

## Synthesis and spectroscopic characterization of cobalt (II), nickel (II) and copper (II) complexes with ethyl-5-methyl-1-(2'-pyridyl) pyrazole-3-carboxylate

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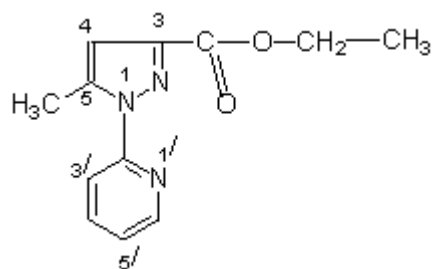
### ABSTRACT

The coordination mode of the title ligand, 1 ( synthesised for the first time and abbreviated as EMPyPzC and characterised by elemental analyses, mass, IR and <sup>1</sup>H-NMR spectral parameters), is investigated by way of isolation of its solid complexes of Co<sup>II</sup>, Ni<sup>II</sup> and Cu<sup>II</sup> with various counter ions, X (X = Cl, Br, NO<sub>3</sub>, SCN, BF<sub>4</sub>, ClO<sub>4</sub>, ½SO<sub>4</sub>) and their physicochemical identification. Magnetic and electronic spectral studies classify the reported bis-chelates as six coordinated distorted octahedral ones. A comparative study of IR spectra between the ligand and of its complexes indicate neutral bidentate (NN) behaviour of the ligand in all the species through pyrazolyl 2<sub>N</sub> and pyridyl 1<sub>C</sub> respectively and hence in all the cases the chromophore is MN<sub>4</sub>X<sub>2</sub> (M = Co<sup>II</sup>/ Ni<sup>II</sup>/Cu<sup>II</sup>). The RT e.s.r. spectra of some of the Cu<sup>II</sup> complexes indicate dx<sup>2</sup>-y<sup>2</sup> as ground state rather than dz<sup>2</sup>. Electrochemical studies of some of the Cu<sup>II</sup> species demonstrate easy oxidative nature of Cu<sup>II</sup>.

**Keywords:** Synthesis, spectroscopy, electrochemistry, pyridyl-pyrazolyl carboxylate, bis-chelates, bi-dentate.

### INTRODUCTION

Substituted pyrazoles have long been the focal point of attraction because of their well-acclaimed medicinal values. Subsequently pyrazole derivatives have been shown to be effective as tranquilising agents, anti-convulsants and in retarding growth of malignant tumours in lower animals<sup>1</sup>. In continuation of our earlier reports<sup>2</sup> on the synthesis and characterisation of the transition metal ion complexes, the present communication reports the ligational characteristics of ester derivative of 5-methyl-1-(2'-pyridyl) pyrazole-3-carboxylic acid, namely, ethyl-5-methyl-1-(2'-pyridyl) pyrazole-3-carboxylate by successful complexation with cobalt(II), nickel(II) and copper(II) .



I (EMPyPzC)

### EXPERIMENTAL

All the materials used at different stages for the preparation of the ligands and complexes reported were of analR quality and were used without further purification. Spectrograde solvents

were used for spectral, conductance and electrochemical measurements. D<sub>6</sub>-DMSO (Aldrich) was used for recording <sup>1</sup>H-NMR data.

### Synthesis of EMPyPzC

The ligand, ethyl-5-methyl-1-(2-pyridyl)pyrazole-3-carboxylate (EMPyPzC) was prepared by the condensation of sodium salt of ethylacetylpyruvate and 2-pyridyl hydrazine by following a known method<sup>2a</sup>.

To a solution of sodium salt of ethylacetylpyruvate (18.0g, 0.1mol) dissolved in 100ml water was added 2-pyridyl hydrazine (10.9g, 0.1mol) dissolved by suspending in minimum volume of water followed by drop wise addition of conc. HCl) while stirring in a mechanical manner and being kept in an ice-bath. Few drops of conc. HCl were added to maintain pH ~3, whereby the ester (EMPyPzC) separated out. It was filtered off, washed with water and dried in a desiccator under vacuum. Yield: 90%.

<sup>1</sup>H-NMR: δ 1.26(m, 3H, -CH<sub>3</sub>), 2.56(s, 3H, 5-CH<sub>3</sub>), 4.26(m, 2H, -CH<sub>2</sub>-), 6.74(s, 1H, H4), 7.82(m, 1H, H3'), 8.01(m, 1H, H4'), 7.43(m, 1H, H5'), 8.50(m, 1H, H6'). The product on recrystallisation from ethanol melted at 82°C. Calculated for C<sub>12</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>: C, 62.3; H, 5.6; N, 18.1. Found: C, 62.5; H, 5.5; N, 18.0%

### Synthesis of metal ion complexes: [M (EMPyPzC)<sub>2</sub>X<sub>2</sub>] (M = Co<sup>II</sup>/Ni<sup>II</sup>/Cu<sup>II</sup>; X = Cl, Br, NO<sub>3</sub>, SCN, 1/2SO<sub>4</sub>, BF<sub>4</sub>, ClO<sub>4</sub>)

An ethanolic solution (20ml) of MX<sub>2</sub>.nH<sub>2</sub>O (0.001 mol) was added to solution (20ml) of the ligand (0.46 g, 0.002 mol) in the same solvent. The resultant solution (pH ~5) was concentrated (~15ml) on water bath temperature and cooled to room temperature (~25°C), when microcrystalline compounds separated out in each case. The compound was filtered off, washed with cold ethanol and dried over silica gel.

### Physical measurements

C, H, N analyses were carried out at IACS, Calcutta, with a Perkin-Elmer CHNS/O analyser 2400. Mass spectrum of the ligand was recorded at RSIC, Chennai, with Finnegan Mat 8230 GC-MS. <sup>1</sup>H-NMR spectra were recorded in D<sub>6</sub>-DMSO

with Bucker AM 300L (300 MHz) super-conducting FT NMR. The cobalt content of the complexes was determined gravimetrically<sup>29</sup> as anhydrous CoSO<sub>4</sub>, except for the perchlorate species, where the metal was determined as the CoHg(SCN)<sub>4</sub> after decomposing the complex with conc. HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> mixture. The nickel content of the species was estimated gravimetrically as nickel diethyl glyoximate, after decomposing the metal complex with an acid mixture. The copper content of the complexes were determined iodometrically after decomposing the complex with HNO<sub>3</sub> and HCl mixture followed by boiling with urea. The halogen content of the complexes was determined as silver halide following the standard procedure. Magnetic susceptibilities were measured on a PAR 155 vibrating-sample magnetometer at IACS, Calcutta. The molar conductance values of the complexes in methanolic solution were obtained with a Systronics model 304 digital conductivity meter. The diffused reflectance spectra and the solution spectra of the complexes were recorded on U-3501 spectrophotometer. IR spectra were recorded on a Perkin-Elmer model 883 infrared spectrophotometer in the solid state (KBr pellet). EPR spectra were taken on a Varian E112 spectrometer at RSIC, Calcutta. Cyclic voltammograms were recorded with the PAR model 270/250 Research Electrochemistry Software (version 4.23) at Burdwan University, in methanolic solution of the species (1×10<sup>-3</sup> M) using tetrabutyl ammonium perchlorate (NBu<sub>4</sub>ClO<sub>4</sub>, 0.1M) as supporting electrolyte.

## RESULTS AND DISCUSSION

The new ligand, EMPyPzC has been synthesised by the condensation of sodium salt of ethylacetylpyruvate and 2-pyridyl hydrazine in excellent yield and the synthetic route is stated as follows.

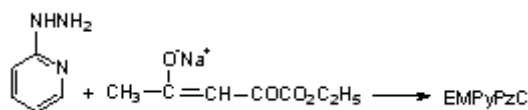
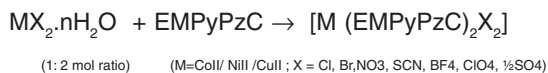


Fig. 1

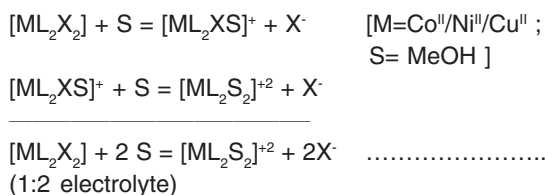
A fair number of solid compounds of varying colours with EMPyPzC have been isolated

in excellent yield and the synthetic route is stated as follows.



The electron impact mass spectra of the title ligand gives a molecular ion peak at *m/z* 231 which corresponds to the molecular formula C<sub>12</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>. In the IR spectra the ligand shows a number of bands appearing in the region 3150-2740 cm<sup>-1</sup> which are probably due to both aliphatic and aromatic C-H stretching vibrations. The very strong band appearing at 1730 cm<sup>-1</sup> is due to the stretching vibrations of C=O group (ν<sub>C=O</sub>) of the ester residue.. The ν<sub>C=N</sub> modes of vibrations of pyridine ring appear at 1595cm<sup>-1</sup> while those of pyrazole ring appear at 1585, 1480 and 1460 cm<sup>-1</sup> respectively. The characteristics pyrazole and pyridine ring vibrations and other usual and expected bands have been helpful to identify the ligand as ethyl-5-methyl-1-(2'-pyridyl) pyrazole-3-carboxylate. The <sup>1</sup>H-NMR spectral features further help to characterise the ligand. Micro analytical results are in line with the proposed formulation.

Cobalt(II) complexes of the title ligand, conform to the general composition [Co(EMPyPzC)<sub>2</sub>X<sub>2</sub>] as ascertained from analytical data (Table 1); the RT (27°C) magnetic moment values fall within the range 4.69-5.13 B.M. (Table 1) are grossly consistent with 6-coordinate high spin cobalt(II) complexes<sup>3</sup>. The somewhat lower magnetic moment values for the perchlorato species (4.69 B.M.) might be explained due to incomplete quenching of the orbital contribution to the magnetic moment<sup>4</sup>. The molar conductance (L<sub>M</sub>) values (Table 1) recorded in dry methanol (L<sub>M</sub> = 160-210 mho cm<sup>2</sup> mol<sup>-1</sup>) are indicative of 1:2 electrolytic nature<sup>5</sup> at least in solution of the said solvent; the data are reconcilable in terms of a solvolysis phenomenon in the said solvent as dictated below.



The diffuse reflectance spectra (d.r.s.) of the present Co<sup>II</sup> species indicate an overall octahedral environment in the complexes. The principal absorption bands in the spectral data are located in the region 8960-9820 and 19,230-20410 cm<sup>-1</sup> which may be assigned as ν<sub>1</sub>[<sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>2g</sub>(F)] and ν<sub>3</sub>[<sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>1g</sub>(P)] transitions<sup>6</sup> respectively. Using the two known relationships<sup>7</sup>, it has been possible to deduce the ligand field parameters (Dq =890-985; B = 676-754cm<sup>-1</sup> and β = 0.72-0.93) from the assigned positions of ν<sub>1</sub> and ν<sub>3</sub> bands; these are quite consistent with those reported earlier<sup>8</sup> for octahedral cobalt (II) species. Using the relationship ν<sub>2</sub> = ν<sub>1</sub> + 10Dq, the position of ν<sub>2</sub> bands are found to lie in the region 17860-19570 cm<sup>-1</sup>, very close to ν<sub>3</sub> bands as expected. In some cases, shoulders or weak bands appearing in the region (27,000-31,900 cm<sup>-1</sup>) are due to CT transitions. The electronic spectral data taken in methanolic solutions indicate that no significant change in geometry occurs on dissolutions of the complexes in the said solvent. The low values of molar extinction co-efficients (ε ≤ 56 dm<sup>3</sup> mol<sup>-1</sup>cm<sup>-1</sup>) found for the spectral bands give additional support to an octahedral geometry.

Nickel(II) complexes of the title ligand, conform to the general composition [Ni(EMPyPzC)<sub>2</sub>X<sub>2</sub>] as ascertained from analytical data (Table 1); the effective magnetic moment values (μ<sub>eff</sub>) (Table 1) of the species fall in the range 2.70-3.10B.M. at RT (27°C) expected for 6-coordinate nickel (II) complexes<sup>9</sup>. The methanolic solutions of these Ni<sup>II</sup> species furnish molar conductances (Λ<sub>M</sub> = 160-210 mhocm<sup>2</sup>mol<sup>-1</sup>) are indicative of 1:2 electrolytic nature<sup>5</sup> (for sulphato species, Λ<sub>M</sub> = 110 mho cm<sup>2</sup> mol<sup>-1</sup> indicating 1:1 electrolyte<sup>5</sup>) at least in solution of the said solvent. The d.r.s. of the reported bis-chelate of Ni<sup>II</sup> consist of three main bands appearing in the region 9,700-10685; 16,300-17670 and 26,700-28,330cm<sup>-1</sup> which can be safely assigned to the transitions <sup>3</sup>A<sub>2g</sub>(F) →

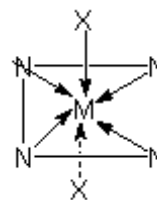


Fig. 2:

Table 1: Elemental and physical data of Co<sup>II</sup>, Ni<sup>II</sup> and Cu<sup>II</sup> complexes

Complex (Colour)	Yield (%)	Analysis(%): Found/(Calc.)				Anion	$\Lambda_M$ (**)	$\mu_{\text{eff}}$ at 27° (B.M.)
		C	H	N	M			
1. [Co(EMPYPzC) <sub>2</sub> Cl <sub>2</sub> ] (Pink)	90	48.8 (48.6)	4.2 (4.4)	14.0 (14.2)	9.8 (9.9)	12.1 (11.9)	160	4.82
2. [Co(EMPYPzC) <sub>2</sub> Br <sub>2</sub> ] (Bright Pink)	90	42.3 (42.2)	3.8 (3.8)	12.3 (12.3)	8.7 (8.6)	23.6 (23.4)	180	5.12
3. [Co(EMPYPzC) <sub>2</sub> (SCN) <sub>2</sub> ] (Pale Pink)	85	50.2 (50.2)	4.1 (4.0)	17.4* (17.6)	9.1 (9.2)	-	200	4.75
4. [Co(EMPYPzC) <sub>2</sub> (BF <sub>4</sub> ) <sub>2</sub> ] (Brownish red)	80	41.6 (41.4)	3.8 (3.7)	12.1 (12.0)	8.4 (8.5)	-	180	4.92
5. [Co(EMPYPzC) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ] (Brownish red)	80	40.2 (40.0)	3.5 (3.6)	11.5 (11.6)	8.3 (8.1)	-	210	4.69
6. [Ni(EMPYPzC) <sub>2</sub> Cl <sub>2</sub> ] (Green)	90	48.7 (48.6)	4.5 (4.3)	14.1 (14.2)	10.0 (9.9)	12.2	210	2.95
7. [Ni(EMPYPzC) <sub>2</sub> Br <sub>2</sub> ] (Deep green)	90	42.5 (42.3)	3.7 (3.8)	12.2 (12.3)	8.7 (8.6)	23.5 (23.7)	200	3.10
8. [Ni(EMPYPzC) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ] (Pale blue)	85	44.8 (44.6)	4.1 (4.0)	17.3 (17.4)*	9.1 (9.2)	-	160	2.86
9. [Ni(EMPYPzC) <sub>2</sub> SO <sub>4</sub> ] (Light pink)	85	46.4 (46.7)	4.1 (4.1)	13.6 (13.5)	9.3 (9.2)	-	110	2.70
10. [Ni(EMPYPzC) <sub>2</sub> (SCN) <sub>2</sub> ] (Sky blue)	80	49.3 (49.0)	3.9 (4.0)	17.4 (17.6)*	9.0 (9.2)	-	200	2.78
11. [Ni(EMPYPzC) <sub>2</sub> (BF <sub>4</sub> ) <sub>2</sub> ] (Sky blue)	85	41.6 (41.4)	3.6 (3.7)	12.0 (12.1)	8.6 (8.4)	-	190	3.02
12. [Ni(EMPYPzC) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ] (Light green)	85	40.2 (40.0)	3.8 (3.6)	11.8 (11.7)	8.3 (8.1)	-	170	2.98
13. [Cu(EMPYPzC) <sub>2</sub> Cl <sub>2</sub> ] (Yellowish green)	90	48.3 (48.2)	4.3 (4.3)	13.8 (14.0)	10.4 (10.6)	12.1 (11.9)	150	1.90
14. [Cu(EMPYPzC) <sub>2</sub> Br <sub>2</sub> ] (Dark green)	90	42.0 (42.2)	3.8 (3.9)	12.1 (12.2)	9.0 (9.2)	23.5 (23.3)	140	2.02
15. [Cu(EMPYPzC) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ] (Yellowish green)	85	44.5 (44.3)	3.9 (4.0)	17.0 (17.2)*	10.1 (10.2)	-	120	1.92
16. [Cu(EMPYPzC) <sub>2</sub> (BF <sub>4</sub> ) <sub>2</sub> ] (Bright green)	90	41.3 (41.1)	3.8 (3.7)	12.0 (12.0)	9.0 (9.1)	-	160	1.72
17. [Cu(EMPYPzC) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ] (Bright green)	85	39.9 (39.7)	3.4 (3.4)	11.4 (11.6)	8.5 (8.7)	-	200	1.79

\*including nitrogen present in the anions; \*\* conductivity in MeOH (mho cm<sup>2</sup> mol<sup>-1</sup>)

${}^3T_{2g}(F)$  ( $\nu_1$ ),  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$  ( $\nu_2$ ) and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$  ( $\nu_3$ ) respectively in an  $O_h$  symmetry. The weak bands or shoulder appearing at  $12,000\text{ cm}^{-1}$  are probably due to the spin-forbidden transition<sup>10</sup>. An additional band appearing around  $32,000\text{ cm}^{-1}$  could be due to LMCT transitions. The ligand field parameters ( $Dq = 975\text{-}1068\text{ cm}^{-1}$ ;  $B = 863\text{-}1028\text{ cm}^{-1}$ ,  $\beta = 0.79\text{-}0.95$  and  $\nu_2/\nu_1 = 1.61\text{-}1.68$ ) substantiate an overall octahedral geometry for the reported  $\text{Ni}^{II}$  species<sup>9,11</sup>. All the present bis-chelates of  $\text{Ni}^{II}$  on dissolution in methanol afford green solutions and suggest that there is no gross departure from the stereochemical environment..

The copper(II) complexes of the title ligand, conform to the composition  $[\text{Cu}(\text{EMPYPzC})_2\text{X}_2]$  as ascertained from analytical data (Table 1) furnish the RT ( $27^\circ\text{C}$ ) magnetic moment values ( $\mu_{\text{eff}}$ ) in the range 1.72-2.02 B.M. (Table 1). It is well authenticated<sup>12</sup> that for mono-nuclear  $\text{Cu}^{II}$  complexes, the magnetic moment values lie in the range 1.72-2.20 B.M. having no major interactions between two  $\text{Cu}^{II}$  ions. The molar conductance ( $\Lambda_M$ ) values of the reported species in dry methanol ( $\Lambda_M = 140\text{-}210\text{ mho cm}^2\text{ mol}^{-1}$ ) (Table 1) are indicative of 1:2 electrolytic in nature<sup>5</sup> of the species at least in the said solvent.

The reflectance spectra of the present  $\text{Cu}^{II}$  complexes exhibit a strong broad band in the region  $12,180\text{-}12,953\text{ cm}^{-1}$ ; the nature of the curve in such case; clearly indicates that more than one transitions are buried under the absorption envelope. Studies<sup>13</sup> on the electronic spectra of  $\text{Cu}^{II}$  complexes have indicated that the three transitions  ${}^2B_1 \rightarrow {}^2A_1$  ( $\nu_1$ ),  ${}^2B_1 \rightarrow {}^2B_2$  ( $\nu_2$ ) and  ${}^2B_1 \rightarrow {}^2E$  ( $\nu_3$ ) are close in energy often giving rise to a single broad band envelope. Thus, the present  $\text{Cu}^{II}$  species are best regarded as having distorted octahedral structures with a symmetry lower than  $O_h$  though the extent of distortion is not known. An additional band in all these cases appearing in the region  $25,575\text{-}27,855\text{ cm}^{-1}$  could be due LMCT transition. However, electronic spectral data in methanol indicate that there is no stereochemical change on dissolution. To have an insight into the points of attachments of the ligand molecule to the central metal ions in the present  $\text{Co}^{II}$ ,  $\text{Ni}^{II}$  and  $\text{Cu}^{II}$  complexes, i.r. spectra have been recorded in the region  $4000\text{-}200\text{ cm}^{-1}$  for the ligand, EMPYPzC as well as for its complexes.

A scrutiny of the spectral data of all the metal ion complexes reveals that a +ve shift of ( $\Delta\nu = 5\text{-}25\text{ cm}^{-1}$ ) vibration takes place as compared to the free ligand; this result is quite consistent with the non-participation of the ester group in complexation through the carbonyl oxygen<sup>14</sup>. The  $\nu_{\text{C=N}}$  (pyrazole) in all the species suffers a +ve shift ( $\Delta\nu = 5\text{-}20\text{ cm}^{-1}$ ),  $\nu_{\text{N-N}}$  (pyrazole) attains +ve shift ( $\Delta\nu = 5\text{-}15\text{ cm}^{-1}$ ) and  $\nu_{\text{C=N}}$  (pyridine) also gains +ve shift ( $\Delta\nu = 10\text{-}25\text{ cm}^{-1}$ ) in the i.r. spectra of the metal ion complexes. These observations clearly indicate that the tertiary N atoms i.e. pyrazolyl  $2_N$  and pyridyl  $1'_N$  are the points of attachment<sup>15</sup> to the central metal ions respectively. The far i.r. data down to  $200\text{ cm}^{-1}$  for the metal ion complexes show non-ligand bands which can be safely assigned to  $\nu_{\text{M-N}}$  ( $270\text{-}300\text{ cm}^{-1}$ ; pyrazolyl  $2_N$ )<sup>14</sup>,  $\nu_{\text{M-N}}$  ( $250\text{-}270\text{ cm}^{-1}$ ; pyridyl  $1'_N$ )<sup>16</sup> respectively. The mode of attachment of the anions (X) [X = Cl, Br,  $\text{NO}_3$ , SCN,  $\text{ClO}_4$ ,  $\text{BF}_4$ ,  $\frac{1}{2}\text{SO}_4$ ] in the reported metal ion species can be qualitatively inferred from the i.r. spectroscopy. The spectra of the halo complexes show metal-halogen stretching frequencies around  $300\text{ cm}^{-1}$  [differentiable from  $\nu_{\text{M-N}}$  (ring)] which might be attributed to  $\nu_{\text{M-X}}$  stretches<sup>17</sup>.

The i.r. spectra of  $\text{Ni}^{II}$ ,  $\text{Cu}^{II}$  nitrate species exhibit three bands of which two ( $1300\text{-}1380\text{ cm}^{-1}$ ) could be components of  $\nu_3$  and the third ( $\sim 800\text{ cm}^{-1}$ ) be the  $\nu_2$  vibration of a monodentate nitrate group in  $\text{C}_{2v}$  symmetry<sup>18</sup>. The spectra of thiocyanato complexes  $\text{Co}^{II}$ ,  $\text{Ni}^{II}$  and  $\text{Cu}^{II}$  exhibit strong bands around  $2100$  and  $800\text{ cm}^{-1}$  respectively which could be assigned to  $\nu_{\text{C=N}}$  vibration<sup>19</sup> and  $\nu_{\text{C-S}}$  stretch of N-bonded<sup>20</sup> NCS. In the far i.r. spectra a band around  $500\text{ cm}^{-1}$  which can be assigned to  $\delta_{\text{N-C-S}}$  mode of vibration of N-bonded thiocyanate group<sup>21</sup>. The sulphato complex of  $\text{Ni}^{II}$  show three bands in the region  $1050\text{-}1165\text{ cm}^{-1}$  and one strong band around  $1000\text{ cm}^{-1}$ ; the first three bands can be assigned to split components of  $\nu_3$  and the strong band around  $1000\text{ cm}^{-1}$  due to the  $\nu_1$  vibration of a coordinated sulphato group in  $\text{C}_{2v}$  symmetry<sup>22</sup>. The fluoborato complexes of  $\text{Co}^{II}$ ,  $\text{Ni}^{II}$  and  $\text{Cu}^{II}$  exhibit three bands in the region  $1150\text{-}1070\text{ cm}^{-1}$  which support the presence of a monodentate  $\text{BF}_4$  in  $\text{C}_{3v}$  symmetry<sup>23</sup>.

Perchlorato complexes of  $\text{Co}^{II}$ ,  $\text{Ni}^{II}$  and  $\text{Cu}^{II}$ , show the components of  $\nu_{\text{Cl-O}}$  in  $\text{C}_{3v}$  symmetry have been found at  $\sim 1160$ ,  $\sim 1100$  and  $\sim 1060\text{ cm}^{-1}$

respectively ;these indicate clearly the monodentate nature of perchlorate ion<sup>24</sup> in these reported species.

The ESR spectra of some of the Cu<sup>II</sup> complexes, [Cu (EMPyPzC)<sub>2</sub>X<sub>2</sub>] (X= Cl, BF<sub>4</sub>, ClO<sub>4</sub>) in polycrystalline form at RT (~30°C) do not show any hyperfine splitting. The nitrate- and perchlorato-species furnish similar spectral features with two g-values (g<sub>||</sub> > g<sub>⊥</sub>) (table 2) which are characteristics of tetragonally distorted geometry<sup>25</sup> with d<sub>x<sup>2</sup>-y<sup>2</sup></sub> ground state. G values for the nitrate- and perchlorato species are 2.91 and 3.17 respectively (table 2) and indicate strong exchange interactions. Fluoborate-species has e.s.r. spectrum with three g-values G = 3.18 recommending exchange interactions<sup>26</sup>.

Electrochemistry of some Cu<sup>II</sup> species of the series, [Cu( EMPyPzC)<sub>2</sub>X<sub>2</sub>] ( X = Cl, BF<sub>4</sub>, ClO<sub>4</sub>) in dry MeOH in the potential range +1.20 to -1.20 V vs. SCE provides that in each case, Cu<sup>II</sup> gets reduced to Cu<sup>I</sup> irreversibly around ( Table 3 ) -0.50 V vs. SCE. The well-defined redox couple formed in the +ve potential area is due to Cu<sup>III</sup>/Cu<sup>II</sup> system<sup>27</sup>; the anodic peak potential corresponds to the oxidation of Cu<sup>II</sup> (3d<sup>9</sup>) to Cu<sup>III</sup> (3d<sup>8</sup>) and the cathodic counterpart is due to quasi-reversible one-electron change process, since the ratio I<sub>p</sub><sup>red</sup>/I<sub>p</sub><sup>ox</sup> is very close to one and is expressed as Cu<sup>II</sup>  $\rightleftharpoons$  Cu<sup>III</sup> + e. The metallic copper deposited in the electrode surface gets irreversibly oxidised in the potential range -0.05 to +0.05 V vs. SCE in each run.

**Table 2: ESR spectral parameters of some of the representative**

S.No	Complex	g <sub>  </sub>	Cu <sup>II</sup> complexes		
			g <sub>⊥</sub>	g <sub>av</sub>	G
1.	[Cu(EMPyPzC) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	2.20	2.07	2.11	2.91
2.	[Cu(EMPyPzC) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ]	2.36	2.11	2.19	3.17
3.	[Cu(EMPyPzC) <sub>2</sub> (BF <sub>4</sub> ) <sub>2</sub> ]	2.32	2.10	2.17	3.18

**Table 3: Cyclic voltammetric results of some of the representative**

S.No	Complex	E <sub>a</sub> (V)	Cu <sup>II</sup> complexes		
			E <sub>c</sub> (V)	ΔE (V)	E <sub>1/2</sub> (V)
1.	[Cu(EMPyPzC) <sub>2</sub> Cl <sub>2</sub> ]	0.47	0.21	0.26	0.34
2.	[Cu(EMPyPzC) <sub>2</sub> (BF <sub>4</sub> ) <sub>2</sub> ]	0.45	0.25	0.20	0.35
3.	[Cu(EMPyPzC) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ]	0.55	0.12	0.43	0.33

E<sub>a</sub> and E<sub>c</sub> are the anodic and cathodic peak potentials respectively;

$$\Delta E = E_a - E_c; E_{1/2} = \frac{1}{2}(E_a + E_c)$$

## CONCLUSION

Thus in the light of the discussion from spectral data (4000-200 cm<sup>-1</sup>) it appears that the central metal ions has an overall octahedral geometry. The ligand, EMPyPzC, in the bis-chelates of Co<sup>II</sup>, Ni<sup>II</sup> and Cu<sup>II</sup> exercises a neutral bidentate (NN) through pyrazolyl 2<sub>N</sub> and pyridyl 1<sub>N</sub> respectively, the ester group (-COOC<sub>2</sub>H<sub>5</sub>) remains

non-participating in the chelates. Fate of the of the anions (X) is coordinated. The chromophore; MN<sub>4</sub>X<sub>2</sub> in all the bis-chelates is best represented by the following figure II.

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