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Characterization, synthesis, X-ray and thermal studies of some Schiff base of Ni (II) and Cu (II) transition metal complexes

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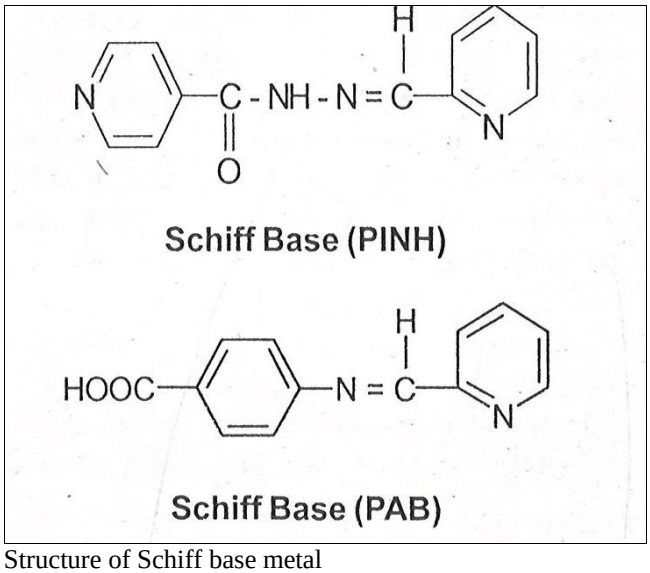
Abstract
New bi-and tridentate Schiff bases have been synthesized by condensing 2-pyridine carboxaldehyde with isonicotinic acid hydrazide and 4-amino benzoic acid. The 1:1 or 1:2 metal complexes were obtained as a result of interaction of ligand and the metal ions: Ni (II) and Cu (II). The complexes have been characterized and studied by elemental analysis, molar conductance, electronic spectra, IR, ESR spectroscopy and FAB mass. Thermal data show degradation pattern of the complexes. The complexes are colored and stable. The ligand Schiff base exhibit bitridentate nature, coordinating through N.O donor atoms. The reactivity and substitution behavior of the synthesized complexes have been studied. The crystal system lattice parameters, unit cell volume and number of molecules in unit cell of [Ni (PINH) (H_2O)] Cl, complexes have been determined by XRD, this complex crystallizes as tetragonal system.

Keywords: Transition metal, Schiff base, spectroscopic techniques, thermal study, XRD

Introduction
Schiff bases are an important class of ligands in coordination chemistry [1]. A large number of Schiff bases and their metal complexes have been found to possess important biological and catalytic activity [2-3], Due to their great flexibility and diverse structural aspects, a wide range of Schiff bases have been synthesized and their complexation behavior was studied [4]. The coordination complexes of hydrazones are of great interest due to their novel structural features, unusual magnetic properties and relevance to biological processes [5-6] Schiff base metal complexes of hydrazones have their utility as antiamoebic agents [7-10], Isonicotinic acid hydrazide has been one of the most effective anti tubercular agents since 1952 [11]. Pyridine derivative play important role in many bio-chemical reactions. 2-pyridine carboxaldehyde has been found involved in enzyme reactions as medicine [12-13].



Structure of Schiff base metal

Materials and Methods
All chemicals and solvents were used in grade. Elemental analysis and FAB mass were done at CDRI (Central Drug Research Institute), Lucknow. Electronic spectra (in MeOH) were recorded on Perkin-Elmer lambda-2B-spectrophotometer. Molar conductance (10^{-3}M) was measured on Elico Conductivity Bridge at room temperature. FT-IR (in KBr) spectra were recorded at SAIF (Sophisticated Analytical Instrumentation Facility), CDRI (Central Drug Research Institute), Lucknow and Chandigarh. ESR spectra were recorded at 1.1.T. (Indian Institute of Technology) Mumbal. TGA was carried out under nitrogen atmosphere with a heating rate 20°C min^{-1} on Mettler Toledo Star Thermal Analyzer at NIPER (National Institute of Pharmaceutical Education and Research) Chandigarh. X-ray spectra were recorded at SAIF (Sophisticated Analytical Instrumentation Facility). R.T.M (Rastriya Santa Tukajirao Maharaj) Nagpur University, Nagpur.Two Schiff bases (PINH, PAB) have been synthesized by adding 50ml methanolic solution of 2-pyridine carboxaldehyde (0.06 mole) with 50ml methanolic solution of isonicotinic acid hydrazide 4-amino benzoic acid (0.06 mole) in equimolar ratio. The reaction mixture was then refluxed on a water bath for 6hrs. The condensation product was filtered, thoroughly washed with ethanol and ether, recrystallized with ethanol and dried under the reduced pressure over anhydrous $CaCl_2$, the purity of the synthesized compounds was monitored by TLC using silica gel *G*. The metal complexes have been prepared by mixing the (50ml) methanolic solution of respective metal salt [$MCI_2.nH_2O$] (where M=Ni (II), Cu (II)) with the (50ml) methanolic solution of Schiff bases (PINH, PAB) in 1:1 or 1:2 metal ligand ratio. The resulting mixture was refluxed on water bath for 8 hrs. A colored product appeared on standing and cooling the refluxate. The precipitated complex was filtered and washed with ether. The complexes were recrystallized twice with ethanol, washed with ether and dried under the reduced pressure over anhydrous $CaCl_2$ in dessicator.

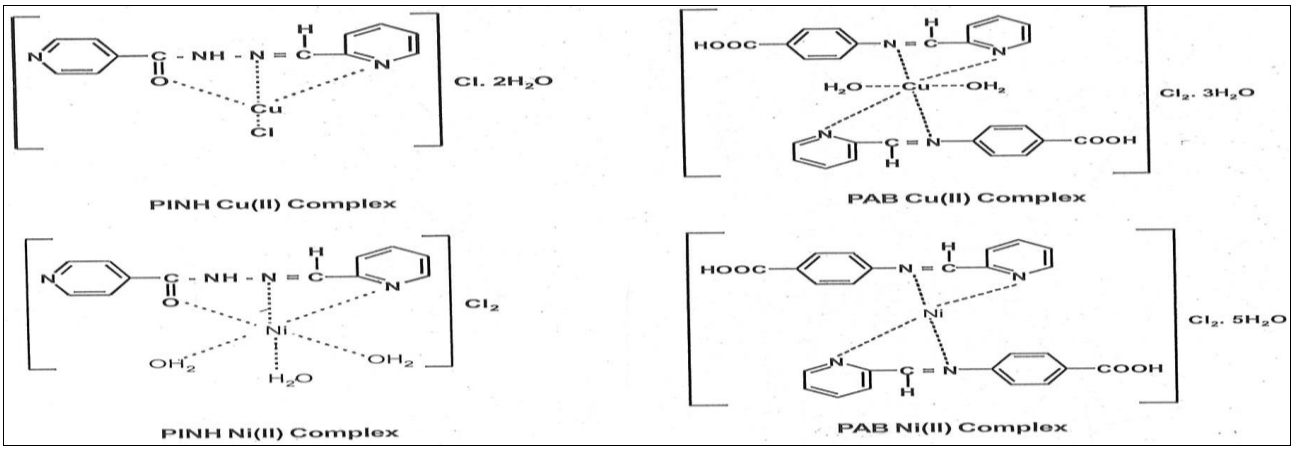
Table-1: Analytical and physical data of ligand and metal complexes.

Compound	color	M. P. (dec)^{0}C	Elemental Analysis found/(cal)%			Conductane Ohm^1 cm^2 mol-1	Yield %
			C	H	N		
PINH 226.0	white	160	63.61 (63.71)	4.31 (4.42)	24.62 (24.77)	-	85
$[Ni(PINH)(H_2O)_3CL_2$ 409.7	Parrot Green	200	35.20 (35.14)	3.45 (3.90)	14.76 (14.12)	123.8	83
$[Cu(PINH)Cl.2H_2O$ 396.5	Green	270	36.41 (36.31)	3.25 (3.53)	14.76 (14.12)	65.0	80
PAB 226.0	Light Green	220	69.20 (69.00)	4.11 (4.42)	12.31 (12.38)	-	94
$[Ni(PAB)_2]Cl_2.5H_2O$	Yellow	270	46.42 (46.44)	4.32 (4.46)	7.96 (8.33)	80.5	85
$[Cu(PAB)_2(H_2O)_2]Cl_2.3H_2O$ 676.5	Green	110	46.40 (46.11)	4.35 (4.43)	7.91 (8.27)	76.0	82

Results and Discussion

All the metal complexes are colored, solid, stable towards air and moisture at room temperature. They decompose on heating at high temperature and more or less soluble in common organic solvents. The analytical data of the complexes are consistant with proposed molecular formula shown in Table-1. The metal complexes exhibit 1:1 or 1:2 (metal-ligand) stoichiometry. The IR- spectra of the complexes were compared with those of the free ligand in order to determine the involvement of coordination sites in chelation. Characteristic peaks in the spectra of the ligand and complexes were considered and compared [14], IR spectrum of the PINH ligand exhibit bands at 3293 cm^{-1} due to UN-H stretching frequency. A strong absorption band appearing at 1666 cm (C = 0 amide 1) in ligand (Schiff base) has shifted to lower side by 25-30 cm^{-1} in the complexes. This indicates the involvement of C=O group in coordination. A band at about 1630 cm^{-1} due to $u_{c=n}$ (azomethine) group in ligand shift down by 25-30 cm^{-1} due to u_c = N in the complexes. This suggests coordination of nitrogen to metal atom due to donation of electron density from nitrogen to metal d-orbitals. Pyridine ring shows absorption band at 1463 and 1065cm^{-1} in the ligand spectrum. These band show positive, (1481± 10 cm^{-1} and 1078±10 cm^{-1} in the complexes suggesting participation of nitrogen in complexation. The broad band around 3455±10 cm^{-1} in the spectra of complex may be due to $U_{str\ (OH)}$. A medium intensity band at 680 cm^{-1} suggests the presence of coordinated water in Ni (II) complex. This band has been found absent in the Cu (II) complex. The new bands at 510±10 and 490±10 cm^{-1} have been assigned to υM-O and υM-N modes, respectively [15-20] .IR Spectrum of PAB ligand show a strong band at 1700 cm^{-1} due to C=O (carboxylic acid group) which practically remains unchanged in the spectra of complexes. The free ligand band of medium intensity at 1628 cm^{-1} is assignable to $u_{c=n}$ (azomethine group). This has shifted to lower wave number (1610±10) cm^{-1} in the spectra of complexes. This indicates the involvement of azomethine nitrogen in coordination with metal ion. The pyridine ring vibration (1476 and 1009 cm^{-1}) in the ligand has shifted to higher frequency by 10-15 cm^{-1} in the complexes. This indicates participation of pyridine ring nitrogen on coordination with the metal atom in both the complexes. The band around 3460 cm^{-1} in the spectra of complexes is due to $U_{str\ (OH)}$A medium intensity band at 647 cm^{-1} suggest the presence of coordinated water in the Cu (II) complex. This band is absent in the Ni (II) complex.

The new bands at 585±10 cm^{-1} and 475±10 cm^{-1} in the complexes have been assigned to υM-O and υM-N vibration [17,19-20].



Structure of Schiff bases metal complexes

The nature of the ligand field around the metal ion and the geometry of the complexes have been deduced from the electronic spectra. The electronic absorption spectra of the complexes were recorded at room temperature using methanol as solvent.

The electronic spectrum of Ni (II)-PINH complex show three bands at 12376, 22276 and 26720 cm^{-1} corresponding to transitions ^3A_2g (F) - ^3T_2g (F)(υ_1),^3A_2g(F)-^3T_1g(F)(υ_2),) and ^3A_2g(F)-^3T_1g(P)(υ_2) respectively The value of various ligand field parameters, 10Dq, B, β, υ_2/υ_1, and LFSE are as

12376, 791.2, 0.73, 1.79,(-)273cm^{-1} and 177.4 kJ mol^{-1} respectively. The magnetic moment of this complex is 3.08 B.M. These finding are in favor of an octahedral geometry for the Ni (II) complex.

Cu (II)-PINH complex gives one band at 13513 cm^{-1}, which is assignable to ^2B_1g - ^2B_2g transition. The magnetic moment value for is 1.83 B.M. This favors the square planar VIgeometry.

The electronic spectrum of Ni (II)-PAB complex one band at 12610 cm^{-1} assignable ^1A_1g - ^1Eg transition. Since the complex is diamagnetic square planar geometry has been suggested.

The Cu (II)-PAB complex exhibit band at 12559 cm^{-1}. This has been assigned to ^2Eg- ^2T_2g transition. The value of ligand field parameters *viz* 10Dq. λ. LFSE are as 12559, (-) 435 cm^{-1} and 90.02 kJ mol^{-1} respectively. Its magnetic moment is 1.85 B.M. Thus, octahedral geometry has been suggested for this complex [21-22]. Solution of the complexes was made in methanol to check the reactivity and substitution behavior against hydroxy, aquo, amine, chloro and thiocyanato ligand. The reactions were monitored by observing change in color or precipitation [21-22].

PINH-Ni (II) complex does not react with dil HCl on keeping for 1 hr at room temperature while PINH-Cu (II), PAB-Ni (II), Cu (II) complexes react rapidly under the similar conditions. All the three complexes react well on heating except PINH-Ni (II) complex. PAB-Ni (II) complex also does not react with NaOH at room temperature. But PAB-Cu (II) and PINH-Cu (II) and Ni (II) complexes react quickly at room temperature. All the three complexes react well on heating except PAB-Ni (II) complex. All the four complexes however, react rapidly on adding slight amount of NH_4OH at room temperature. Further they react well on heating KSCN does not react with PAB-Ni (II) complex on keeping for 1 hr at room temperature. But PAB-Cu (II), PINH-Cu(W) Ni (11) complexes react quickly under the similar conditions All the complexes react appreciably on heating Nevertheless, PAB-Ni (II), Cu (II) and PINH-Ni (II) complexes were found to react with water rapidly at room temperature but PINH-Cu (II) complex does not react with water under the similar conditions. All the three complexes react well on heating except PINH-Cu (II) complex. Similarly, PAB-Ni (II) complex does not react with thiourea on keeping for 1 hour at room temperature, while PAB-Cu (II) and PINH-Cu (II) react fast at room temperature. All the complexes react appreciably on heating [24-25.27].

The FAB mass spectrum of Ni $(PAB)_2]$ $Cl_2.5H_2O$ complex has been studied as one of the representative cases. The peaks of appreciable intensity have been observed at m/z value 676, 652, 599, 545, 510, 279, 226, and 89 suggesting the fragmentation pattem. The m/z value 676 corresponds to nearest composition [Ni $(PAB)_2]Cl_2$ $5H_2O$;652 [Ni$(PAB)_2]$ $Cl_2.4H_2O$; 599 to [Ni$(PAB)_2]$ $Cl_2.H_2O$: 545 to [Ni$(PAB)_2]$ Cl; 510 to [Ni$(PAB)_2]$; 279 to [Ni$(PAB)_2]$ 226 to ligand alone and 89 to some chelated ligand moiety as also reported elsewhere[23-24].

X-ray powder diffractogram of only one complex [N](P|NH) $(H_2O)]Cl_2$ was recorded using Cuka in the range 50.99 (20) X-ray crystal system has been worked out by trial and error method, for finding the best fit between observed and calculated Sin^20 values. The crystal system, lattice parameters, unite cell volume and number of molecules in unit cell have been determined with the help of diffraction data. Crystal data for [Ni (PINH) $(H_2O)]$ Cl_2 are as a = b = 13.3103A^{0,} c=35.6441A^0 and v=6314.88A^{0,} ^{Dobs} =1.4003g cm^{-3}. D_{cal} =1.4315 g cm^3 Z = 13, this reflects that this comlpex has crystallized in tetragonal system [24-25].

The ESR spectra of Cu (II) provide information about the extent of the delocalization of unpaired electron. ESR spectra of both the Cu (II) complexes have been recorded on x-band and their mathfrak g II g1, Δg A g_{av}. and G values been calculated. The values of ESR parameters for PINH Cu (II) complex are gII g1, Δg gav and G, 2.2057, 2.1198, 2.1484, 0.0859 and 1.7294 respectively. Similarly, the corresponding values for PAB-Cu (II) complex are 2.1909 2.1061, 2.1344, 0.0848 and 1.8143 (Table-2). ESR spectra of the complexes revealed two g values9(gII and g_1). The trend, gII>g_1 shows that the electron is delocalised in dx^2 - y^2 orbital in the ground state of Cu (II) and spectra characteristic of axial symmetry. The gII > 2.3 is characteristic of an ionic environment and gII > 2.3 indicates a covalent environment in metal-ligand bonding. In the present compounds gII indicate the prevalence of covalent character in metal- ligand bond. The G values are less than 4 (G < 4), suggests the strong- field nature of the ligand [27-29].

Table-2: Electronic Spin Resonance Parameters of the Cu (II) complex.

Metal Complex	g_{II}	g1	g_{av}	G	Δg
Cu (II) PINH complex	2.2057	2.1198	2.1484	1.7294	0.0859
Cu (II) PAB complex	2.1909	2.1061	2.1344	1.8143	0.0848

The nonisothermal heating of the complex [Cu $(CH_{12}H_{10}N_4O)$ Cl]CI.$2H_2O$ show that its thermal degradation starts at 60^0. Pyrolysis curve shows that two water molecules from lattice come out between 60-130 ^{0}C temperature, (Remaining wt.% obs/cal. 96/90.93) The complex does not show any loss in weight between 130 - 210 ^{0}C After 220 ^{0}C a loss in weight has been observed in general up to 330 ^{0}C corresponding to the loss of partially decomposed ligand part from the complex. (Remaining wt.% obs/cal. 41/37.96) Above 330^{0}C an inflection occurs in the curve and loss in weight goes up to 470^{0}C This indicates the elimination of the remaining 1 thermally degradable part of the complex. Above this temperature, the curve shows a constant weight region which may be due to metal oxide as an ultimate pyrolysis product (Remaining wt.% obs/cal. 29.0/25.35) [30-31]

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