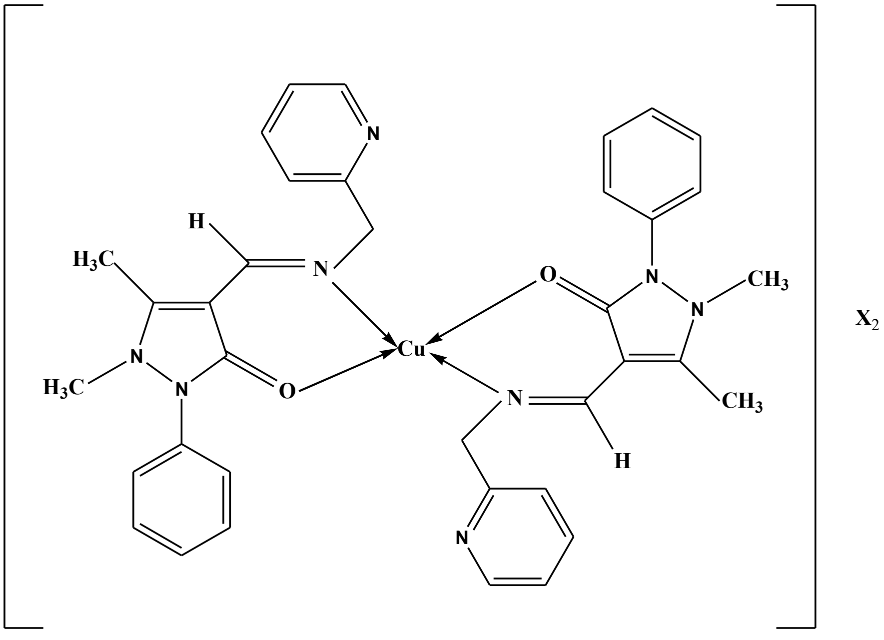


Figure 2 $[Cu(DFAPP)_2]\ X_2$ (where X = NO_3^- or ClO_4^-)(**3** and **4**)

EPR spectra

EPR spectral studies give information about the distribution of unpaired electrons and hence the nature of bonding between metal ion and its ligands. The EPR spectra of the complexes **1-4** are given in **Figure 3** and the calculated parameters are given in Table 1.

The EPR spectra of the complexes **1-4** have been evaluated and relevant spin-Hamiltonian parameters computed. All the complexes have a well resolved $g_{\parallel}$ and a broad $g_{\perp}$ region. In all the spectra no hyperfine splitting from ligand part is observed.

The trend $g_{\|} > g_{\perp} > 2.0023$ indicates that the unpaired electron is most likely in the $d_{x^2-y^2}$ orbital [20]. The covalency parameter α^2 is found to be in the range 0.75-0.78 indicating fairly covalent nature of metal-ligand bond. The shape of EPR spectra indicates that the geometry around copper(II) ion is square planar in perchlorate and nitrate complexes and elongated octahedron in chloride and bromide complexes as evident from the less intense low field side and more intense high field side [21].

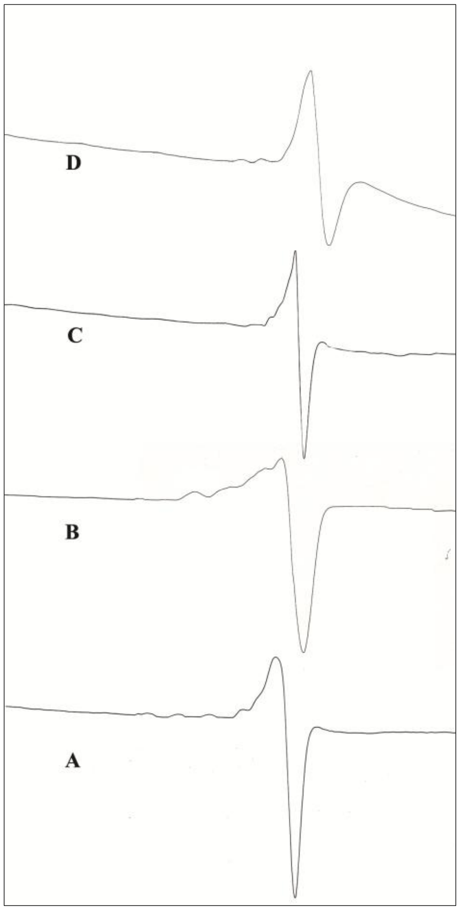


Figure 3 EPR spectra of copper(II) complexes of DFAPP A = [Cu(DFAPP)$_2$Cl$_2$] (**1**), B = [Cu(DFAPP)$_2$Br$_2$] (**2**), C = [Cu(DFAPP)$_2$](ClO$_4$)$_2$ (**3**) and D = [Cu(DFAPP)$_2$](NO$_3$)$_2$ (**4**)

Conclusion

In this paper, we have explored the synthesis and coordination chemistry of a series of copper(II) complexes of the Schiff base 2,3-Dimethyl-4-formyl-[2'-(aminomethyl)pyridine]-1-phenyl-3-pyrazolin-5-one (DFAPP). The complexes are characterized by elemental analysis, molar conductance studies, CHNS analysis, spectroscopic techniques, magnetic susceptibility measurements and thermal analysis data. The ligand to metal ratio in all the complexes is found to be 1:2. In complexes Schiff base acts as bidentate ligand with NO donor sites forming chelate rings. The complexes **1** and **2** have octahedral geometry and **3** and **4** have square planar geometry with both the anions as counter ions.

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