Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2015, 4 (3): 958-964

(International Peer Reviewed Journal)

Synthesis, Spectroscopic, Thermal and Antimicrobial Studies of Some Transition Metal mixed ligand Complexes of Schiff Base

P.R.Shirode[1*] and P.M.Yeole[2]

1. Department of Chemistry, Pratap College, Amalner, North Maharashtra University,
Jalgaon, Maharashtra, **INDIA**
2. R.L.College, Parola, North Maharashtra University, Jalgaon, Maharashtra, **INDIA**

Email: prshirodepca@gmail.com

Accepted on 7th January 2015

ABSTRACT

Some new Schiff base metal complexes of Cr(III), Mn(II),Fe(III)Co(II), Ni(II) and Cu(II) derived from ortho hydroxyacetophenone semicarbazone and pyruvic acid semicarbazone have been synthesized by conventional methods. These compounds have been characterized by elemental analysis, FT-IR, molar conductance, electronic spectra, magnetic susceptibility, thermal, electrical conductivity. The complexes are colored and stable in air. Analytical data revealed that all the complexes exhibited 1:1:1(metal: ligand: ligand) ratio with the coordination number 6. The Schiff base and metal complexes show a good activity against the Gram-positive bacteria; Staphylococcus aureus and Gram-negative bacteria; Escherichia coli and fungi Aspergillus niger and Candida albicans. The antimicrobial results also indicate that the metal complexes are better antimicrobial agents as compared to the Schiff bases.

Keywords: Schiff base complexes, semicarbazone ligand, Spectral studies, Thermodynamic parameters, Biological activities.

INTRODUCTION

Metal complexes have been receiving considerable attention for many years due to their interesting characteristics in the field of material science and biological systems. Optoelectronic, electrical and magnetic properties of the metals and metalloids can be tailored by reacting them with different ligands. A large number of Schiff bases and their complexes may exhibit the properties like- to reversibly bind oxygen, transfer of an amino group, as nano precursors and varied complexing/redox ability. The Schiff bases have high affinity to chelate with the transition metal ions, hence are attracting attention due to potential applications in areas viz. biology, catalysis, thermal, electrical, optical , magnetic etc [1-4]. A Transition metal complexes which usually contain nitrogen, sulphur/or oxygen as ligand atoms are becoming increasingly important because these Schiff base can bind with different metal centers involving various coordination sites and allow successful synthesis of metallic complexes with interesting stereochemistry.

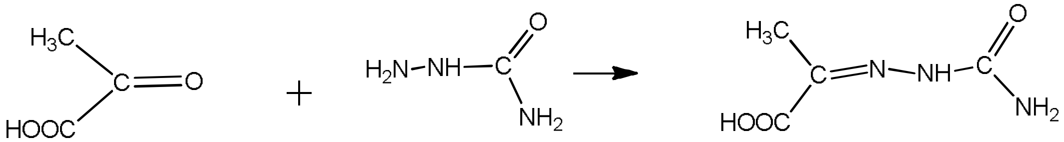
Heterocyclic compounds are widely distributed in the nature and essential to many biochemicals, analytical and industrial processes. Compounds containing these heterocycles have important properties in the field of material science and biological systems [5-8].

In this study we are reporting the synthesis and physicochemical characterization of Cr (III), Mn(II). Fe(III),Co(II), Ni(II) and Cu(II) complexes with ligands derived from semicarbazone of ortho hyroxy acetophanone and pyruvic acid.

MATERIALS AND METHODS

The compounds pyruvic acid, ortho hydroxyacetophenone and semicarbazide hydrochloride and chlorides of Cr(III),Mn (II),Fe(III),Co(II),Ni(II) and Cu(II) used were of analytical grade. The amount of metals are determined volumetrically by EDTA using double burette technique for optimum utilization of reagents. Indicator Eriochrome Black T is used for Cr(III), Mn(II), ammonium thiocynate for Fe(III), xylenol orange for Co(II) and muroxide for Ni(II) and Cu(II).Carbon, hydrogen and nitrogen analysis were carried from SAIF, Mumbai. IR spectra of the complexes were recorded on Perkin Elmer FTIR instrument using KBr pellets in the region 400-4000 cm^{-1} from Department of Physics, Pratap College, Amalner. The Electronic spectral data of complexes is shown in table 4. Electronic spectra of complexes were recorded on Systronics UV-VISIBLE Spectrophotometer in the Department of Chemistry, Pratap College, Amalner. The IR spectral data of complexes is shown in table 5.. Thermo gravimetric analysis was carried out on SHIMAdZU STA 6000.Antimicrobial activities are determined by using three microbial nutrients.
Ligands L_1 and L_2 were prepared and the methods of their preparation are given below.

Ligand L_1: To a mixture of aqueous 25mL solution of pyruvic acid and 20mL (0.1M) sodium acetate solution 25mL (0.1M) aqueous solution of semicarbazide hydrochloride were slowly added with constant stirring. This mixture was ice cooled for 20-25min.On cooling white solid product was separated out. It was filtered, washed with cold ethanol, dried in air and recrystallized from hot water.



Ligand L_2: To a mixture of hot ethonalic 25mL (0.1M)solution of ortho hydroxyacetophenone and 20mL (0.1M) solution of sodium acetate, 25mL(0.1M) aqueous solution of semicarbazide hydrochloride was added slowly with constant stirring. Then the reaction mixture was refluxed for 15-20 min on a water bath. After cooling thoroughly, white solid product was precipitated out from the solution. This solid obtained was filtered, washed with cold ethanol and dried in air and recrystallized from ethanol.

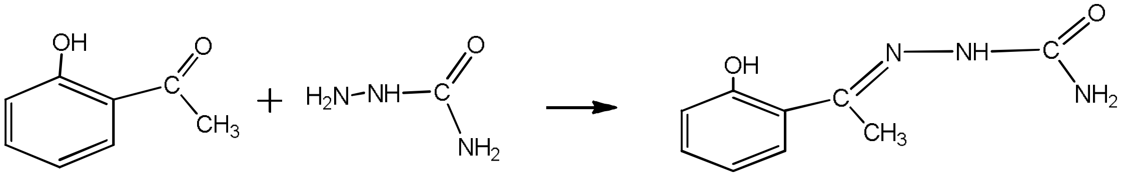


Table I: Physical properties of ligands.

Name of the ligand	Symbol	Colour and nature	Method purification.	M.P.^{0}c(observed) reported	Mol. wt	Molecular formula
Pyruvic acid semicarbazone	PASC	White shining crystals	Recrystallization from water	(214) 215	145	$C_4H_7N_3O$
O-Hydroxy acetophenone semicarbazone	OH ACPHS C	White Crystals	Crystallized from aq. Ethanol	210(209)	193	$C_9H_{11}N_3O$

RESULTS AND DISCUSSION

Generally, the complexes were prepared by reacting the respective metal salts as chloride with the ligands using 1:1:1 mole ratio, i.e. one mole of metal chloride: one mole of orthohydroxy acetophenone semicarbazone and one mole of pyruvic acid semicarbazone.

The synthesis of mixed ligand Metal complexes may be represented as follows:

$$\mathbf{OHYACPHSC+PYACSC+MCl_2 \rightarrow\rightarrow [M(OHYACPHSC)_1(PYACSC)_1]Cl_2}$$

(where OHYACPHSC is orthohydroxy acetophenone semicarbazone and PYACSC is pyruvic acid semicarbazone and Cr(III), Mn(II), Fe(III)Co(II), Ni(II) and Cu(II)

The formula weights and melting points, are given in Table1.Based on the physicochemical characteristics, it was found that all the complexes were non-hygroscopic, stable at room temperature indicating a strong metal-ligand bond. The solubility of the complexes of ligands was studied in various solvents. The complexes are soluble in dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF) while insoluble in water .The observed molar conductance values measured in(DMF) in 10^{-3} M solution lie in the (3.0-17.25)Ω^{-1} cm^2mol^{-1} range, the conductivity measurements in DMF indicated the non electrolyte behavior [9]. The Characterization data of the complexes was given in table 2.

Table 2: Characterization data of the complexes found (Calculated.) %

Ligand/ Complex	**Colour**	**Mole. wt**	**%Yieldof the comp.**	**%of metal (Calculated)**	**%of C**	**%of H**	**%of N**
Cr[$(PYACSC)_1$ $(OHACPHSC)_1$]	Light Brown	460.99	62	11.27(11.95)	33.84(33.79)	3.90(3.88)	18.22(18.19)
Mn [$(PYACSC)_1(OHACPHSC)_1$	Light Brown	469.93	74	11.84(12.00)	33.62(33.55)	3.87(3.82)	18.01(17.97)
Fe[$(PYACSC)_1(OHACPHSC)_1$	Orange	500.35	67	11.16(11.72)	31.17(31.15)	3.59(3.53)	16.78(16.71)
Co [$(PYACSC)_1$ $(OHACPHSC)_1$]	Light Pink	467.93	78	12.59 (12.96)	33.33(33.28)	3.84(3.81)	17.95 (17.91)
Ni[$(PYACSC)_1(OHACPHSC)_1$]	Green	467.69	62	12.59 (12.96)	33.33(33.26)	3.83(3.79)	17.95 (17.93)
Cu[$(PYACSC)_1$ $(OHACPHSC)_1$]	Pale Green	472.54	68	13.44(13.97)	33.01(32.97)	3.80(3.76)	17.77 (17.73)

Magnetic moment and Electronic spectra: The magnetic moments of the complexes shown in table 3 were calculated from the measured magnetic susceptibilities after employing diamagnetic corrections. [10-13].

The magnetic moments obtained at room temperature for the complexes of Cu(II), Ni(II), Co(II),Fe(II),Mn(II) and Cr(III) are listed (Table 3).Cu(II) complex exhibits magnetic moment of (2.17B.M) which is less than the normal value (2.20 -1.84). The lowered magnetic moment value observed for Cu (II) complex under present study is due to distorted octahedral geometry[11]The Co(II) complex shows magnetic moment of 4.475B.M the spin free octahedral complex are reported to exhibit magnetic moment in the range of 4.46- 5.53 B.M[17] .The Ni(II) complex shows magnetic moment of 3.316 B.M. The magnetic moment of octahedral Ni(II) complex are reported to exhibit magnetic moment in the range of 2.80– 3.40 B.M. 3.316 including spin orbital coupling contribution from$^3A_{2g}$ and higher $^3T_{2g}$ states. Hence the observed magnetic moment for the Ni(II) complex suggest that it may have octahedral geometry [13] . The Fe (III) complex shows magnetic moment of 5.426 B.M. The magnetic moment of octahedral Fe(III) complex are reported to exhibit magnetic moment in the range of 5.70– 6.00 B.M. 5.426

including spin orbital coupling contribution from$^3A_{2g}$ and higher ^{3} T_{2g} states. Hence the observed magnetic moment for the Fe(III)complex suggest that it may have octahedral geometry [13] . The Mn(II) complex shows magnetic moment of 5.717 B.M . The magnetic moment of octahedral Mn(II)complex are reported to exhibit magnetic moment in the range of 5.65– 6.00 B.M. 5.717 including spin orbital coupling contribution from$^3A_{2g}$ and higher ^{3} T_{2g} states.Hence the observed magnetic moment for the Fe(II)complex suggest that it may have octahedral geometry [13] . The Cr(III) complex shows magnetic moment of 3.90 B.M . The magnetic moment of octahedral CR(III) complex are reported to exhibit magnetic moment in the range of 3.70– 3.90 B.M. 3.90B.M. including spin orbital coupling contribution from$^3A_{2g}$ and higher ^{3} T_{2g} states.Hence the observed magnetic moment for the Cr(III)complex suggest that it may have octahedral geometry [13] .

Typical spectral data of the metal salts, ligands and complexes of Transition metal complexes have been investigated in DMf and shown in table 3.

Table 3. Magnetic moment and molar conductance values of the complexes

Ligand/ Complex	Magnetic moment	Molar cond.$\Omega^1cm^2mol^1$ at RT.(29^0C)	Molar cond.$\Omega^{-1}cm^2mol^1$ at RT + 10^0C(39^0C)
Cr[$(PYACSC)_1$ $(OHACPHSC)_1$]	3.90	2.4	3.0
Mn [$(PYACSC)_1(OHACPHSC)_1$	5.717	15.12	17.25
Fe[$(PYACSC)_1(OHACPHSC)_1$	5.426	5.25	6.05
Co [$(PYACSC)_1$ $(OHACPHSC)_1$]	4.475	1.97	3.4
Ni[$(PYACSC)_1(OHACPHSC)_1$]	3.316	3.4	4.1
Cu[$(PYACSC)_1$ $(OHACPHSC)_1$]	2.17	2.51	6.4

The electronic spectra of the pyruvic acid thiosemicarbazone displays absorption bands at 262, and 345 which is assigned to ($\pi - \pi^*$) and ($n - \pi^*$) electronic transitions respectively. The electronic spectra of the ortho hydroxy acetophenone semicarbazone displays absorption band at 297nm, which is assigned to ($\pi \rightarrow \pi^*$) electronic transition. [1-9-13]

The electronic spectra of Cr (III) complexes shows peak at 356nm due to charge transfer. Other peaks at 410nm and 872 nm were found to be caused by (d-d) electronic transition type ($T_{2g} \leftarrow A_{2g}$), ($T_{1g} \leftarrow A_{2g}$) and $T\ _{1g}(P) \leftarrow A_{2g}$).

The electronic spectra of Mn (II) complexes are indicating peaks at 293nm due to charge transfer band while peaks at 387nm and 876nm are observed due to (d-d) electronic transition type $^4A_{1g,}$ $^4E_g(G)_{\rightarrow}$ $^6A_{1g}$ and $^4E_g(D)_{\rightarrow}$ $^6A_{1g}$

The electronic spectra of Fe (III) complexes shows peaks at 346nm charge transfer. Other peaks at observed at 410nm and 843nm due to (d-d) electronic transition type ($^6A_{1g} \rightarrow {}^4T_{1g}$), $^6A_{1g} \rightarrow {}^4E_{2g}$ (^4G) , $^6A_{1g} \rightarrow {}^4E_{2g}(^4D)$. The electronic spectrum of Co(II) complex shows peak at 411 nm due to charge transfer. Other three peaks at 490 nm, 668 nm and 960 nm were found to be caused by (d-d) electronic transition type $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, $^4T_{1g}(F) \rightarrow$ $^4A_{2g}(F)$ and $^4T_{1g}(F)$ $\rightarrow$ $^4T_{2g}(F)$ respectively [14].The spectrum of Ni(II)complex absorption peak is appeared at 356 nm was related to charge transfer, then other two peaks at551 nm and 843nm were assigned to electronic transition type $^3A_{2g}(F)$ $\rightarrow$ $^3T_{1g}(P)$ and $^3A_{2g}(F)$ $\rightarrow$

$^3T_{1g}$(F)respectively [7]. The spectrum of Cu (II) complex gave absorption peak at 305nm due to charge transfer. The peak at 372 nm was caused by electronic transition [9-14]$^2E_g \rightarrow {}^2T_{2g}$. The results were given in table 4.

Table 4: Electronic Spectra

Sr.no.	Name of the Complex	ν_1	ν_2	ν_3	B	β	ν_2/ν_1
1	Cr[(PYACSC)$_1$(OHACPHSC)$_1$]	11467	24339	28089	766.93	0.789	2.12
2	Mn [(PYACSC)$_1$(OHACPHSC)$_{1]}$	11405	25839	34129	990.627	0.961	2.25
3	Fe[(PYACSC)$_1$(OHACPHSC)$_1$	11862	25125	28089	885.195	0.759	2.11
4	Co [(PYACSC)$_1$(OHACPHSC)$_1$]	10428	20408	24330	696.93	0.843	1.95
5	Ni[(PYACSC)$_1$(OHACPHSC)$_1$]	11862	18125	28089	885.195	0.859	1.52
6	Cu[(PYACSC)$_1$(OHACPHSC)$_1$]	12048	26881	32786	1049.94	1.0193	2.231

IR Spectra: The assignments of the significant IR spectral bands (4000-400cm^{-1}) of ligand and its metal complexes are presented in following table 5

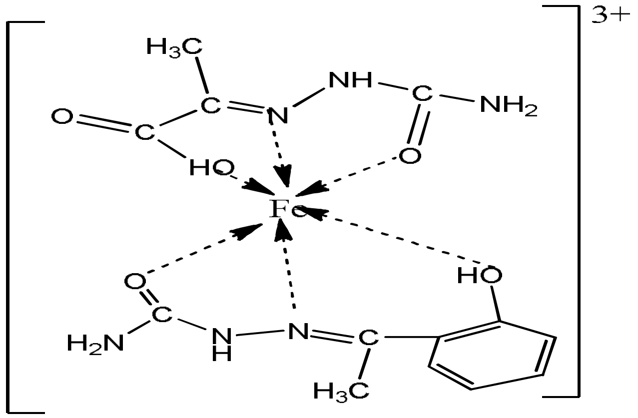
Table 5: IR Spectra

Sr.no.	**Name of the Ligand/Complex**	**V$_{N-H}$**	**V$_{(C=N)}$**	ν-cooH	**V$_{(C=O)}$**	**V$_{(C-O)}$**	**V$_{(N-N)}$**	**ν$_{M-N}$ and ν$_{M-O}$**
1	OHACPHSC	3410	1618		1678		1208	
2	PYACSC	3430	1611	2360	1699	1356	1201	
3	Cr[(PYACSC)$_1$(OHACPHSC)$_1$]	3180	1548	2360	1641	1242	1186	672
4	Mn [(PYACSC)$_1$(OHACPHSC)$_{1]}$	2923	1595	2361	1679	1236	1156	680
5	Fe[(PYACSC)$_1$(OHACPHSC)$_1$	3223	1548	2359	1654	1252	1156	671
6	Co [(PYACSC)$_1$(OHACPHSC)$_1$]	2922	1564	2359	1738	1302	1216	589
7	Ni[(PYACSC)$_1$(OHACPHSC)$_1$]	3344	1598	2361	1644	1217	1166	617
8	Cu[(PYACSC)$_1$(OHACPHSC)$_1$]	3265	1595	2359	1642	1231	1158	672

The assignments of the significant IR spectral bands (4000-400cm^{-1}) of ligand and its metal complexes are presented in Table 5. In order to study the binding mode of the Schiff base ligands (PYACSC AND OHACPHSC) to the metal ion in complexes .The IR spectrum the free ligand was compared with the spectra of the complexes. The IR spectrum of (PYACSC AND OHACPHSC) show bands in the regions3406cm^{-1} and 1734cm^{-1}The position of bands provides significant indications regarding the bonding sites of the ligand molecule when complexes with Cr(III),Mn (II),Co(II),Ni(II) and Cu(II) metal ions. . In principle, the ligand can exhibit keto-enol tautomerism since it contains a amide −NH−C=O functional group. The ν(O−H) band at 2565 cm^{-1} is absent in the IR spectrum of ligand but $\nu_{(-NH)}$ band at 3320 cm^{-1} is present, indicating that in the solid state, the ligand remains as the ketone tautomer. The position of $\nu_{(C=N)}$ band of the ligand(L1) appeared at 1611cm^{-1} is shifted towards lower wave number in the complexes indicating coordination via the azomethine nitrogen [16] . This is also confirmed by the appearance of bands in the range of 589-680 cm−1, this has been assigned to the $\nu_{(M-N)}$ (16) . The position of this band is shifted towards higher wave number in the spectra of complexes. It is due to the increase in the bond strength, which again confirms the coordination via the azomethine nitrogen. The position of $\nu_{(-OH)}$ band of the (L1) appeared at 3410cm−1 is shifted towards lower wave number in the complexes indicating coordination via oxygen of phenolic group. It indicates that ketonic oxygen coordinates to the metal ion [27-28] . Thus, it may be concluded that the both the ligand behaves as tridentate chelating agent coordinating through phenolic oxygen, azomethine nitrogen and ketonic oxygen. The IR bands of medium intensity within range 589-680 cm^{-1} are attributed to V_{M-N} and $V_{M-O.}$

The thermograms (TG) of the compounds have been recorded in flowing nitrogen atmosphere at the heating rate of 10°C/min on approximately 10 mg samples. Thermogravemetric analysis is carried out on SHIMAdZU STA 6000 shows absence of water molecule in the complexes supports the octahedral nature of complexes.

Structure of the complex



APPLICATIONS

Biological Activity: The compound synthesized in the present investigation has been subjected to various antimicrobial screening programs based on their structural features so as to ascertain their activity against different microorganisms. The solvent used was DMF, and the sample concentrations were 200, 100, 50, 25, 12.5 ppm. The results of preliminary study on antimicrobial activity indicated that most of the compounds were highly and few were moderately active against these organisms.

Table No.6

Ligand/Complex	*Staphylococcus aureus*			*Escherichia coli*			*Aspergillusniger*			*Candida albicans.*		
	25 ppm	50 ppm	100 ppm	25 ppm	50 ppm	100 ppm	25 ppm	50 ppm	100 ppm	25 ppm	50 ppm	100 ppm
OHACPHSC	16	18	20	15	17	20	12	16	16	10	12	14
PYACSC	13	15	22	18	24	34	17	22	28	14	14	14
Cr[(PYACSC)$_1$(OHACPHSC)$_1$]	14	16	19	10	15	17	18	21	25	12	15	18
Mn [(PYACSC)$_1$(OHACPHSC)$_{1]}$	17	20	21	14	16	18	23	28	28	17	22	30
Fe[(PYACSC)$_1$(OHACPHSC)$_1$	22	28	35	24	31	42	21	25	27	23	27	29
Co [(PYACSC)$_1$(OHACPHSC)$_1$]	17	19	20	21	33	39	31	42	55	28	39	45
Ni[(PYACSC)$_1$(OHACPHSC)$_1$]	20	27	39	23	29	34	19	29	41	15	17	18
Cu[(PYACSC)$_1$(OHACPHSC)$_1$]	34	39	50	27	35	48	22	29	34	21	25	31

ACKNOWLEDGEMENTS

I am grateful to Principal, Pratap college, Amalner AND the Head, Department of Chemistry; Head, Department of Physics Pratap college, Amalnerfor providing necessary facilityand Head, SAIF, IIT Mumbai for elemental analysis.

REFERENCES

[1] S.G.Shirodkar, P.S. Mane, T.K. Chondhekar, *Indian J. Chem,* **2001,** 40, 1114
[2] A.A.Soliman, G.G. Mohamed, *Thermochim Acta,* **2004**, 421, 151.
[3] S.Chandra, U. Kumar, *Spectrochim. Acta.* 2**005,** 61A, 219. **DOI:**10.1016/j.tca.2004.03.010
[4] A.P.Mishra, R. Jain, *J. Saudi Chem. Soc,* (In press). **DOI:**10.1016/j.jscs.2011.09.013
[5] C.Spinu, A. Kriza, L. Spinu, *Acta Chim. Slov,* **2001,** 48, 257.
[6] R.R.Coombs, S.A. Westcott, A. Decken, F.J. Baerlocher, *Trans. Met. Chem,* **2005,** 30, 411.**DOI:** 10.1007/s11243-004-7625-4
[7] M.M.Omar, G.G. Mohammed, *Spectrochim. Acta,* **2005,** 61A, 929.
[8] N. Raman, S.J. Raja, J. Joseph, J.D. Raja, *J. Chil. Chem. Soc,* **2007,** 52, 1138, **DOI:**10.1016/ j.saa.2004.05.040
[9] W.J.Geary, “The use of conductivity measurements in organic solvents for the characterization of coordination compounds”, *Coordination Chemistry Reviews,* **1971**,7 (1), 81–122, 50–58.
[10] A.B.P. Lever,” *Inorganic Electronic Spectroscopy*”, Elsevier, Amsterdam, **1984.**
[11] R.M. Silverstein, “*Spectrophotometric identification of organic compounds*”, John Wiley, NewYork, **2009**.
[12] 12. Dyer J.R,“*Application of absorption spectroscopy of organic compounds*”, Prentice Hall of Ind. Pvt.Lt,(**2009**).
[13] Liwang Jiwen Cai, Zon-Wang Mao, Xiao-Long Feng and Jim- Wang Huang, (2004) nickel complexes bridge by unusual(N,O,O’)-coordinated -amino acids: Syntheses, structural characteri zation and magneticproperties, *Trans. Met. Chem,* 29, p 418.
[14] Ahmed Jasim M.Ai-karwai, AdilAhmed A.Al-Dulimi, Ali MohamadAli, A.Al-Mokaram, “Synthesis,Characterization and thermal properties of sodium pyruvate thiosemicarbazone and some of its metal complexes”, *Journal of King Saud*, Nitrogen-oxygen and Nitrogen-Sulpher-Ligands, *Transition Metal University –Science,* **2012,** 24(1), 25-31.
[15] Sulekh Chandra and Krishna K. Sharma: Cobalt (II) and Nickel (II) Complexes of Some Chemistry, **1984,** 9, 1-3.
[16] P.K.Panchal and M.N.Patel ,Synthesis,Spectroscopy ,and Antibacterial Activity of some Transition Metal Complexes With Tridentate(ONS) and bidentet(NN) Donar Schiff Base, *Pharmaceutical Chemistry Journal,* **2006,** 40, 10.

AUTHORS’ ADDRESSES

1. **Shri.P.R.Shirode**
Associate Prof, Dept.of Chemistry,
Pratap College, Amalner.
Mob.no: 09404056845 Email: prshirodepca@gmail.com
2. **Dr.P.M.Yeole**
Assistant Prof, Dept.of Chemistry,
R.L.College,Parola.
Mob.no:09421517102, Email: pmy_chem@rocketmail.com