

Synthesis and Characterization of New Complexes of Co^{+2} , Ni^{+2} and Cu^{+2} with Schiff Base Ligand

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ABSTRACT

New α -(2-pyridyl)benzylidene (5-nitropyrid-2-yl)amine (L) ligand has been synthesized by condensation of 2-benzoyl pyridine and 2-amino-5-nitro pyridine in 1:1 molar ratio in ethanol. Further the Co^{+2} , Ni^{+2} and Cu^{+2} complexes were synthesized by reacting above ligand with metal chloride in (1:1) (1:2) or (2:2) (Ligand:metal) molar ratio in ethanolic medium. The ligand and their complexes were characterized by electronic and IR spectra, magnetic susceptibility measurements, molar conductance and metal content analysis. The complexes (1-3) and (7-9) are found to be non ionic in nature while the complexes (4-6) are found to be (1:2) electrolyte. The magnetic moment and electronic spectral studies show a tetrahedral geometries for the complexes (1-6) and octahedral geometries for the rest of the complexes.

Keywords: 2-amino-5-nitro pyridine, 2-benzoyl pyridine.

Cu^{+2}	Ni^{+2}	Co^{+2}
-2	(-2- -5)	(-2)-
(1:1)	(1:1)	-5- -2
		Cu^{+2} Ni^{+2} Co^{+2}
		(2:2) (1:2)
(4-6)		(1:2)
		(6-1)
	-2	-5- -2 :

INTRODUCTION

Schiff base ligands are excellent coordinating ligands. During the past three decades, a considerable attention has been paid to the chemistry of the complexes of the Schiff bases containing nitrogen and other donor atoms. This may be attributed to their stability, biological activity and potential applications in many fields, such as oxidation catalysis and electrochemistry making the behavior of Schiff base complexes with transition metals a worth of research topic (Yamada,1999; Gaber *et al.*,1989; Thaker *et al.*, 2005; Khaddar *et al.*, 2005).

Complexes of nickel (II) with N,N'-disalicylidene-3,4-diamino- toluene (H_2L^1), N,N'-bis(3,5-di-t-butyl salicylidene)-1,3-diaminopropane (H_2L^2), tetrathiaflavalene-N,N'-phenylene bis (salicylideneimine) (H_2L^3) and 1-phenylbutan-1,3-dione mono 5-methyl isothiosemicarbazone with 5-phenylazo-2-hydroxybenzaldehyde (H_2L^4) have been synthesized and characterized by elemental analysis, electronic, IR,¹HNMR spectra, magnetic susceptibility and molar conductance measurements by Prakash *et al.*, (2011). These studies show tetrahedral and octahedral geometries of the complexes.

The conformationally rigid nickel (II)-based cationic molecular square of the type $[Ni(HL)]_4^{+4}$ and copper (II) based neutral molecular rectangle $[Cu_2LCl_2]_2$ were achieved via self-assembly from novel rigid pentadentate N_4S ligand bis{phenyl(2-pyridyl)methanone}thio-carbazone (H_2L). Crystal structure analyses show that the tetranuclear nickel (II) cation $[Ni(HL)]_4^{+4}$ is located at the inversion center with four nickel atoms in the corners of square of each metal center being octahedrally coordinated by sulfur,pyridine nitrogen and carbazone nitrogen atom from two perpendicular HL- ligands (Cheng *et al.*, 2000).

An efficient method was developed to prepare series of zinc-Schiff base complexes. Introduction of pyridyl group as bridging unit as well as incorporation of ethynyl and electron donating group. The salicylidene moiety in these complexes moderately enhances the photoluminescence intensity and the quantum yield. The crystal structure of the pyridine adduct of a salen Zn complex is determined by X-ray diffraction analysis (Chang *et al.*, 2004).

The one step synthesis of Schiff base macrocyclic complexes bearing a primary amino group in the pendant arm via a template condensation between diacetyl pyridine and tripodal aliphatic tetramines. The resulting complexes, however experience, have a significant steric strain due to an imperfect match the rigid, planar, conjugated bis-iminepyridine fragment and the incorporated 3d-metal ion, were demonstrated by X-ray data and molecular mechanics calculations, (Herrera *et al.*, 2003).

Transition metal complexes of Cr(III), Fe(III), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with a tridentate ligand. (4-hydroxy-4-methyl-2-pentanone-1H-benzimidazole-2-yl-hydrazone (H-HpBH) derived from condensation of 2-hydrazino benzimidazole and diacetone alcohol) were synthesized. Characterization has been done on the basis of analytical, conductance, thermal magnetic data, infrared, ¹HNMR, electronic, mass and ESR spectral data. Divalent complexes of the general formula $[M(HpBH)Cl(H_2O)_2]$ in octahedral geometry, $[M(HpBH)Cl]$ in tetrahedral and square planar stereochemistry and trivalent complexes $[M(HpBH)Cl_2(H_2O)]$ in octahedral disposition was studied by Neelama *et al.*, 2011.

THE EXPERIMENT

All chemicals were A.R grade. Solvents were dried over an appropriate reagent and distilled prior to use.

Physical measurements

The IR spectra were recorded on Bruker Tensor 27CO FTIR spectrophotometer in the 4000-200 cm^{-1} range using CsI disc. Electronic spectra were recorded on Shimadzu UV 160 spectrophotometer for 10^{-3} M solution of complexes in dimethyl sulfoxide DMSO using 1cm quartz cell. Conductivity measurements were made on conductivity meter 4070 Jenway for 10^{-3} M solution of the complexes using DMSO. The magnetic measurements were carried out at 25°C on the solid state by Faraday's method using Burker BM6 instrument. Melting point or decomposition temperatures were recorded on a Buchi 510 melting point apparatus and were uncorrected. The metal content was estimated spectrophotometrically using Shimadzu atomic absorption 670 AA.

Preparation of the ligand(L).

To a solution of 2-benzoylpyridine (1.83 g, 0.01 mol) in absolute ethanol (10 ml) a solution of 2-amino-5-nitropyridine (1.39 g, 0.01 mol) in absolute ethanol (10 ml) was added dropwise. After the addition was completed, the mixture was boiled under reflux for 2h. The solid creamy product formed on cooling was filtered off, washed with ethanol and diethylether, then dried under vacuum over P_2O_5 .

Preparation of $[\text{MLCl}_2]$ and $[\text{M}(\text{L})_2]\text{Cl}_2$ complexes: M= Co(II), Ni(II), Cu(II)

These complexes were prepared according to the following general procedure. To a solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.24g, 0.001 mol) or $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.24g, 0.001 mol), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.17g, 0.001 mol) in ethanol (10 ml), a solution of the ligand (1 or 2 mmol) in ethanol was added. The mixture was stirred under reflux for 2hs. The solid thus obtained was filtered off, washed with ethanol and diethylether then dried under vacuum for several hours.

Preparation of $[\text{M}_2(\text{L})_2\text{Cl}_4(\text{H}_2\text{O})_2]$ complexes

A solution of the ligand (0.60g, 2mmol) in ethanol (10ml) was treated with a solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.48g, 2mmol) or $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.48g, 2mmol), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.34 g, 2 mmol) in ethanol (10 ml). The reaction mixture was refluxed for 3hs. The completion of the reaction was checked by TLC. The solution was concentrated to about 5ml. The complexes were precipitated, filtered off, washed with ethanol and diethylether, then dried under vacuum for several hours.

RESULTS AND DISCUSSION

The resulting Schiff base and their Co(II), Ni(II) and Cu(II) complexes are colored and soluble in DMF and DMSO. They have sharp melting points or decomposition temperatures, stable at room temperature and are non-hygroscopic. The compounds are pure as both ligand and complexes moves as a single spot indicating the presence of one component and hence their purity. The analytical data (Table 1) of the metal complexes show that the metal chelates have 1:1, 1:2 or 2:2 metal to ligand stoichiometry. Conductance measurements were carried out to ascertain the electrolytic nature of metal complexes.

Molar conductance values of the complexes in 0.001 M DMSO solution suggest their non-electrolytic nature (Geary 1971), except for the complexes (4-6) which are (1:2) electrolyte.

The infrared spectrum of the ligand shows strong bands located at 1629 and 1572 cm^{-1} assigned to $\nu(\text{C}=\text{N})$ (exo) and $\nu(\text{C}=\text{N})$ (ring) respectively.

The IR spectra of all complexes show a positive shift of $\nu(\text{C}=\text{N})$ (exo) (7-12) and a negative shift of $\nu(\text{C}=\text{N})$ (ring) by (8-25) cm^{-1} which suggest the involvement of azomethine nitrogen as well as the azothemine nitrogen ring in the coordination (Neelamma *et al.*, 2011).

The far IR spectra of all the metal chelates contain non ligand bands around 290-340 cm^{-1} and these are assigned to $\nu(\text{M}-\text{Cl})$. The spectra of all complexes show non-ligand bands in the region 400-500 cm^{-1} . This was assigned to $\nu(\text{M}-\text{N})$ band (Nasari *et al.*, 2009).

The IR spectra of the complexes show absorption bands of the coordinated water at 3411 and 870, 670 cm^{-1} for wagging and rocking vibration of H_2O and a new band at 561 signed to $\nu(\text{M}-\text{O})$.

The magnetic properties of the complexes provide valuable information for distinguishing their stereochemistry. The magnetic moment of Co(II) complexes (1, 4 and 7). The $3d^7$ system showed an effective magnetic moments of (4.33, 4.48 and 5.44)B.M. confirming tetrahedral geometries for complexes (1, 4) and octahedral geometry for complex (7). The magnetic moments of Ni(II) complexes (2,5 and 8) were found to be (3.6, 3.53 and 2.9) B.M. which suggest tetrahedral geometries for complexes (2,5) and octahedral geometry for complex (8). The magnetic moment values of the Cu(II) complexes (3, 6 and 9) are (2.03, 1.58 and 2.18) B.M. These values reveal the presence of one unpaired electron (Hussein *et al.*, 2011).

The electronic spectral bands of the ligand and their complexes are listed in Table 2. The UV-visible spectra of the ligand showed a bands at (24630 and 29761) cm^{-1} assignable to $\pi-\pi^*$ or $n-\pi^*$ within the ligand molecule.

The bands of the ligand were slightly shifted to a higher wave length (red shift) in all complexes and the new bands were observed in the visible region for the complexes due to d-d transition.

The Co(II) complexes (1 and 4) show bands in the visible region at (15625 and 15479) cm^{-1} generally correspond to the transition from singlet level of ^4F state $^4\text{A}_2$ to the P state $^4\text{T}_1$ which is consistent with tetrahedral geometry, similar to those reported for $[\text{CoCl}_4]^{2-}$ and $[\text{CoI}_4]^{2-}$ (Lobana 2007), while the complex (7) exhibited two bands at 16722 and 25252 cm^{-1} which correspond to the transitions $^4\text{T}_1\text{g}(\text{F}) \rightarrow ^4\text{A}_2\text{g}(\text{F})$ and $^4\text{T}_1\text{g}(\text{F}) \rightarrow ^4\text{T}_1\text{g}(\text{p})$ respectively, in the octahedral environment (Baranwal and Gupta, 2002) .

The electronic spectra of Ni(II) complexes (2 and 5) show bands at (16181 and 16129) cm^{-1} due to the transition $^3\text{T}_1(\text{F}) \rightarrow ^3\text{T}_1(\text{P})$ in tetrahedral geometry, while the Ni(II) complex (8) shows absorption bands in the region 14730, 16380 and 26315 cm^{-1} . These bands are assigned to $^3\text{A}_2\text{g} \rightarrow ^3\text{T}_2\text{g}$, $^3\text{A}_2\text{g} \rightarrow ^3\text{T}_1\text{g}(\text{F})$ and $^3\text{A}_2\text{g} \rightarrow ^3\text{T}_1\text{g}(\text{P})$ transitions respectively in an octahedral geometry (Kullearni *et al.*, 2012). In case of Cu(II) complexes (3 and 6) only one band each at lower frequency was at 15873 and 15723 cm^{-1} assigned to d-d transition ($^2\text{T}_2 \rightarrow ^2\text{E}$ transition) in addition to charge transfer bands at 25773-30487 cm^{-1} . respectively The magnetic moment and electronic spectra of Cu(II) complexes supported the tetrahedral geometry of Cu(II).

The electronic spectrum of Cu(II) complex (9) shows bands in the region (14900-16030) cm^{-1} . The position and shape of these bands suggest the merging of two electronic transitions ${}^2A_{1g} \longrightarrow {}^2B_{1g}$ and ${}^2B_{1g} \longrightarrow {}^2E_g$, which indicate that the Cu(II) complex has octahedral geometry.

The results of this study clearly indicate that the M^{+2} ions are surrounded by two Cl^- and two (C=N) nitrogen of the ligand to form tetrahedral mononuclear complexes (1:1) and (1:2), while in case of (2:2) the metal ions are surrounded by six (C=N), two Cl^- ions and two H_2O molecules to form octahedral geometry as shown in Fig (1).

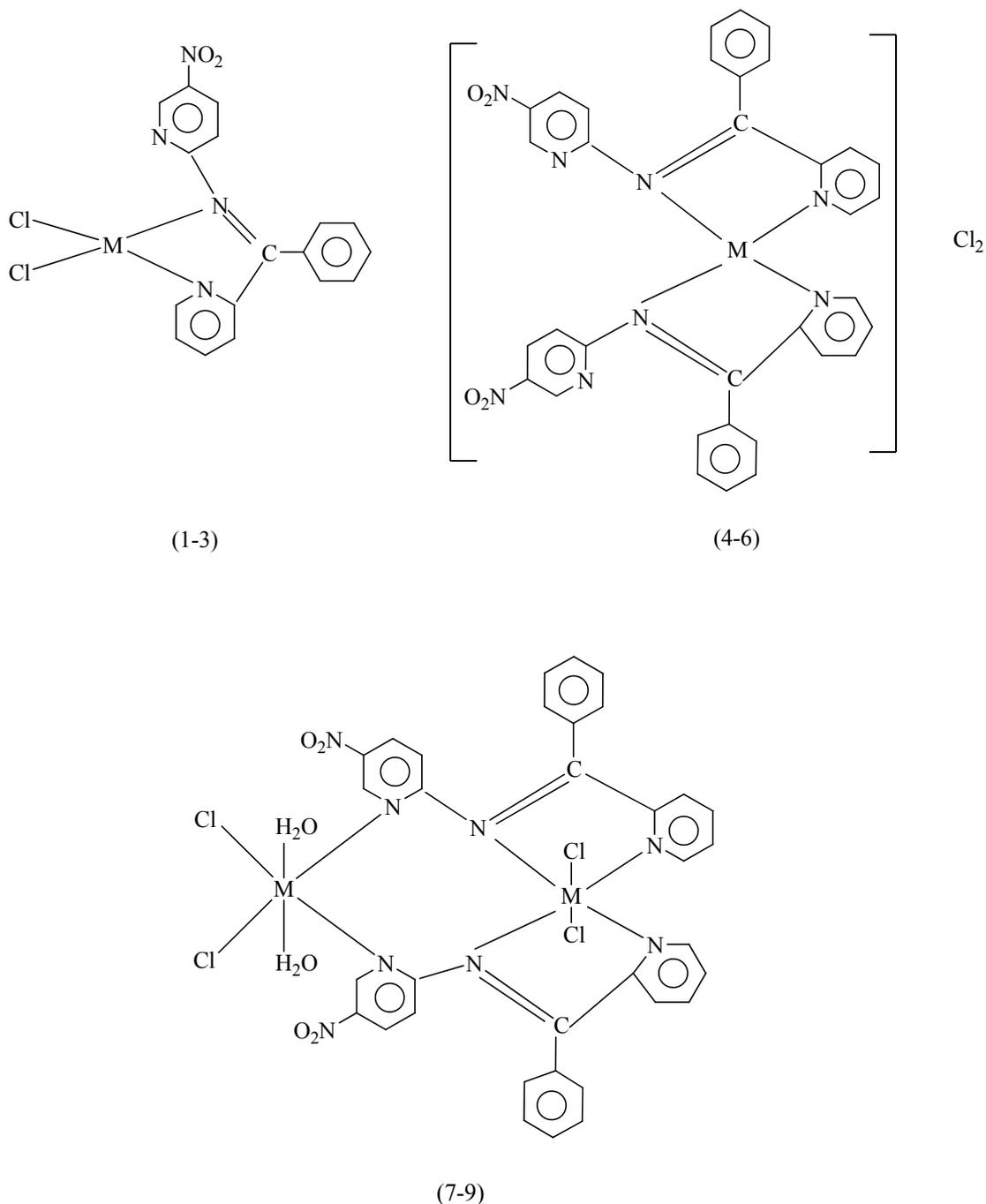


Fig 1: The suggested structures of the complexes

Table 1: Some physical properties of organic salts and their ionic salts

Seq.	compound	m.p (°C)	Color	Yield	% Metal found (calc.)	Λ $\text{cm}^2 \cdot \text{ohm}^{-1} \cdot \text{mol}^{-1}$	μ_{eff}
L	$[\text{C}_{17}\text{H}_{12}\text{N}_4\text{O}_2]$	178	Yellow	84	---	---	---
1	$[\text{Co}(\text{L})\text{Cl}_2]$	160-162	Bright green	74	13.31 (13.59)	14	4.33
2	$[\text{Ni}(\text{L})\text{Cl}_2]$	270 _(d)	Yellow	72	13.42 (13.58)	20	3.60
3	$[\text{Cu}(\text{L})\text{Cl}_2]$	158-160	Green	68	14.18 (14.38)	22	2.13
4	$[\text{Co}(\text{L})_2]\text{Cl}_2$	160-162	Brown	68	7.91 (7.99)	70	4.48
5	$[\text{Ni}(\text{L})_2]\text{Cl}_2$	281 _(d)	Yellow	75	7.89 (7.94)	80	3.53
6	$[\text{Cu}(\text{L})_2]\text{Cl}_2$	155-160	Olive	72	8.34 (8.49)	75	1.58
7	$[\text{Co}_2(\text{L})_2\text{Cl}_4(\text{H}_2\text{O})_2]$	260-262	Pale green	76	6.92 (6.98)	22	5.44
8	$[\text{Ni}_2(\text{L})_2\text{Cl}_4(\text{H}_2\text{O})_2]$	246 _(d)	Yellow	79	6.90 (6.93)	18	3.01
9	$[\text{Cu}_2(\text{L})_2\text{Cl}_4(\text{H}_2\text{O})_2]$	143-145	Olive	84	7.38 (7.42)	12	2.18

Table 2: The IR spectra and electronic spectral data of the ligand and its complexes

Seq.	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{N})_{\text{ring}}$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{Cl})$	UV.vis. absorbance bands (cm^{-1})
L	1625 _(s)	1593 _(s)	---	---	29761, 24630
1	1639 _(s)	1610 _(s)	498 _(m)	300 _(w)	29761, 16778
2	1649 _(s)	1605 _(s)	459 _(m)	330 _(w)	29761, 26315, 16181
3	1649 _(s)	1610 _(m)	465 _(w)	340 _(w)	15873, 16722
4	1639 _(s)	1614 _(m)	492 _(m)	295 _(w)	15479, 16780
5	1649 _(s)	1611 _(m)	498 _(s)	290 _(w)	29761, 15723, 25000
6	1633 _(s)	1610 _(s)	494 _(s)	300 _(w)	2944, 14925, 16722, 25252
7	1649 _(s)	1605 _(s)	494 _(w)	310 _(w)	16129, 25125
8	1650 _(s)	1605 _(s)	490 _(m)	330 _(w)	15822, 16666
9	1648 _(s)	1615 _(s)	495 _(m)	320 _(w)	14900, 16030

S = strong , m = medium, w = weak

REFERENCES

- Baranwal, B.P.; Gupta, T. (2002). Synthesis and characterization of some trinuclear cobalt (II) thiocarboxylates. *Synth. React. Inorg. Met-Org. Chem.* **23**(10), 1855-1864.
- Chang, K.; Huang, C.; Liu, Y.; Hu, Y.; Chon, P.; Lin, Y-Chih (2004). Synthesis of photoluminescent Zn(II) Schiff base complexes and its derivative containing Pd(II) moiety. *J. Chem. Soc. Dalton Trans.* 1731- 1738.
- Cheng, H.; Chun-Ying, C.; Chem-Jic, F.; Yony-jiany, L.; Qing-jin, M. (2000). Self-assembled macrocyclic tetranuclear square $[\text{NiHL}]_4^{+4}$ and molecular rectangle $[\text{Cu}_2\text{Cl}_2\text{L}]_2$. *J. Chem. Soc. Dalton Trans.*, 1207- 1212.
- Gaber, M.; Isaa, R.M.; Aly, F.A.; Ayad, M.I. (1989). Studies of Ti(IV) and Zr(IV) chelates with N_2O_2 Schiff bases of 2-hydroxy-1- naphthaldehyde with aromatic diamine Thermo. *Chem. Acta*, **155**, 309-316.
- Greavy, W.J. (1971). The use of conductivity measurements in organic solvent for characterization of coordination compounds. *Coord. Chem. Rev.*, **7**, 81-122.
- Herrera, A.M.; Kalayda, G.V.; Disch, S.J.; Wikstrom, J.P.; Korendovych, I.V.; Staples, R.J.; Haas, T.E.; Akimova, E.V. (2003). Reactions at the azomethine C=N bonds in the nickel (II) and copper (II) complexes of pyridine-containing Schiff base macrocyclic ligands. *J. Chem. Soc. Dalton Trans.*, 4482-4492.
- Hussein, S.S.; Mostafa, M.; Stefan, S.L.; Abdel-Aziz, E. (2011). Structural diversity of 3d complexes of a isatinic hydrazone. *Res. J. Chem. Sci.*, **1**(5), 67-72.
- Khaddar, A.; Hosseni, S.A.; Zarei, S.A. (2005). Synthesis characterization and x-ray crystal structures of copper(II) and nickel (II) complexes with potentially hexadentate Schiff base ligands, *Inorg. Chem. Acta*, **358**, 3211-3220.
- Kulkarni, P.A.; Habib, S.I.; Saraf, V.D.; Deshpande, M.M. (2012). Synthesis, spectral analysis and antimicrobial activity of some new transition metal complexes derived from 2,4-dihydroxy acetophenones. *Res. J. Pharm., Biog. Chemical Sci.*, **3**(1), 107-113.
- Lobana, T. (2007). Stereochemical terads of metal derivatives of some heterocyclic thiones, *Proc. Indian. Acad. Chem. Sci.*, **112**, 323-329.

- Nasari, M.S.; Mirsatteri, S.N.; Saberyan, K. (2009). Template synthesis and characterization of host (nanocavity of zeolite-yl) geneot $[\text{Cu}[18] \text{ and } \text{N}_4\text{S}_2]^{+2}$, $[\text{Cu}[20] \text{ and } \text{N}_4\text{S}_2]^{+2}$, $[\text{Cu}(\text{BzO}_2.[20]) \text{ and } \text{N}_4\text{S}_2]^{+2}$, nanocomposite materials. *Bull Korean Chem. Soc.*, **30**, 2, 348-354.
- Neelamma, M.; Rao, P.V.; Anuradha, G.H. (2011). Syntesis and structural studies on transition metal complexes derived from 4-hydroxy-4-methyl-2-pentanone-1H-benzoimidazol-2-yl-hydrazone. *E. J. Chem.*, **8**(1), 29-36.
- Prakash, A.; Gangwav, M.P.; Singh, K.K. (2011). Synthesis spectroscopy and biological studies of nickel (II) complexes with tetradentate Schiff bases having N_2O_2 donor group. *T. Develop. Biol. and Tissue. Eng.*, **3**(2), 13-19.
- Thaker, B.T.; Tandal, P.K.; Patel, A.S.; Vyas, C.J.; Jesani, M.S.; Patel, T.M. (2005). Synthesis and mesomorphic characterization of Cu(II), Ni(II) and Pd(II) complexes with azomethine and chalcone as bridging group. *Indian J. Chem.*, **44A**, 265-270.
- Yamada, S. (1999). Advancement in stereochemical aspects of Schiff base metal complexes. *Coord. Chem. Rev.*, 192-237.