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## Synthesis, characterization and biological studies on divalent transition metal complexes of schiff bases derive from condensation of pyridine derivatives

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### Abstract

New Schiff-base ligand derived from the condensation of 1, 2, 3 triamino propane 1, 3 diamino propane 2ol with 2 fomyl pyridine (=FPTN and FPTNOL) and 2-acetyl pyridine (=APTN and APTNOL) and their Copper (ii) and Nickel(ii) transition metal complexes have been synthesized and characterized by IR spectra, electronic spectra, magnetic susceptibility molar index and elemental analysis.

All complexes contain a 1:1 ratios of tetra dentate ligand to metal (II) salt. Copper (II) complexes of the type [Cu(L)I] ClO<sub>4</sub> and formed to be five coordinated, while (CuL) (ClO<sub>4</sub>)<sub>2</sub> are formed tetragonal or square planner in structure. The IR spectra of Cu(II) and Ni(II) Cheates support the Schiff base formulation of the ligands and provide evidence for the co-ordination of the pyridine groups. A tetragonal crystal field model provides a basis for the interpretation of the visible and near IR, Electronic spectra of Ni(II) complexes with the tetradentate ligand occupying the square planer arrangement. The complex NiL<sub>x</sub>nH<sub>2</sub>O where L= FPTN, FPTNOL, APTN, APTNOL, X= Cl, NO<sub>2</sub> or NCS<sup>-</sup> behaves as 2:1 electrolytes in aqueous solution and give rise to a common species [Ni(L)(H<sub>2</sub>O)<sub>2</sub>]<sup>+2</sup>. In aqueous the complex ion [Ni(L)(H<sub>2</sub>O)<sub>2</sub>]<sup>+2</sup> reacts with neutral dentate donors to yield [Ni(L) (donor)<sub>2</sub>]<sup>+2</sup> the <sup>1</sup>H and <sup>13</sup>C n.m.r. spectral data confirmed the suggested structure for the Schiff base ligand and mass spectra results confirmed the proposed structure of the legend. The antimicrobial activities, properties of the ligand and their metal complexes have been studied.

**Keywords:** Synthesis, characterization and biological, pyridine derivatives

### Introduction

Recently Cu II & Ni II complexes with bi & tridentate Schiff base has been reported <sup>[1, 2]</sup>, In the present work we have isolated some copper (II) and Nickel(II) complexes of neutral tetradentate Schiff bases derived by the condensation of 2 formylpyridine with trimethylenemine (FPTN) 1, 3 di amino propane-2-ol (=FPTNOL) and also of the Schiff bases devived by the condensation of 2-acetyl pyridine with trimethylenediamine (=APTN), and 1, 3 diamino propane-2-ol (=APTNOL). A recent publication <sup>[5]</sup> on the Nickel (II) complexes of polydentate Schiff bases promoted us to report our results. This paper described the preparation, properties and structural elucidation and biological activities of some Copper (II) and Nickel (II) complexes of the above mentioned four ligands. A survey of literature reveals that amongst the different class of N, O containing ligands play an important role in the determination of Copper (II) and Nickel (II) metals. Attempt were made to improve upon the selectivity and sensitivity of the reactions –C=N linkage with these metals.

### Experimental

All the chemicals used where supplied from CDH, Aldrich, sigma samples of 1, 2, 3 triaminopropane, 1, 3 diaminopropane-2ol, 2-formyl pyridine, 2-acetylpyridine (fluka) were employed. Nickel (II) and Copper (II) salts uses were of A.R. grade while solvents of reagent grade.

Copper content have been determined by absorption spectroscopy and Nickel content by applying precipitation method after the decomposition of the complexes with concentrated minimal acids <sup>[6, 7]</sup>.

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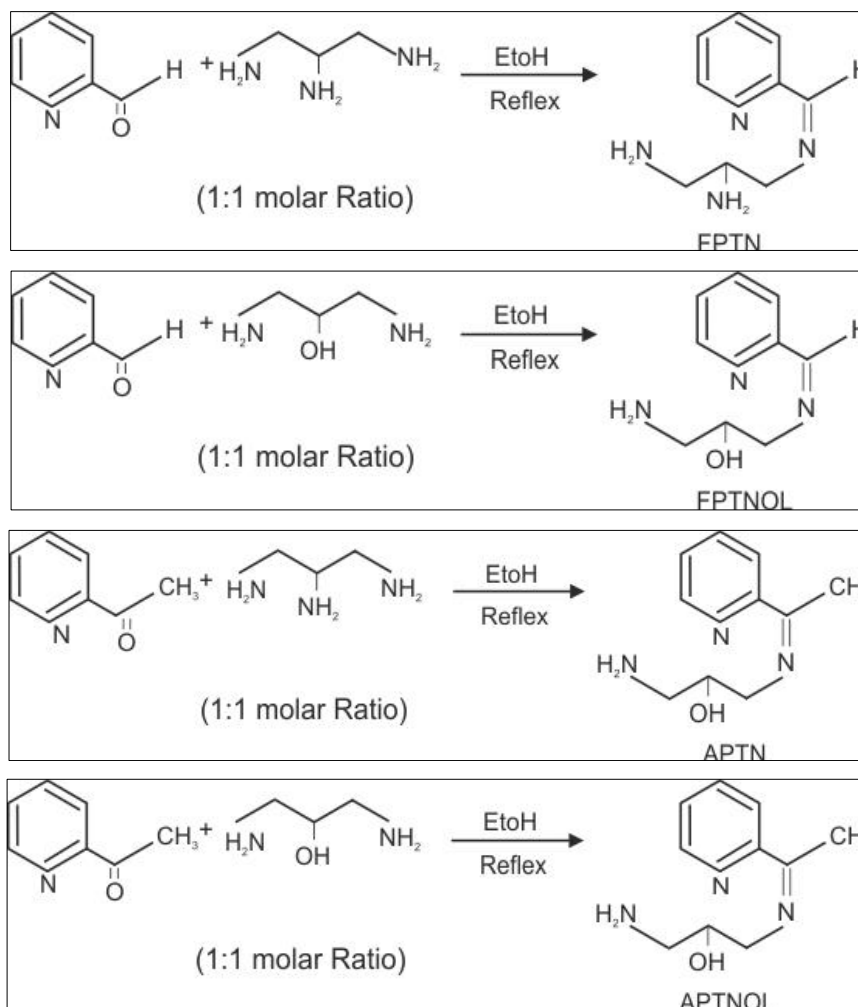
Relative molecular weight of the ligand and their complexes have been determined cryoscopically<sup>[8]</sup>. Molar diffraction measurements have been carried out with Alago illumination Alago Co. Ltd Japan Using  $10^{-3}$  M EtOH solvent. Conductivity measurement have been carried out with an electrolytic conductivity measuring Toshiwal conductivity bridge type CL 01/02 A using  $10^{-3}$ M  $\text{CH}_3\text{NO}_2$ , MeOH, EtOH and  $\text{H}_2\text{O}$  solvents at 27 °C, Elemental analysis were performed on a carlo Eraba 1106 elemental analysis.

The IR spectra of the compounds have been recorded as nujol mull on a pye unicam sp-3-300 spectrophotometer in range 200-4000  $\text{cm}^{-1}$  using KBr disc. Electronic spectra has been recorded on pye unicam sp-5-560 visible spectrophotometer for  $10^{-3}$ M solution of the ligand and thin complexes in DMFO

at 27 °C using a 1 cm cell. Magnetic susceptibility of the complexes have been measured at room temperature by Gouy's balance method using  $\text{CoHg}(\text{SCN})_4$  as standard.  $^1\text{H}$  and  $^{13}\text{C}$  N.M.R. spectra were recorded on a varian FTXL-200 n.m.r. instrument.

#### Preparation of ligands (Schiff bases)

The 0.1 mole of amine was dissolved in absolute EtOH (20 ml). It was reflux for about 30 min on a water bath than it was mixed with 0.1 mole of aldehyde (20 ml). The mixture was refluxed for 3-4 hours. A coloured solution was obtained. The Schiff base ligand was isolated by crystallisation after volume reduction. The crystalline product was dried under vacuum desiccator under reduced pressure at room temperature.



#### Preparation of the complexes

**Copper (II) complexes:**  $\text{CuL}(\text{ClO}_4)_2$  where L=FPTN: APTN (III); FPTNOL (V) and APTNOL (VII). An ethanol solution of the ligand was prepared from a mixture of 2-formylpyridine (0.02 mole) or 2-acetylpyridine and 1, 2, 3 triaminopropane or 1, 3 diaminopropane-2-ol and then diluted with 300 ml. This solution was then added slowly to a stirred ethanol solution (500 ml) of copper perchlorate hexa hydrate (10.0 g). The pale yellow, green blue and dark green compound were filtered. Wash with ethanol and dried in vacuum desiccator.

$[\text{Cu}(\text{L})\text{I}]\text{ClO}_4$  (Where L=FPTN, (II); L=APTN, (IV); FPTNOL, (VI); and APTNOL (VIII)): These solution of the above complexes eg.  $\text{Cu}(\text{FPTN})(\text{ClO}_4)$  (0.05 g) in acetonitrile (50 ml) was treated with a solution of tetra ethylammoniumiodide (0.25 g) in acetonitrile (10 ml) and the

mixture was evaporated on a water bath (15, ml). This solution, on keeping in a refrigerator, gave Pale yellow, red wine, straw colour and dark green crystals, which was filtered off, wash with acetonitrile and dried in vacuum desiccator.

Nickel (II) complexes,  $\text{Ni}(\text{L})\text{Cl}_2 \cdot n\text{H}_2\text{O}$  (Where L=FPTN, (IX); APTN, (XI); FPTNOL, (XII); and APTNOL, (XIV); n=0 or 1): 2-formyl pyridine or 2-acetyl pyridine (50m mole) dissolved in 10 ml of isopropyl alcohol was added dropwise to a solution of diamine (25mmole) in 10~15 ml of the same solvent, which previously cooled in a icemixture 0 °C. The resulting solution was stirred at room temperature for 2 hrs (in same cases refluxing is necessary at this stage); and then added to a hot solution of Nickel(II) chloridehexahydrate (25m mole) in 80 ml of absolute ethanol. After slow evaporation to 50-70 ml followed by cooling blue, purple, green, and red crystals were obtained. These were filtered,

washed with isopropyl alcohol and dried in vacuum desiccators at 60 °C.

For the complex (XI) about 30 ml of n-butylalcohol was added in the reaction mixture and slowly evaporated to get the desired complex, which was washed with water-ethanol-butanol mixture.

For the complexes (XII) and (XIV) the NiCl<sub>2</sub>·6H<sub>2</sub>O is large excess of absolute ethanol was boiled (~2 hrs) with ~100 ml of 2, 2 dimethoxypropane prior to the addition to the ligand solutions. The rest of the procedure was same as described above.

Ni(L) (X<sub>2</sub>) (Where L=FPTN & X=NO<sub>2</sub>, (x); L=FPTNOL & X=NCS, (XIII); and L=APTANOL & X= NO<sub>2</sub>, (XV): The metathesis of the chloro complexes with appropriate sodium salt in methanol gave these chelates as blue, light blue, red or brown crystals. The biological activity of synthesized Schiff base and their metal complexes have been studied for thin antimicrobial and antifungal activities. Bacillus subtilis 1MG

22 (bacterium), Saccharomyces cerevisiae WET 136 (Yeast), Exchericha coli DM (bacterium). Klebsiella pneumoniae DIG 1319 (bacterium) and micrococcus luteus LA 2971 (bacterium) were used as the test organism in an antimicrobial study [9] the bacteria and yeast strain were inoculated into nutrient both (Difco) and malt extract both (Difco) and incubate for 48 hrs, respectively. In the Disc diffusion method. The Sterile Mueller Hinton Agar (Oxide) for bacteria and Sabouraud dextrose Agar for yeast were separately inoculated with the test microorganism. The compound dissolved in DMF as 100 µg/disc solution and absorbed on the sterile paper antibiotic discs were placed in wells (6mm. diameter) cut in the agar media and the plates were incubated at 30 °C for bacteria (20-24 hrs) at 25 °C for yeast (72 hrs). The resulting inhibition zone on the plates were measured after 48 hrs Table 6. The control samples were only absorbed in DMF. The data reported are the average of their experiments.

**Table 1:** Elemental Analysis of Copper (II) and Nickel (II) chelates

S. No.	Complex	M. Wt. cal (obs)	Colour	% Found Cu/Ni	N	% Cal. Cu/Ni	N
1.	[Cu(FPTN)](ClO <sub>4</sub> ) <sub>2</sub>	440.5(431.6)	yellow green	12.80	11.20	12.34	10.88
2.	[Cu(FPTN)I](ClO <sub>4</sub> )	468(446.2)	Pale Yellow	11.50	10.40	11.71	10.33
3.	Cu(APTN)(ClO <sub>4</sub> ) <sub>2</sub>	454.5(448.3)	dirty yellow	11.40	10.12	11.70	10.32
4.	[Cu(APTN)I](ClO <sub>4</sub> )	482(476.6)	Red wine	10.98	10.10	11.14	9.82
5.	[Cu(FPTNOL)](ClO <sub>4</sub> ) <sub>2</sub>	455.5(447.6)	green blue	12.00	10.89	11.97	10.56
6.	[Cu(FPTNOL)I](ClO <sub>4</sub> )	483(476.6)	Strong colour	11.25	9.92	11.39	10.03
7.	[Cu(APTNOL)](ClO <sub>4</sub> ) <sub>2</sub>	455.5(436.3)	dark green	11.41	10.30	11.37	10.02
8.	[Cu(APTNOL)I](ClO <sub>4</sub> )	483 (472.4)	green	10.38	9.29	10.82	9.55
9.	Ni (FPTN) Cl <sub>2</sub> H <sub>2</sub> O	325.7(310.2)	blue	14.80	13.98	14.53	14.04
10.	Ni(FPTN)(NO <sub>2</sub> ) <sub>2</sub>	328.7(313.6)	brown	11.60	21.08	11.47	20.89
11.	Ni (APTAN)Cl <sub>2</sub>	321(309.6)	purple	14.56	13.99	14.18	13.70
12.	Ni (FPTNOL)Cl <sub>2</sub>	322 (311.6)	dark green	14.00	13.90	14.61	14.10
13.	Ni (APTANOL)(NCS) <sub>2</sub>	367.7(344.2)	light blue	13.32	18.86	13.12	19.01
14.	Ni (APTANOL)Cl <sub>2</sub>	322.7(309.7)	red	18.80	13.40	13.65	13.17
15.	Ni (APTANOL)(NO <sub>2</sub> ) <sub>2</sub>	343.7(324.7)	red brown	12.80	18.21	13.00	18.84

**Table 2:** Molar conductive at 27°C and Magnetic Moments

Complex No.	Solvent	Molecular Conductivity 10 <sup>-1</sup> M solution Ω <sup>-1</sup> cm <sup>2</sup> mole <sup>-1</sup>	Electrolytic nature	Temp °c	µ <sub>eff</sub> (B.M.)
1.	CH <sub>3</sub> NO <sub>2</sub>	164	2:1	25	1.85
2.	CH <sub>3</sub> NO <sub>2</sub>	88	1:1	27	1.90
3.	CH <sub>3</sub> NO <sub>2</sub>	168	2:1	25	1.88
4.	CH <sub>3</sub> NO <sub>2</sub>	90	1:1	25	1.82
5.	CH <sub>3</sub> NO <sub>2</sub>	168	2:1	25	1.92
6.	CH <sub>3</sub> NO <sub>2</sub>	92	1:1	27	1.88
7.	CH <sub>3</sub> NO <sub>2</sub>	160	2:1	27	1.92
8.	CH <sub>3</sub> NO <sub>2</sub>	82	1:1	27	1.90
9.	H <sub>2</sub> O/CH <sub>3</sub> OH	190/88	2:1/1:1	25	3.20/-
10.	H <sub>2</sub> O	180	2:1	25	3.09
11.	H <sub>2</sub> O/CH <sub>3</sub> OH	188/90	2:1/1:1	25	3.23/-
12.	H <sub>2</sub> O	188	2:1	27	3.22
13.	-	-	-	27	-
14.	H <sub>2</sub> O	192	2:1	27	3.30
15.	H <sub>2</sub> O	198	2:1	27	3.19

**Table 3:** Electronic Spectral Data

	Complex	Solvent	Bond Position in (KK(log ε mol))*
I	Cu(FPTN)OCl <sub>4</sub>	CH <sub>3</sub> NO <sub>2</sub>	16.5(1.95)
II	[Cu(FPTN)I](ClO <sub>4</sub> )	CH <sub>3</sub> NO <sub>2</sub>	13.0(2.29)
V	Cu(FPTNOL)(ClO <sub>4</sub> )	CH <sub>3</sub> NO <sub>2</sub>	16.55(1.88)
VI	[Cu(FPTNOL)I](ClO <sub>4</sub> )	CH <sub>3</sub> NO <sub>2</sub>	12.95(2.18)
IX	Ni (FPTN) Cl <sub>2</sub> H <sub>2</sub> O	Nujol mull H <sub>2</sub> O	9.0, 11.98(sh), 13.0, 17.5(sh), 26.5(sh), 32.0, 33.7 (sh), 40.00, 10.00 (sh), 12.5, (1.0), 3.2 (0.9), 18.5 (0.8)
X	Ni (FPTN) (NO <sub>2</sub> ) <sub>2</sub>	Nujol mull H <sub>2</sub> O	12.5, 30.0(sh), 33.0, 40.0, 10.1(0.5), 12.8 (1.2), 13.5(1.0), 19.0(0.9)
XI	Ni (APTAN) Cl <sub>2</sub>	H <sub>2</sub> O	9.8 (0.48), 12.8(0.9), 13.5(0.9), 17.8(sh), 19.5(0.7)
XIII	Ni (FPTNOL) (NCS) <sub>2</sub>	Nujol mull	9.2, 11.09, 12.7, 17.8(sh), 31.9, 39.5

XIV	Ni (APTNOL) Cl <sub>2</sub>	Nujol mull	11.3, 12.8(sh), 18.6, 32.5, 40.0 (sh)
XV	Ni (APTNOL) (NO <sub>2</sub> ) <sub>2</sub>	H <sub>2</sub> O	9.7(0.5), 13.0(1.0), 13.5 (0.9), 17.6(sh), 19.5(0.6)
XII	Ni (FPTNOL) Cl <sub>2</sub>	Nujol mull H <sub>2</sub> O	12.6, 31.2(sh), 33.0, 40.0, 10.3(0.7)] 12.5(1.3), 13.5(sh), 19.0(1.0)

1 KK=1000/cm

**Table 4:** Infrared frequency assignment for the nitrate and thio cyanate ions in the Nickel (II) complexes

Ni(FPTN)(NO <sub>2</sub> ) <sub>2</sub> (x)	Ni(FPTN)(NO <sub>2</sub> ) <sub>2</sub> (xv)	Ni(FPTN)(NCS) <sub>2</sub> (xiii)	Assignment
1380	1379	-	$\gamma_{as}NO_2$
1150	1350(sh), 1190, 1155	-	$\gamma_sNO_2$
820	821	-	$\delta NO_2$
-	-	2100, 2090	$\gamma^{C-N}$
-	-	810, 795	$\gamma^{C-S}$
-	-	Not clearly observed	$\delta^{NCS}$

(X), (XV), (XIII) (complex No'S)

**Table 5:** Visible and near-Infrared spectral Data of some Nickel (II) complexes with assignments

	Complex	Solvent	KK (log $\epsilon$ ) mol	
			$\gamma_1$	$\gamma_2$
(IX)	Ni (FPTN) Cl <sub>2</sub> H <sub>2</sub> O	Nujolmull H <sub>2</sub> O	9.0, 11.98(sh), 13.0, 10.0(sh), 12.05(1.0), 13.2 (0.9)	1.75 (sh), 18.5 (8)
(X)	Ni (FPTN) (NO <sub>2</sub> ) <sub>2</sub>	Nujolmull H <sub>2</sub> O	12.5, 10.1 (0.5), 12.8(1.2), 13.5 (1.0)	19.(0.9)
(XI)	Ni (APTN) Cl <sub>2</sub>	H <sub>2</sub> O	9.8 (0.48), 12.8(0.9), 13.5 (0.9)	17.8 (sh) 19.5 (0.7)
(XIII)	Ni (FPTNOL) Cl <sub>2</sub>	Nujolmull H <sub>2</sub> O	11.3, 12.8 (sh), 9.7 (0.5), 13.0 (1.0), 13.5 (0.9)	18.6, 17.6 (sh), 19.5 (0.6)
(XV)	Ni (APTNOL) (NO <sub>2</sub> ) <sub>2</sub>	Nujolmull H <sub>2</sub> O	12.6, 10.3 (0.7), 12.5 (1.3), 13.5 (sh)	- 10.0(1.0)

(Killo kaiser) 1KK= 1000cm<sup>-1</sup>

## Result and Discussion

**Copper II complexes:** The copper II complexes are quite stable in air. The analytical data table-1 reveals a 1:1 ratio Schiff base ligand to metal ratio for all of the complexes. The conductivity of (I), (III) (V) and (VII) in nitromethane are all in the usual range for 2:1 electrolytes in this solvent table-2. On the other hand the conductivity of (II), (IV), (VI) and (VIII) complexes are all in the usual range for 1:1 electrolytes in the same solvent table 2.

All the compound of the type [Cu(L)]ClO<sub>4</sub> possibly have a five coordinate structure in the solid and in solution of nitro methane as revealed from their electronic spectral data (Table-3). Analysis five co-ordinate geometry has also been reported for a series of copper (II) chelates of the type [Cu(FPEN)L]<sup>+</sup> (L=Br, I) [9]. However, it is difficult to say the types of distorted geometry these chelates will adopt without ray crystallographic study. It may be mentioned that bromo methoxy-compound, [Cu (FPEN, ROH) Br]. ClO<sub>4</sub>, has been shown to have the five co-ordinated structure by a single crystal three dimensional X-ray structure determination [12] however the structure of this compound is grossly distorted from either of the regular five co-ordinated geometries. Such into intermediate geometry appears to be quite common feature of five coordinated metal-chelate complexes [13]. The analogous structure may be proposed for the present copper (II) Chelates [Cu(L)]ClO<sub>4</sub>.

The Copper (II) complexes Cu(L)(ClO<sub>4</sub>)<sub>2</sub> (Table-1) show a single relatively sharp absorption band in the spectra of these chelation at ~16500 cm<sup>-1</sup> (Table-3) which closely resembles that in the tetramine copper (II) compounds, which have a tetragonal (4+2) geometry, perchlorate ion in these chelates are found to be ionic (infra-red data, very slightly split bond around 1000-1150 cm<sup>-1</sup>) Accordingly, these compounds are tentatively assigned on essentially square planar four coordinate geometry, with the usual implied reservations about weak interactions from other ligands, such as the perchlorate or the solvent molecule in the remaining tetragonal sites. However, we are not sure about the conformations of the neutral tetradentate Schiff base ligands in these chelates.

Nickel (II) complexes: They are stable in air and the analytical data (Table-1) reveal a 1:1 ration of Schiff base ligand to metal salt for all of the complexes.

The molar conductivity values (Table-2) support 2:1 electrolytic nature of Ni(L)X<sub>2</sub>. nH<sub>2</sub>O complexes in water. On the other hand, these chelates behaves as 1:1 electrolytic in EtOH (Table-2). The deduction of electrolyte type was made by comparing the observed molar conductivities values reported for various salt at similar concentration [10], and for various complex ions [16]. The magnetic moments of the Nickel (II) complexes (Table-2) fall within the range 3.09-3.30 B.M. reported for octahedral complexes of Nickel (II) [11].

The IR spectra of the present ligand system and their Nickel (II) and Copper (II) complexes exhibit bands typical of 2-substituted pyridines [11, 12]. These pyridine bands are the four ring stretching vibration in the range 1610-1435 cm<sup>-1</sup>, the ring breathing vibration around ~1000 cm<sup>-1</sup> (mixed up with ClO<sub>4</sub><sup>-</sup> vibrations in some copper (II) chelates), and the out of plane C-H deformation around 790 cm<sup>-1</sup>. The C=N stretching vibrations observed at 1650-1540 cm<sup>-1</sup> position and assignment of these bands are in agreement with those reported [6, 11], for FPEN and N-methy pyridine-2-carboxalimine. The characteristics change observed in pyridine vibrations of the ligands together with the absence of splitting in the ring stretching modes indicates that both the pyridine moieties are coordinated in all the complexes. Further the presence of C=N stretching bonds in the chelates, together with the absence of NH and C=O bonds (arising as a result of the partial or complete hydrolysis of the C=N bond) support the Schiff base nature of the ligands.

The OH stretching bonds in the complexes of FPTNOL and APTNOL and also in the complex (IX) observed for the nitrite and thiocyanate complexes along with tentative assignments are given in (Table-4). The assignments were made by comparison to the extensive literature data for nitrite [12] and thiocyanate complexes. From the stretching frequency assignment (Table-4) the presence of oxygen-bonded NO<sub>2</sub> group in [Ni (FPTN) (ONO)<sub>2</sub>(X) and [Ni



(APTNO<sub>L</sub>)](ONO)<sub>2</sub>(XV) may be infrared. The IR frequencies observed for (X) are similar to the values reported for trans [Ni(Py)<sub>4</sub>(ONO)<sub>2</sub>] and the analogous picoline complexes. We are unable to explain the splitting of NO<sub>2</sub> absorption band observed in (XV). No bands were found for this complex, which would be ascribed to the presence of non-bonded NO<sub>2</sub> group [14], which would be present for both bridging and chelating nitrite ions [5, 14].

The assignment C-S stretching and NCS bonding vibration in Ni (FPTNO<sub>L</sub>)(NCS)<sub>2</sub> (XII) Table-4 suggest and bonded thiocyanate group in this chelate. Again the splitting of the thio cyanate bond is not clear to us, although it could be due to the present of both bridging and non bonded thiocyanate or to the presence of Cis-, N-bonded thio cyanate ion [18].

The detailed electronic absorption bands for the Nickel (II) chelates are set out in (Table-3), while (Table-5) indicates the bands in 9000-20000 cm<sup>-1</sup> range along with their assignments. The higher energy bands are not assigned as they may be due to various transitions eg. red-shifted anion transition [13], charge transfer transitions, ligand-transition and Nickel (II) transition. The band in the 900-20000 cm<sup>-1</sup> range are very weak (ε ~10) and has been assigned to Nickel (II) d-d<sup>1</sup> transitions in terms of octahedral or tetragonal configuration [12, 14]. The nujolmull and solution spectra the Nickel (II) complexes in the near IR spectra and visible region consists of two principal band γ<sub>1</sub> and γ<sub>2</sub> (Table-5).

Splitting of the parent octahedral transition <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>2g</sub> into <sup>5</sup>B<sub>1g</sub> → <sup>3</sup>B<sub>2g</sub> (function of in-plane donor strength) and <sup>3</sup>B<sub>1g</sub> → <sup>3</sup>E<sub>g</sub> (function of the axial donor strength) depends on the strengths of the equatorial and axial ligands. For a series of a complexes in which only the weaker axial donor and varied, the energy of the in-plans transition should remain roughly constant, while the energy of the axial transition decreasing in going poorer axial donors [4, 15]. For in plane an axial ligands of comparable donor strength, the separation of the tetragonal levels becomes too small to be observed. Although the no. of Nickel (II) bands observed in the nujolmull spectra of the present chloro- complexes is too low to permit detailed analysis, a tentative assignment can be made using this tetragonal crystals field model assuming D<sub>4h</sub> local symmetry (However, the actual asymmetry may be C<sub>2</sub> or lower). The lowest energy component corresponds to the axial <sup>3</sup>B<sub>1g</sub> → <sup>3</sup>E<sub>g</sub> transition and the remaining more instance higher energy component to the in-plane <sup>3</sup>B<sub>1g</sub> → <sup>3</sup>B<sub>2g</sub>

transition.

For the nitro and thiocyanate complexes γ<sub>1</sub> and γ<sub>2</sub> may be assign to be <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>2g</sub> and <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub> (F) transition of octahedral Nickel (II) and the shoulder observed on γ<sub>1</sub> to the spin-forbidden <sup>3</sup>A<sub>2g</sub> → <sup>1</sup>E<sub>g</sub> transition. The apparent lack of tetragonal splitting in γ<sub>1</sub> can be ascribed to the smaller difference between the planar and axial ligand field strengths [5, 15].

The spectra of the present Nickel (II) chelates are all approximate identical in aqueous solutions (Table-5). All of the Ni(L)X<sub>2</sub> complexes are formulated as 2:1 electrolytes in aqueous solution (Table-2). From this observations a common species in water may be formulated as [Ni(L)(H<sub>2</sub>O)<sub>2</sub>]<sup>+2</sup> and

them the splitting of γ<sub>1</sub> bond (Table-5) may be explained as discussed above. The weak shoulder 13500 cm<sup>-1</sup> is assign to a spin forbidden transitions. It has also been observed that the

splitting in γ<sub>1</sub> bond is almost suppressed when the spectra of the aqueous solution are taken in presence of few 'ml' of pyridine. This reflects other comparable donor strength of axial pyridine and the in-plane nitrogen ligands.

<sup>1</sup>H and <sup>13</sup>C-NMR spectral data for all ligands at room temperature 25 °C were determined by dissolved in DMSO-d<sub>6</sub> (Table-6). The <sup>1</sup>H N.M.R. spectra of the ligands exhibit singlet signal in the 10.8-12.0 ppm range which may be attributed to the OH group proton. The NH and OH proton can be identify easily become they disappear upon D<sub>2</sub>O exchange. In like manner all ligands shown peak due to the pyridine, OH, C=N linkage, methylene, methoxy and amine groups approximately in the expected regions. The <sup>1</sup>H N.M.R. spectrum of the APTN APTNO<sub>L</sub> ligands exhibit a strong singlet at 3.70 and 3.86 attributed to the C-Me group protons. Also in FPTN and FPTNO<sub>L</sub> ligands the singlet observed at 1.4 ppm can be assign to the proton of the t-Bu group. The <sup>13</sup>C-NMR spectra of the ligand exhibit signals in 162.7-164.5 ppm range can be assigned to the C=N group carbon atom (Table-5). The signals due to the carbon atom of the amino propane & pyridine a ring is observed in the 104-158.3 ppm range. The C-atom link with me group lie in the 55.2-56.1 ppm range. The single at 30.4-33.0 ppm due to the C-atom of the propane and t-Bu. group. The quarternary C-atom in the t-Butyl group is observed at 36.0 ppm.

**Table 6:** The <sup>1</sup>H (<sup>13</sup>C) n.m.n. spectral data of the Schiff base ligands compound. Chemical Shift (δ, ppm)

	CH=N	Ph	Py	OH	NH	CMe	CH <sub>2</sub>	NMe <sub>2</sub>	t-BuMe	Quat.C
(FPTN)	8.6 (162.7)	6.2- 7.2 (a)	7.4- 8.0 (a)	11.5- 108	56	3.8 (55.5-56.1)	2.5 (58.7)			
(FPTNO <sub>L</sub> )	8.5 (164.5)	7.6 (a)	7.4- 7.9 (a)	11.4	5.3	3.7 (56.1)	2.6 (60.7)		1.4 (33.0)	30.4
(APTN)	8.8 (164.0)	7.2 (a)	7.3- 8.2 (a)	11.2- 12.0	5.2	3.70 (55.2)	2-4 (58.5)	3.41 (30.4)	1.4 (33.0)	36.0
(APTNO <sub>L</sub> )	8.7 (163.2)	7.3 (a)	7.3- 8.0 (a)	11.0- 11.9	5.1	3.86 (56.4)	2.4 (57.9)	3.46 (32.4)		

<sup>a</sup>The <sup>13</sup>C n.m.n. data of the 1, 3 diaminopropane-2 ol, 2 formyl pyridine and 2 acetyl pyridine of the ligands are observed at 104-152.5 ppm range for L<sup>1</sup>, 110-155.7 ppm range for L<sup>2</sup>, 104.7-158.3 ppm range for L<sup>3</sup> and 104-157.4 ppm range for L<sup>4</sup>, solvent CDCl<sub>3</sub>

**Table 7:** Mass special data of Schiff base ligand and its

S. N.	Compound	Cal mas	Observed mass	Peak
1.	FPTN L <sup>1</sup>	178	178	M
2.	FPTNO <sub>L</sub>	179	179	M
3.	APTN	192	192	M
4.	APTNO <sub>N</sub>	193	193	M
5.	Cu(FPTN)(ClO <sub>4</sub> ) <sub>2</sub>	440	441	M+1
6.	[Cu(FPTN) I] ClO <sub>4</sub>	468	469	M+1

7.	Ni(FPTN)(H <sub>2</sub> O)	325	327	M+2
8.	[Ni(FPTN)(NO <sub>2</sub> ) <sub>2</sub> ]	328.7	330	M+1
9.	Cu(FPTNOL)(ClO <sub>4</sub> ) <sub>2</sub>	440.5	442	M+1
10.	Ni (FPTNOL) Cl <sub>2</sub>	307.7	310	M+2

The mass spectrum data of Schiff base ligand and its metal chelates are given table 7. Mass spectral if the ligand and its metal complexes showed molecular ion peaks, which were in good agreement for expected values. The mass spectra of ligands give some peaks at 178 m/z, 179 m/z, 192 m/z and 193 m/z, respectively which were assigned for [HL] peak.

Copper and Nickel complex give same peak at 441, 469 and 442 m/z which assign as M+1 peak, in all cases while mass spectrum of Ni (ii) complex showed peaks at 327, 330 and 310 m/z which assign for M+1, M+1 and M+2 peaks respectively.

**Table 8:** Antimicrobial effects of the ligand and their complexes Microorganism (Inhibition zone)

Compound	<i>S. Crevial</i>	<i>B. subtilis</i>	<i>E. coli</i>	<i>K Pneumonia</i>	<i>M. luteus</i>	control
(FPTN)	18	32	22	27	21	-
Cu(FPTN)ClO <sub>4</sub>	-	11	-	9	10	-
Ni (FPTN) Cl <sub>2</sub> .H <sub>2</sub> O	-	9	+4	8	8	-
(FPTNOL)	-	15	13	11	16	-
Cu(FPTNOL)(ClO <sub>4</sub> ) <sub>2</sub>	10	11	9	10	-	-
Ni(FPTNOL)(NCS)	-	-	-	9	8	-
(APTN)	19	12	24	21	19	-
Cu(APTN)(ClO <sub>4</sub> ) <sub>2</sub>	-	-	14	14	19	-
Ni(APTN)(NO <sub>2</sub> ) <sub>2</sub>	-	10	11	10	11	-
(APTNOL)	9	11	10	11	10	-
[Cu(APTNOL)I](ClO <sub>4</sub> )	-	-	6	8	7	-
Ni(APTNOL)(NO <sub>2</sub> ) <sub>2</sub>	-	-	6	8	7	-

<sup>a</sup>concern=100µg/disc<sup>b</sup> Including disc diameter (6 mm)

The symbol '-' reveal that the compound have not any activity against to the microorganism.

Antimicrobial activities of the Schiff base ligands and their metal complexes against bacteria and yeast are recorded in Table-8. In this study one of the striking features is that while FPTN, APTN and APTNOL and the Copper (II) complexes FPTNOL have activity against *Saccharomyces cerevisiae*, the FPTN and other compounds have no such activity against the same organism. It is apparent that the FPTN, APTN and APTNOL ligands containing two free hydroxyl groups are more active than the FPTNOL ligand containing one hydroxyl group. Since the hydroxyl group substituent is known to increase the activity of compounds [11, 16]. We have shown that the activity decreased on undergoing complex action, since, chelation reduces that partial sharing of its position charge with the oxygen atom of the free hydroxyl group and nitrogen atom of the -C=N group some complexes are not showing activity against bacteria and yeast, are not mentioned in the Table-6.

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