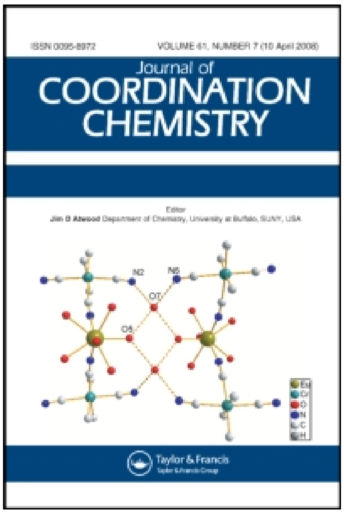

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Synthesis, spectroscopic and thermal investigation of Schiff-base complexes of Cu(II) derived from heterocyclic β-diketone with various primary amines

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The mononuclear complex [Cu(PMFP)(bipy)]ClO_4 was prepared by reaction of $Cu(NO_3)_2 \cdot 5H_2O$ with ligand PMFP and 2,2′-bipyridine. The corresponding Schiff bases were prepared by condensation of [Cu(PMFP)(bipy)]ClO_4 with ethylenediamine, ethanolamine and glycine with general formula [Cu(PMFP-SB)(bipy)]ClO_4 (where PMFP = 1-phenyl-3-methyl-4-formyl-2-pyrazolin-5one; bipy = 2,2′-bipyridine). All the compounds have been characterized by elemental analysis, magnetic susceptibility, conductometry measurements and ^{1}H-NMR, FT-IR, ESR, electronic spectra and mass spectrometry. Electronic spectra and magnetic susceptibility measurements indicate square planar stereochemistry. Thermal stability, order of kinetics, heat capacity and activation energy of thermal degradation for these complexes were determined by TGA and DSC. Hamiltonian and bonding parameters from ESR spectra indicate the metal ligand bonding is partially covalent.

Keywords: Mononuclear Cu(II) complexes; FT-IR; ESR; Mass spectrometry; Thermal studies; Kinetic parameters

1. Introduction

The chemistry of pyrazolone derivatives has attracted attention because of structures and application in diverse areas [1–10], such as laser materials, ^{1}H-NMR shift reagents, chromatographic materials and in the petrochemical industry [11–15]. Photochromism of pyrazolone derivatives has also been reported [16]. Many of these ligands exhibit keto enol tautomerisum, and show interesting structural and spectroscopic properties [17, 18]. Pyrazolone-based Schiff-base chemistry is less extensive and our laboratory has been exploring this chemistry [19–21]. In the present article we report the pyrazolone derivative 1-phenyl-3-methyl-4-formyl-2-pyrazolin-5-one (PMFP), mononuclear mixed ligand complexes of Cu(II) and their Schiff-base complexes.

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2. Experimental

Solvents were purified using standard methods [22]. 1-Phenyl-3-methyl-2-pyrazoline-5-one and 2,2′-bipyridine (E-Merck); ethylenediamine, ethanolamine and glycine (BDH) were used as received. The cupric nitrate was from BDH. Elemental analyses (C, H, N) were performed at CDRI, Lucknow with a Carlo Erba 1108 analyzer. Infrared spectra were recorded with a Perkin-Elmer IR spectrophotometer (4000–400 cm^{-1}) using KBr pellets. ^1H-NMR spectra of the compound were recorded with a JEOL-GSX-400 using $CDCl_3$ as solvent and TMS as an internal reference at SAIF, IIT Madras, Chennai. Mass spectra (EI) of the compounds were recorded at SAIF, IIT Madras, Chennai with VG 70-250S mass spectrometer. Electronic spectra in the 200–800 nm range were obtained in acetone on a "SHIMADZU" UV 160A using a 1 cm^3 quartz cell. Magnetic measurements were carried out at room temperature by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant. Molar conductances of the Schiff-base complexes were determined on Systronics direct reading conductivity meter type CM–82T. TGA was carried out on a universal V3.0G TA instrument in the range 0–700°C at a heating rate of 10°C min^{-1} under nitrogen. DSC was carried out on a universal V3.0G TA instrument in the range 0–300°C. ESR spectra of all complexes were recorded by ESR laboratory, RSIC, IIT, Bombay, at room temperature and liquid nitrogen temperature for polycrystalline samples and solutions.

2.1. *Synthesis of ligand (PMFP)*

1-Phenyl-3-methyl-4-formyl-2-pyrazolin-5-one was prepared by condensation of 1-phenyl-3-methyl-2-pyrazoline-5-one with DMF and $POCl_3$ [22]. 1-Phenyl-3-methyl-2-pyrazoline-5-one (8.7 g, 0.05 mol) in DMF (10 cm^3, 0.05 mol) was cooled to 0°C in an ice bath. To this phosphoryl chloride (5.5 cm^3, 0.06 mol) was added dropwise at a rate to maintain the temperature between 10 and 20°C. After the addition was complete, the reaction mixture was heated on a steam bath for 1.5 h and then poured into 1 L of ice water. The resulting mixture was allowed to stand overnight and product was collected by filtration, washed with water, and dried. Crystallization was done from ethanol. Yellow compound PMFP, yield 83%, m.p. 176°C. Calcd: C, 65.3; H, 4.9; N, 13.0. Found: C, 65.9; H, 5.0; N, 12.9. ^1H-NMR ($CDCl_3$) δ (ppm), 1.2 (s, 3H, CH_3), 7.3–7.9 (m, 5H, Ph), 8.45 (br, 1H, OH), 9.85 (s, 1H, CHO). MS (EI): m/e 202 $[M]^+$, 203 $[M + 1]^+$ (Calcd for $[M]^+$ 202). IR (cm^{-1}), ν_{max} (KBr): 3400–3300m, 2816–2755vs (doublet), 1625vs, 1541vw cm^{-1}.

2.2. *Synthesis of mononuclear mixed ligand complexes*

To PMFP (2.02 g, 0.01 mol) in 50 cm^3 methanol was added 2,2′-bipyridyl (1.56 g, 0.01 mol) in 50 cm^3 methanol followed by an aqueous solution of $Cu(NO_3)_2 \cdot 5H_2O$ (2.77 g, 0.01 mol). The reaction mixture was refluxed for 30 min and then a saturated solution of sodium perchlorate was added. The precipitated complex was further digested on water-bath for 30 min. The resulting solution was filtered and reduced to 1/3 volume and allowed to stand over night at room temperature. A solid mass separated out on addition of ether. The crude compound was recrystallized from methanol and dried over $CaCl_2$.

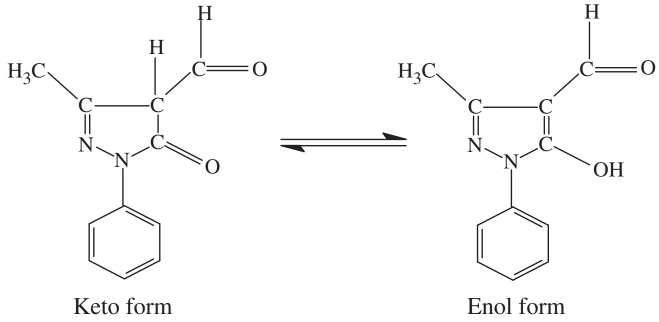
2.3. *Synthesis of Schiff-base complexes*

The Schiff-base complexes were prepared by 1 : 1 interaction of the complex with ethylenediamine, ethanolamine or glycine.

To the mixed ligand complex (6.49 g, 0.0125 mol) in 20 cm^3 methanol was added ethylendiamine (0.75 g, 0.0125 mol), ethanolamine (0.76 g, 0.0125 mol) or glycine (0.93 g, 0.0125 mol). The solution was allowed to stand for 10 min at room temperature and then refluxed for 2 h on a water bath. The solution was reduced to 1/3 volume and allowed to stand overnight at room temperature. A solid mass separated, was collected and washed by ether. Crystallization was done with CH_3OH and the complex dried over $CaCl_2$.

3. Results and discussion

The elemental analyses (table 1) are in good agreement with the proposed formulas. The ligand PMFP has the following tautomeric forms:



IR spectra show a broad band at 3400–3300 cm^{-1} due to ν(OH). Free ν(OH) is generally observed between 3500 and 3600 cm^{-1}; the observed lower value is due to intramoleculer H-bonding. The IR spectrum of the ligand shows a doublet at 2755 and 2816 cm^{-1} (Fermi resonance) assigned to the aldehydic ν(C–H), whereas two moderately intense bands are observed at 3020 and 2877 cm^{-1}, due to aromatic and aliphatic ν(C–H), respectively. The very sharp absorption band at 1624 cm^{-1} is assigned to ν(C=O) which is shifted to lower wavenumber because of intramolecular hydrogen bonding. The ^{1}H-NMR spectrum of PMFP show a broad singlet at δ 8.49 ppm due to –OH proton, indicating the ligand is in the enol form. The spectrum also shows the phenyl multiple at δ 7.3 to 7.9 ppm, a sharp singlet at δ 1.2 ppm assigned to methyl protons of the pyrazoline ring, and the aldehyde proton at 9.85 ppm. PMFP is in the enol form only. PMFP is also characterized by mass spectral studies with a molecular ion peak at 202(M^+). A weak peak at m/e 201 is due to the formation of $(C_{11}H_9N_2O_2)^+$, elimination of H from the molecule. One intense peak at m/e 185 is due to removal of OH and formation of $(C_{11}H_8ON_2)^+$, A distinct but less abundant peak observed at ($m/e = 174$) due to elimination of CO from the parent compound. Prominent peaks for $(C_6H_5N)^+$ and $(C_6H_5)^+$ ions are observed at $m/e = 91$ and 77.

Table 1. Elemental analysis and some physical properties of the solid complexes.

Complexes	Color	Yield (%)	Melting point (°C)	FW	Analysis found % (calculated %)				Mass peak m/e	Λ (ohm $^{-1}$ cm^2 mol^{-1})	μ_{eff} (BM)
					C	H	N	M			
[Cu(PMFP)(bipy)]ClO_4	Green	87	122	519.95	49.12 (48.46)	3.92 (3.27)	9.96 (10.77)	11.89 (12.22)	–	87.7	1.95
[Cu(PMFP-en)(bipy)]ClO_4	Dark Green	82	146	561.99	48.68 (49.10)	4.05 (4.09)	14.81 (14.94)	10.23 (11.30)	561	76.0	1.99
[Cu(PMFP-EA)(bipy)]ClO_4	Green	84	137	562.99	49.46 (49.02)	3.94 (3.91)	12.54 (12.43)	10.39 (11.28)	559	87.0	1.96
[Cu(PMFP-Gly)(bipy)]ClO_4	Dark Green	87	128	576.99	48.25 (47.83)	3.49 (3.46)	12.23 (12.13)	10.14 (11.01)	570	79.0	1.92

3.1. *IR spectra*

The FT-IR spectral data of the Cu(II) complex and the Schiff-base complexes are given in table 2. The Cu(II) mononuclear mixed ligand complex does not show a band between 3600–3400 cm^{-1} indicating the –OH hydrogen of PMFP at the fifth position is deprotonated after complexation. A new band in all complexes at 1350–1300 cm^{-1} is due to the enolic group ν(C–O) [23, 24]. On coordination ν(C=N) shifts to lower wavenumber 1545–1598 cm^{-1} from 1600–1659 cm^{-1} for free C=N. The band at 3327 cm^{-1} shows that NH_2 group of ethylendiamine Schiff-base complex is not coordinated to the metal ion. The sharp band at 3510 cm^{-1} in ethanolamine complex of Cu(II) correspond to free –OH of ethanolamine. In the glycine complex broad bands at 3400–3100 cm^{-1} and 1666 cm^{-1} are assigned for undissociated carboxylic group of glycine. The presence of counter ion perclorate (ClO_4^-) is confirmed through a weak band at 914 cm^{-1} due to the symmetrical stretching mode (IR-forbidden) and an asymmetrical stretching mode at 1100 cm^{-1} (IR-allowed). This shows that ClO_4^- has T_d symmetry [25].

3.2. *Electronic spectra and magnetic moment*

Uv-visible spectra of the metal complexes were obtained in methanol (table 2). Electronic spectra of the Cu(II) complex show a broad band at 14609–14787 cm^{-1} due to the combination of the three transitions ($^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$). The value of extinction coefficient ($\varepsilon = \sim 70$) indicates a d–d transition, not a charge transfer. In the UV region four bands appear at 47,846, 41,379, 33,557 and 31,372 cm^{-1}. The first three bands may be due to interligand transitions and the last may be due to charge transfer. The electronic spectra of [(PMFP-en)Cu(dipy)] ClO_4, [(PMFP-EA)Cu(dipy)]ClO_4 and [(PMFP-Gly)Cu(dipy)]ClO_4 exhibit broad bands at 18,832, 16,502 and 15,291 cm^{-1} for ethylenediamine, ethanolamine and glycine, respectively. The formation of Schiff-base complexes shifts the band in visible range to lower wavelength or higher wavenumber indicating the formation of a strong M–N bond. The band shift in the sequence ethylendiamine > ethanolamine > glycine, indicates that ethylenediamine Schiff base with PMFP is more stable. It may be concluded that all complexes have square-planar geometry [26]. This is further supported by magnetic moment values $\mu_{eff} = 1.92$ to 1.99 BM (table 1), within the required range for d^9 systems [27].

3.3. *Mass spectra*

The characteristics fragments were observed as follows:

3.3.1. [Cu(PMFP-en)(dipy)]ClO_4. The molecular ion peak is observed at $m/e =$ 561 $[M]^+$, the removal of noncoordinated ClO_4^{-1} is indicated by $m/e = 461$ and of 2,2′-bipyridine by $m/e = 405$.

3.3.2. [Cu(PMFP-EA)(dipy)]ClO_4. The molecular ion peak is observed at $m/e =$ 560 $[M]^+$, the removal of noncoordinated ClO_4^{-1} is indicated by $m/e = 460$ and of 2,2′-bipyridyl by $m/e = 402$.

Table 2. Infrared and electronic data of the complexes.

Complexes	ν(OH)	$\nu(NH_2)$	ν(C=N) coord.	ν(C=N) (cyclic)	ν(C=O)	ν(C–O) Str.	d–d (cm^{-1})	Charge transfer band (cm^{-1})
[Cu(PMFP)(bipy)]ClO_4	–	–	–	1593	1600	1353	23,255, 14,609, 21,978	47,846, 41,379, 33,557
[Cu(PMFP-en)(bipy)]ClO_4	–	3388	1624	1588	–	1353	15,770, 23,378, 18,832	42,379, 35,460
[Cu(PMFP-EA)(bipy)]ClO_4	3510	–	1624	1594	–	1349	23,121, 15,290	40,983, 35,211
[Cu(PMFP-Gly)(bipy)]ClO_4	–	–	1608	1598	1726	1348	15,658, 16,501	35,663

3.3.3. [Cu(PMFP-Gly)(dipy)]ClO$_4$. The molecular ion peak is observed at $m/e=570$ [M]$^+$, the removal of noncoordinated ClO_4^{-1} by $m/e=470$ and of 2,2′-bipyridine by $m/e=416$.

The other fragments are also observed due to rearrangements and recombination of the molecules.

3.4. *Thermogravimetric analysis*

Figure 1 shows DSC curves of the complexes which all exhibit an endothermic process. The area of the endothermic peak corresponding to the heat of fusion and the peak temperature corresponds to the melting point. The melting (T_p), transition temperature (T_1, T_2), heat of reaction (ΔH), order of reaction (C_s), activation energy (E^*) and heat capacities (C_p) of the complexes were calculated from TGA/DSC and the results are given in table 3. TGA of the solid complexes indicate that the complexes decomposed in one step without formation of stable intermediates. The decompositions start within the range of 119–128°C and end between 389 and 678°C (oxide formation). The metal percentages of the complexes were calculated from the residual metal oxide formed in the final step and were found to be in good agreement with those obtained by the wet combustion method of MacDonald [28].

3.4.1. Determination of reaction order of decomposition. The Horowitz and Metzger [29, 30] equation, $C_s=(n)^{1/(1-n)}$, where C_s is the mass fraction of the substance,

$$C_s=\frac{W_s-W_f}{W_0-W_f}$$

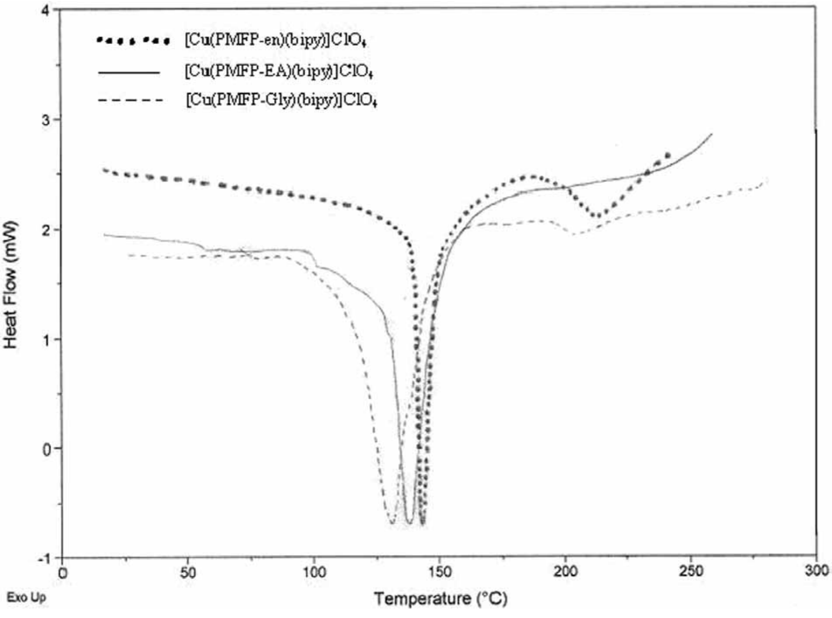


Figure 1. The DSC curve of Cu(II) Schiff-base complexes.

Table 3. The thermodynamic and decomposition parameters for Cu(II) Schiff-base complexes.

Complex	C_p (kJ g^{-1} C^{-1})	T_s	T_1	T_2	T_p	E^* (kJ mol^{-1})	H^* (kJ mol^{-1})	C_s
[Cu(PMFP-en)(bipy)]ClO_4	2.06	128	126	161	146	128.69	72.44	0.29
[Cu(PMFP-EA)(bipy)]ClO_4	2.82	124	120	153	137	86.56	93.28	0.34
[Cu(PMFP-Gly)(bipy)]ClO_4	2.35	119	111	149	128	96.25	89.56	0.33

Table 4. g and G values of powder ESR spectra of Cu(II) complexes at R.T. and N_2(P).

	R.T.				N_2(P)			
Complex	$g_{\|\|}$	$g_{\perp}$	$\|g\|^a$	G^b	$G_{\|\|}$	$G_{\perp}$	$\|g\|^a$	G^b
[Cu(PMFP)(bipy)]ClO_4	2.11	2.03	2.08	2.22	2.10	2.03	2.08	2.23
[Cu(PMFP-en)(bipy)]ClO_4	2.12	2.05	2.07	2.45	2.11	2.05	2.07	2.25
[Cu(PMFP-EA)(bipy)]ClO_4	2.12	2.06	2.08	2.03	2.12	2.06	2.08	2.03
[Cu(PMFP-Gly)(bipy)]ClO_4	2.11	2.05	2.07	2.25	2.11	2.05	2.07	2.25

[a] $|g| = 1/3(g_{||} + g_{\perp})$, [b] $G = (g_{||} - 2.002)/(g_{\perp} - 2.002)$.

Table 5. g and A value of solution[a] ESR spectra of Cu(II) complexes.

Complex	$g_{\|\|}$	$g_{\perp}$	$\|g\|$	$A_{\|\|} \times 10^{-4}$ (cm^{-1})	$A_{\perp} \times 10^{-4}$ (cm^{-1})	$\|A\| \times 10^{-4}$ (cm^{-1})	$g_{\|\|}/A_{\|\|}$
[Cu(PMFP)(bipy)]ClO_4	2.20	2.08	2.12	191.26	99.2	202.32	99
[Cu(PMFP-en)(dipy)]ClO_4	2.21	2.03	2.09	192.0	99.0	205.65	115
[Cu(PMFP-EA)(dipy)]ClO_4	2.21	2.08	2.09	214.10	149.7	171.23	98
[Cu(PMFP-Gly)(dipy)]ClO_4	2.19	2.07	2.11	213.34	186.86	195.69	102

[a] (60% pyridine + 40% toluene).

can be used for determination of the reaction order. W_s, is the mass remaining at a given temperature, W_0 and W_f are initial and final masses of the substance, respectively. The values of C_s for the thermal decomposition of Cu(II) complexes are in the range 0.29–0.39 indicating that the decomposition follows first order kinetics [30].

The thermodynamic activation parameters of the complexes such as activation energy (E^*) were evaluated by employing the Horowitz and Metzger [30] methods.

3.5. *Electron spin resonance spectra*

As we could not get well-shaped single crystals, the EPR spectra were recorded only for powder and solution samples for the Schiff-base complexes at RT and N_2(P); the results are described in tables 4 and 5. The powder samples were recorded in quartz tubes to avoid Mn(II) or Fe (II) impurities and solution spectra were recorded in pyridine : toluene (40 : 60) mixed solutions in capillary tubes. The solution spectra were recorded to confirm that the complexes do not undergo structural change in solution.

The powder ESR spectra are shown in figure 2. Hamiltonian parameters $g_{||}$, $g_{\perp}$, $A_{||}$, $A_{\perp}$ and A_{iso} were calculated and are included in table 4. For Cu(II) $g_{||}$ indicates covalence with $g_{||} < 2.3$ for covalent complexes and $g_{||} \geq 2.3$ for ionic [32]. $g_{||}$ values (table 5) of the Schiff-base Cu(II) complexes of 2.19–2.21 indicates covalency

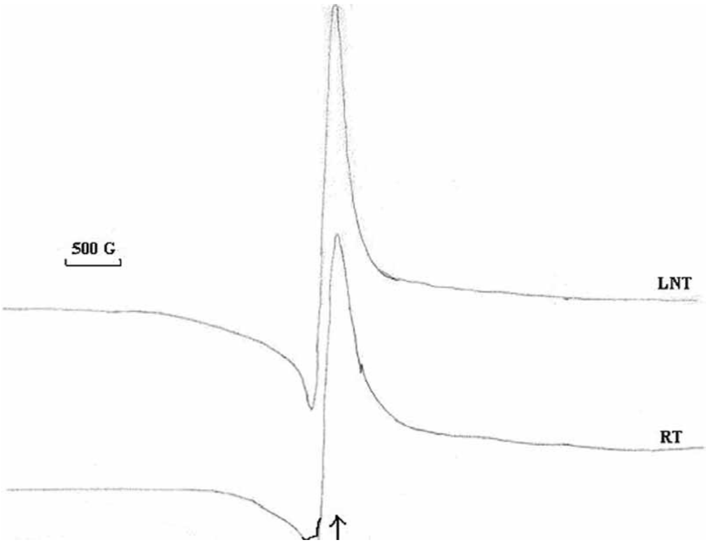


Figure 2. X-band ESR spectra of [Cu(PMFP-EA)(dipy)]ClO_4 complex in polycrystalline at RT and LNT.

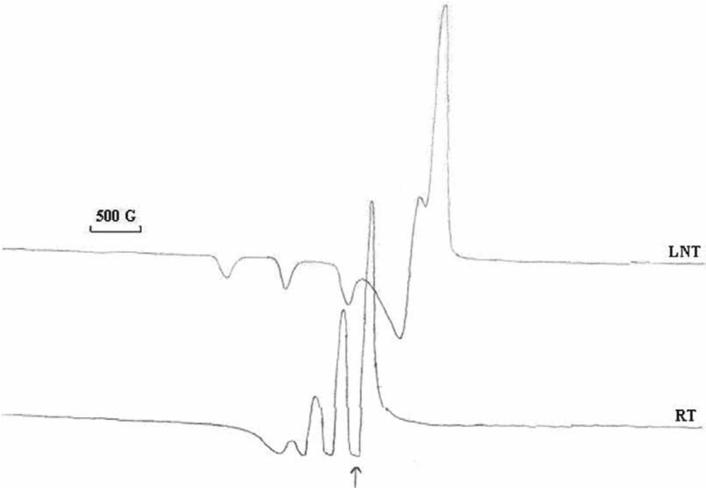


Figure 3. X-band ESR spectra of [Cu(PMFP-EA)(dipy)]ClO_4 complex in solution at RT and LNT.

for the M–L bond. The nature of ligand is evaluated from G value (table 4),

$$G = \frac{g_\parallel - 2}{g_\perp - 2} \cong 4.0$$

For $G < 4.0$, the ligand forming the complex is regarded as a strong field ligand. For square planar complexes G is usually in the range of 2.03–2.45 [32], in good agreement with our results. The results for polycrystalline Schiff-base complexes are not much different at RT and LNT. The solution ESR spectra in pyridine : toluene (40 : 60) mixed solvent are given in figure 3. The RT ESR consists of four asymmetrical but equally spaced hyperfine lines characteristic of the Cu(II) nuclear hyperfine interaction (Cu = I = 3/2 for ^{63}Cu and ^{65}Cu). From these solution ESR spectra, we have calculated average values of A_{av} and g_{av}. The g_{av} and A_{av} values for a tetragonal complex are given by,

$$g_{\mathrm{av}} = \frac{1}{3}(g_{\parallel} + 2g_{\perp}) \quad \text{and} \quad A_{\mathrm{av}} = \frac{1}{3}(A_{\parallel} + 2A_{\perp})$$

The ESR parameters obtained from solution spectra for the Cu(II) complexes are summarised in table 5. The ratio of $g_{||}/A_{||}$ is used to find the structure of a complex. In present Cu(II) complexes, the ratio obtained is in the range 98–115 cm, which falls in the range 90–140 cm for square-planar copper(II) complexes [32].

Molecular orbital co-efficient, α^2 (covalent in-plane σ-bonding) and β^2 (covalent in-plane π-bonding) were calculated by using the following equations [31, 32]

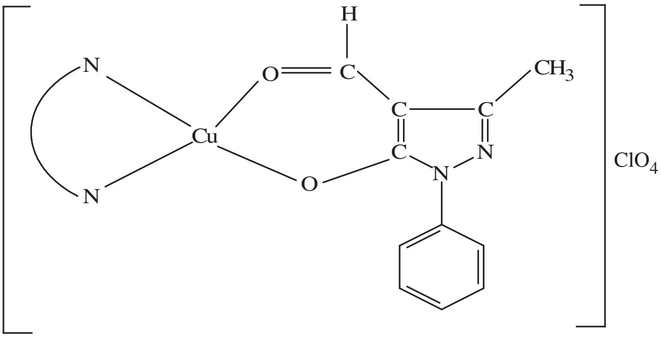
$$\alpha^2 = -(A_{\parallel}/0.036) + (g_{\parallel} - 2.0023) + \frac{3}{7}(g_{\perp} - 2.0023) + 0.04$$
$$\beta^2 = (g_{\parallel} - 2.0023)E/(-8\lambda\alpha^2)$$

The α^2 and β^2 values are given in table 6. The α^2 value measures the fraction of the unpaired electron density on copper(II). The smaller the value of α^2, the more covalent bonding. The α^2 values here indicate that the Cu(II) complexes of

Table 6. Bonding parameters of Cu(II) complexes.

Complex	α^2	β^2	$K \times 10^{-4}\,\mathrm{cm}^{-1}$
[Cu(PMFP)(bipy)]ClO$_4$	0.722	0.627	106
[Cu(PMFP-en)(dipy)]ClO$_4$	0.793	0.635	109
[Cu(PMFP-EA)(dipy)]ClO$_4$	0.775	0.612	108
[Cu(PMFP-Gly)(dipy)]ClO$_4$	0.849	0.604	109

α^2, β^2 were calculated by using $P = 0.036\,\mathrm{cm}^{-1}$ and $\lambda = 828\,\mathrm{cm}^{-1}$.



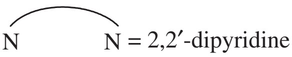
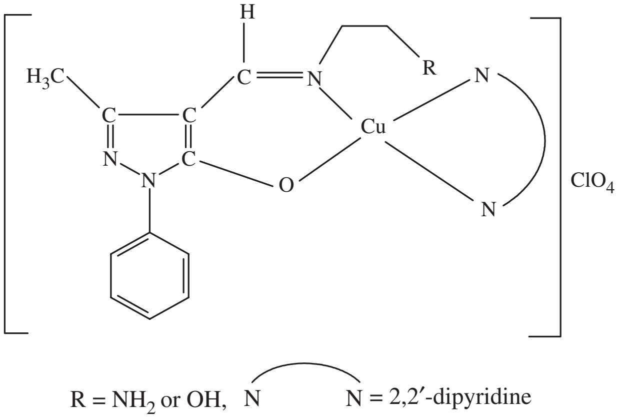

N = 2,2′-dipyridine

Figure 4. Mononuclear mixed ligand complex.



R = NH_2 or OH, N⌒N = 2,2′-dipyridine

Figure 5. Mononuclear Schiff-base complexes.

[(PMFP-en)Cu(dipy)]ClO_4 ($\alpha^2 = 0.793$) and [(PMFP-EA)Cu(dipy)]ClO_4 ($\alpha^2 = 0.775$) are more covalent than [(PMFP-Gly)Cu(dipy)]ClO_4 ($\alpha^2 = 0.849$). The β^2 is regarded as in-plane π-bonding parameter and are almost the same for all three Schiff-base Cu(II) complexes.

4. Conclusion

Based on the above results, the structures can be formulated as shown in figures 4 and 5.

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