

# SYNTHESIS AND SPECTRA CHARACTERIZATION OF MIXED-LIGAND COMPLEXES DERIVED FROM N-PROPYLIDENE-2-METHYLPYRIDYLAMINE AND TERPYRIDINE

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## ABSTRACT

The Schiff base ligand, N-Propylidene-2-methylpyridylamine was obtained from the condensation of 2-aminomethylpyridine and propanal. Also, its complexes with Cu(II), Ni(II), Zn(II), Co(II) and Mn(II) were prepared with terpyridine as co-ligand by boiling the mixture under reflux. The synthesized ligand and its metal complexes have been characterized by elemental analysis and spectroscopic (i.r. and electronic) methods. An octahedral geometric structure is proposed for the metal complexes. The six coordinate environment of the metals is composed of  $N_5X$  core with three nitrogen atoms from the tridentate terpyridine co-ligand and two from the Schiff base and the anions  $X = NO_3^-$ ,  $CH_3COO^-$  or  $SO_4^{2-}$  completing the octahedral geometry.

**KEY WORDS:** Characterization, Synthesis, Mixed-ligand and Schiff base.

## INTRODUCTION

An imine (Schiff base), forms complexes with metal ions via N and O donor atoms. The steric and electronic effects around the metal core can be finely tuned through the appropriate selection of electron withdrawing or electron donating substituents in the Schiff's bases. These N and O atoms induce two opposite electronic effects: the phenolate oxygen is regarded a hard donor, which stabilizes the higher oxidation states while the imine nitrogen is a softer donor and will hence stabilize the lower oxidation states of the metal ion (Gupta, *et al.*, 2006).

Schiff's bases are considered "privileged ligands" which are active and well-designed. These ligands have been extensively studied in coordination chemistry, and are found to be stable under a variety of oxidative and reductive conditions (Singh, *et al.*, 2007). Schiff's bases are actually able to stabilize many different metals in various oxidation states, controlling the performance of metals in a large variety of useful catalytic transformations (Cozzi, 2004; Shemirani, *et al.*, 2004). Transition metal complexes of these compounds have been used in the catalysis of diverse processes, such as oxygen and atom transfer radical polymerization, enantioselective epoxidation and aziridination. They are used as mediating organic redox reactions and mediators in other oxidation processes. Schiff's bases also have the potentials to be used in different areas such as electrochemistry, bioinorganic, catalysis, metallic deactivators, separation processes and environmental chemistry (Shemirani, *et al.*, 2004). They are becoming increasingly important in the pharmaceutical, dye and plastic industries as well as in the field of liquid-crystal technology (Gupta, *et al.*, 2006).

A special part of nitrogen ligand is the chemistry of oligopyridines. Oligopyridines have attracted special interest in coordination chemistry. Although 2,2'-bipyridine (bpy) has been announced to be "the most used ligand in coordination chemistry" (Humphries, *et al.*, 2005), 2,2':6',2''-terpyridine (tpy) also has a rich chemistry. Almost 70 years ago, Burstall and Morgan reported the first synthesis of 2, 2':6', 2''-terpyridine (Bermejo, *et al.*, 1999).

The kinetics and mechanism of formation of metal complexes and their stability have also been studied (Huynh, *et al.*, 2000; Sanna, *et al.*, 2000). 2,2':6',2''-Terpyridine has found wide application in the field of supramolecular chemistry which has led to the formation of racks, ladders and grids (Hanan, *et al.*, 1996), helicates (Albrecht, 2001), catenanes (Chambron, *et al.*, 2001), knots (Belfrekh, *et al.*, 2000) and dendrimers (Newkome, *et al.*, 2000); and as a result of their chemical and photochemical properties, these metal containing compounds have been extensively studied.

## EXPERIMENTAL

### Preparation of Ligand:

The ligand, N-propylidene-2-methylpyridylamine,  $C_9H_{12}N_2$  (PMPA) was prepared using a similar procedure described by Chen, *et al.*, 2003. 2-aminomethylpyridine (1.08 g; 0.01 mol) was dissolved in ethanol (7ml) in the presence of distilled water (1 ml) and three drop of glacial acetic acid. To this solution, propanal (0.58 g; 0.01 mol) dissolved in ethanol (3 ml) was added. The resultant mixture was boiled under reflux for six hours. The colour of the resulting solution gradually changed from pink to dark brown.

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It was then left to stand overnight at room temperature. The ligand was obtained as dark brown oil after removal of the solvent and drying in vacuo. The purity was checked by IR analysis and compared with standards.

### Preparation of Metal (II) Mixed Ligands Complexes of Cu, Ni, Zn, Mn and Co.

The Complexes N-propylidene-2-methylpyridylamineterpyridylsulphatocopper(II),  $[\text{Cu}(\text{C}_9\text{H}_{12}\text{N}_2)(\text{C}_{15}\text{N}_3\text{H}_{11})(\text{SO}_4)]$ , N-propylidene-2-methylpyridylamineterpyridylacetatonickel(II)-acetate,  $[\text{Ni}(\text{C}_9\text{H}_{12}\text{N}_2)(\text{C}_{15}\text{N}_3\text{H}_{11})(\text{CH}_2\text{CO}_2)]\text{CH}_2\text{CO}_2$ , N-propylidene-2-methylpyridylamineterpyridyl-nitratozinc(II)nitrate,  $[\text{Zn}(\text{C}_9\text{H}_{12}\text{N}_2)(\text{C}_{15}\text{N}_3\text{H}_{11})(\text{NO}_3)]\text{NO}_3$ , N-propylidene-2-methylpyridylamine-terpyridylacetatomanganese(II)acetate,  $[\text{Mn}(\text{C}_9\text{H}_{12}\text{N}_2)(\text{C}_{15}\text{N}_3\text{H}_{11})(\text{CH}_2\text{CO}_2)]\text{CH}_2\text{CO}_2$  and N-propylidene-2-methylpyridylamineterpyridylacetatocobalt(II)acetate,  $[\text{Co}(\text{C}_9\text{H}_{12}\text{N}_2)(\text{C}_{15}\text{N}_3\text{H}_{11})(\text{CH}_2\text{CO}_2)]\text{CH}_2\text{CO}_2$  were prepared by reacting an ethanolic solution of appropriate salts [copper(II)sulphate pentahydrate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ; nickel(II)acetate tetrahydrate,  $\text{Ni}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ ; zinc(II)nitrate hexahydrate,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ; manganese(II)acetate tetrahydrate  $\text{Mn}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$  and cobalt(II)acetate tetrahydrate,  $\text{Co}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ ] (0.02M) with hot ethanolic solution of the mixed ligands (terpyridine and PMPA) (0.02M) respectively. The reaction mixture was stirred under reflux for about six hours and dark brown solutions were formed. The solutions were then precipitated with potassium hydroxide and allowed to settle, filtered, washed several times with ethanol and dried. The precipitates were later dissolved in aqueous ethanol (5ml) and boiled under reflux for two hours and then the products were allowed to cool, filtered, dried and stored in desiccators over  $\text{CaCl}_2$ .

IR spectra were measured with Shimadzu IR Prestige-21 ITIRO and Nicolet Magna-IR spectrometer series (II), electronic spectra were carried out using Perkin-Elmer Lambda 950 UV-visible spectrometer, the elemental analysis of C, H and N were performed on Elemental Analyzer (Carlo Erba), the molar conductance measurement in DMF were carried out using a systronic direct reading conductivity bridge with a conventional dip-type black electrode and the melting points were determined with Thomas-Hoover capillary melting apparatus.

## RESULTS AND DISCUSSION

### N-propylidene-2-methylpyridylamine and terpyridine (mixed ligands) metal (II) complexes.

The physical properties of N-propylidene-2-methylpyridylamine and Terpyridine (mixed-ligand) metal (II) complexes are as tabulated in Table 1. These properties include colour, physical state and melting point. The physical state of the Schiff base ligand is oily (Chen *et al.*, 2003), terpyridine is crystalline while their metal complexes are either powdery or micro crystalline. The melting points of the solid chelates were generally high ( $218^\circ\text{C}$  -  $228^\circ\text{C}$ ). All the complexes melted as indicated by apparent change in colour. The elemental analyses given in Table 2 for C, H, N and metal (M) correspond to the expected molecular formula  $[\text{ML}^1\text{L}^2\text{X}] \cdot \text{X}$ . The data also revealed a 1:1:1 metal-ligand

stoichiometry for the Cu(II), Ni(II), Zn(II), Co(II) and Mn(II) complexes. The solubilities of the complexes were determined in a wide range of solvents. The complexes were all found to be very soluble in coordinating solvents such as DMF and DMSO. The molar conductivities of these complexes fall within the range  $6.00$ – $19.50 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$  suggesting high degree of covalent character.

### Infrared spectra of N-propylidene-2-methylpyridylamine and terpyridine (mixed ligands) metal (II) complexes

The infrared spectra of ligands and their complexes were recorded in the  $200\text{cm}^{-1}$ – $4000 \text{ cm}^{-1}$  range. The selected vibrational bands showed in Table 3 gives the vibration of relevant functional groups of the ligands. The bonds formed between the ligands and the metal(II) ions were elucidated by comparing the spectra of the ligands with that of the metal chelates. The assignment of the bands in the infrared spectra was not straight forward due to overlapping of the vibrational bands. However, through careful diagnostic investigation and comparison with data in literature, tentative assignments have been made. IR spectra of the Schiff bases showed the absence of bands at  $1735$  and  $3420 \text{ cm}^{-1}$  due to carbonyl  $\nu(\text{C}=\text{O})$  and  $\nu(\text{NH}_2)$  stretching vibrations and, instead, appearance of a strong new band at  $\sim 1625 \text{ cm}^{-1}$  assigned to the azomethine,  $\nu(\text{HC}=\text{N})$  linkage (Topal, *et al.*, 2007). It suggested that amino and aldehyde moieties of the starting reagents are absent and have been converted into the azomethine moiety in N-propylidene-2-methylpyridylamine. These deductions are in line with earlier reports (Chen *et al.*, 2003). In the spectra of the metal complexes, the frequencies assigned to C=N and pyridine-ring vibrations have been shifted to higher frequencies by about  $100$  –  $300\text{cm}^{-1}$  relative to that of the free ligand, this confirms bonding of metal ions to the azomethine nitrogen. Similar observation has been made for {N-alkyl-N-[pyridin-2-ylmethylene]amine}dichloro palladium complexes, (Chen *et al.*, 2003). Furthermore, a shift has been observed in the spectra of terpyridine upon coordination to the metal(II) ions from  $1484$  and  $1471 \text{ cm}^{-1}$  to  $1402 \text{ cm}^{-1}$  in the spectra of the complexes. This is considered to be an indication of coordination of terpy-N to the metal ions. Similar observations have earlier been made by (Potts *et al.*, 1990).

### Electronic spectral bands for N-propylidene-2-methylpyridylamine and Terpyridine (mixed-ligand) metal (II) complexes.

The Cu(II) complexes showed three absorption bands between  $10 \text{ Dq}$  band for a distorted octahedral geometry corresponding to the transitions  ${}^2\text{E}_g \longrightarrow {}^2\text{T}_{2g}$  (Lee, 2007). The bands at  $22350$  and  $30575 \text{ cm}^{-1}$  may be due to intra-ligand charge transfer transitions. However, the electronic spectrum of copper (II) is of little value in structural assignment (Drago, 1992), thus the calculation of some ligand field parameters viz:  $10\text{Dq}$ ,  $\text{B}'$ ,  $\beta$ , and L.F.S.E. have not been carried out for the Cu(II) complex.

$[\text{Co}(\text{C}_9\text{H}_{12}\text{N}_2)(\text{C}_{15}\text{N}_3\text{H}_{11})(\text{CH}_3\text{CO}_2)]\text{CH}_3\text{CO}_2^-$  complex gave rise to absorption bands having  $\lambda_{\text{max}}$  at  $8795$ ,  $17850$  and  $30575 \text{ cm}^{-1}$  respectively. These have been assigned to  ${}^4\text{T}_{1g} \longrightarrow {}^4\text{T}_{2g} (\text{F})$ ,  ${}^4\text{T}_{1g}$

$4T_{1g}$   $\longrightarrow$   $4A_{2g}$  and  $4T_{1g}$   $\longrightarrow$   $4T_{1g}$  (P) transitions respectively (Lee, 2007). (Offiong and Martelli., 1995) have reported a similar observation for an octahedral Co(II) complex. In the present study, an octahedral structure has been similarly assigned to  $[Co(C_9H_{12}N_2)(C_{15}N_3H_{11})(CH_3CO_2)]CH_3CO_2^-$ . These spins allowed transition have been used to calculate some ligand field parameters viz:  $10Dq$ ,  $B'$ ,  $\beta$ , and L.F.S.E. The value of  $\beta$  (Table 4) indicates that the covalent character of the metal-ligand bond is low.

Ni(II) ion forms complexes with various stereochemistry. The ground state of Ni (II) in tetragonal coordination is  $3A_{2g}(t_{2g}^6e_g^2)$ . Three transitions are expected for Ni(II) in octahedral field corresponding to  $3A_{2g} \longrightarrow 3T_{2g}$ ,  $3A_{2g} \longrightarrow 3T_{1g}$  (F) and  $3A_{2g} \longrightarrow 3T_{1g}$  (P). The electronic spectra of  $[Ni(C_9H_{12}N_2)(C_{15}N_3H_{11})(CH_3CO_2)]CH_2CO_2^-$  in the present

study shows three bands having  $\lambda_{max}$  at about 10145, 15945, and 29210  $cm^{-1}$  assigned to  $3A_{2g} \longrightarrow 3T_{2g}$ ,  $3A_{2g} \longrightarrow 3T_{1g}$  (F) and  $3A_{2g} \longrightarrow 3T_{1g}$  (P) transitions respectively, being consistent with octahedral geometry of the complex (Drago 1992).

In Mn(II) complex, the intensities of electron transition from ground state  $6S$  to a state of four-fold multiplicity are very weak and since Mn(II) has a  $d^5$  electronic configuration, the same type of energy diagram applies whether the environment is trihedral or octahedral. However, the bands obtained for  $[Mn(C_9H_{12}N_2)(C_{15}N_3H_{11})(CH_3CO_2)]CH_2CO_2^-$  complex has  $\lambda_{max}$  at 18900, 23100, and 29700  $cm^{-1}$ . These may be assigned to  $4T_{1g}(4G) \longrightarrow 6A_1$ ,  $4T_{1g}(4P) \longrightarrow 6A_1$  and  $4T_{1g}(4F) \longrightarrow 6A_1$  transitions in octahedral field (Drago 1992).

**Table 1:** Physical properties of the ligands and their metal (II) complexes

Compound	Colour	Physical state	Melting point( $^{\circ}C$ )	Molar conductance ( $Ohm^{-1}cm^2mole^{-1}$ )
N-propylidene-2-methyl pyridylamine ( $C_9H_{12}N_2$ )	Yellow	Oily	-	-
Terpyridine ( $C_{15}N_3H_{11}$ )	White	Crystalline	80	-
$[Cu(C_9H_{12}N_2)(C_{15}N_3H_{11})SO_4]$	Dark green	Powdery	228	6.00
$[Ni(C_9H_{12}N_2)(C_{15}N_3H_{11})CH_2CO_2] CH_2CO_2$	Blue			
$[Zn(C_9H_{12}N_2)(C_{15}N_3H_{11})NO_3]NO_3$	Dirty-white	Microcrystalline	220	12.60
$[Co(C_9H_{12}N_2)(C_{15}N_3H_{11})CH_2CO_2] CH_2CO_2$	Dark brown	Powdery	222	10.90
$[Co(C_9H_{12}N_2)(C_{15}N_3H_{11})CH_2CO_2] CH_2CO_2$	Dark brown	Microcrystalline	218	10.50
$[Mn(C_9H_{12}N_2)(C_{15}N_3H_{11})CH_2CO_2] CH_2CO_2$	brown	microcrystalline	225	19.50

**Table 2:** Elemental analysis data of the ligands and their metal(II) complexes

Compound	%C	%N	%H	%M
	Found (Calcd)	Found (Calcd)	Found (Calcd)	Found (Calcd)
N-propylidene-2-pyridylamine ( $C_9N_2H_{12}$ )	72.02 (72.97)	18.95 (18.92)	8.11 (8.10)	-
Terpyridine ( $C_{15}N_3H_{11}$ )	- (77.23)	- (18.01)	- (4.75)	-
$[Cu(C_9N_2H_{12})(C_{15}N_3H_{11})(SO_4)]$	53.02 (53.28)	12.59 (12.95)	4.84 (4.26)	11.57 (11.75)
$[Ni(C_9N_2H_{12})(C_{15}N_3H_{11})(CH_3COO)] CH_3COO$	60.20 (60.25)	12.29 (12.55)	5.20 (5.19)	10.32 (10.53)
$[Zn(C_9N_2H_{12})(C_{15}N_3H_{11})NO_3]NO_3$	50.31 (50.49)	17.82 (17.18)	4.93 (4.03)	11.64 (11.46)
$[Co(C_9N_2H_{12})(C_{15}N_3H_{11})(CH_3COO)] CH_3COO$	60.78 (60.22)	12.45 (12.55)	5.88 (5.20)	10.44 (10.56)
$[Mn(C_9N_2H_{12})(C_{15}N_3H_{11})(CH_3COO)] CH_3COO$	60.44 (60.66)	12.36 (12.64)	5.92 (5.24)	9.58 (9.92)

**Table 3:** Selected infrared vibration bands ( $\text{cm}^{-1}$ ) of the ligands and their metal (II) complexes

PMPA	terpy	Co(II)- complex	Ni(II)- complex	Cu(II)- complex	Mn(II)- complex	Zn(II)- complex	Band Assignment
1650		1625	1620	1625	1625	1625	(HC=N) azomethine stretching
1588		1580	1580	1585	1590	1595	(C=N) Pyridine ring stretching
1568	1484 1471	1402	1402	1402	1402	1402	

**Table 4:** Ligand Field Parameters For N-Propylidene-2-Methylpyridylamine And Its Metal (II) Complexes

Complex	10Dq ( $\text{cm}^{-1}$ )	B' ( $\text{cm}^{-1}$ )	$\hat{a}$ ( $\text{cm}^{-1}$ )	L.F.S.E (KJ mol $^{-1}$ )
[CuC <sub>9</sub> H <sub>12</sub> N <sub>2</sub> (C <sub>15</sub> N <sub>3</sub> H <sub>11</sub> )]SO <sub>4</sub>	-	-	-	-
[Ni(C <sub>9</sub> H <sub>12</sub> N <sub>2</sub> )(C <sub>15</sub> N <sub>3</sub> H <sub>11</sub> )CH <sub>2</sub> CO <sub>2</sub> ] (CH <sub>2</sub> CO <sub>2</sub> )	905.5	1469	1.51	105
[Co(C <sub>9</sub> H <sub>12</sub> N <sub>2</sub> )(C <sub>15</sub> N <sub>3</sub> H <sub>11</sub> )CH <sub>2</sub> CO <sub>2</sub> ] CH <sub>2</sub> CO <sub>2</sub>	580	981	0.953	121
[Mn(C <sub>9</sub> H <sub>12</sub> N <sub>2</sub> )(C <sub>15</sub> N <sub>3</sub> H <sub>11</sub> )CH <sub>2</sub> CO <sub>2</sub> ] CH <sub>2</sub> CO <sub>2</sub>	420	762.7	0.887	225

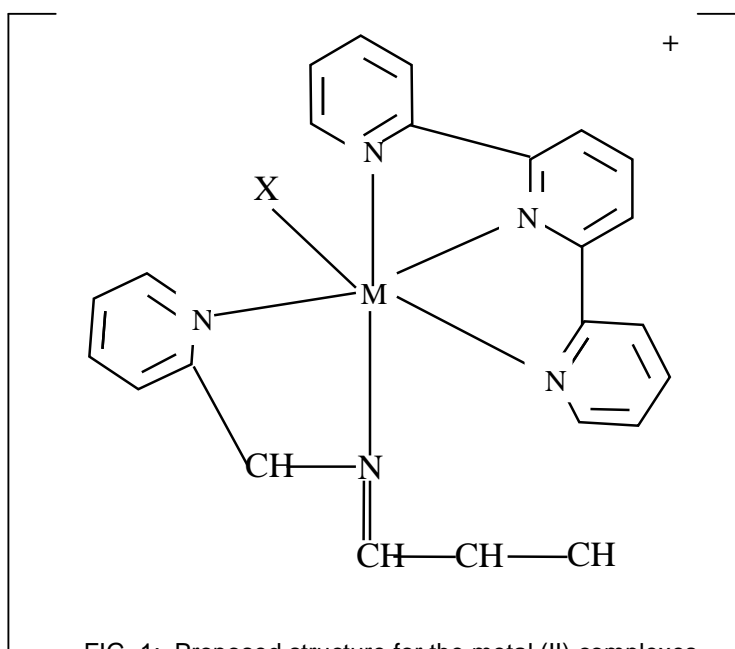


FIG. 1: Proposed structure for the metal (II) complexes.  
X = NO<sub>3</sub>, CH<sub>2</sub>COO or SO<sub>4</sub>

This is further supported by elemental analysis and infrared data. The diamagnetic zinc (II) complexes did not show any d-d bands and their spectra are dominated only by charge transfer bands. The charge transfer bands at 28450  $\text{cm}^{-1}$  was assigned due to

transition  ${}^2E_g \longrightarrow {}^2T_{2g}$  possibly in an octahedral environment geometry (Drago 1992). An octahedral structure as shown in Fig. 1 has been proposed for the metal (II) complexes based on the spectral analyses and literature

**CONCLUSION**

The following conclusions have been drawn from the results of this study: The pyridylimine-type Schiff base ligand N-propylidene-2-methylpyridylamine is bidentate, binding the metal centre through its pyridyl and azomethine nitrogen atoms while the mixed-ligand metal complexes have been deduced to be six coordinate based on spectral characterization. The coordination environment of the metals is composed of five nitrogen atoms three from the tridentate terpyridine co-ligand and two from the Schiff base with the anions ( $\text{NO}_3^-$ ,  $\text{CH}_3\text{COO}^-$  and  $\text{SO}_4^{2-}$ ) completing the octahedral geometry.

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