



SYNTHESIS AND CHARACTERIZATION OF NI (II) COMPLEX WITH 2-METHOXY-6-(8-IMINOQUINOLINYL METHYL) PHENOL

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ABSTRACT :

A Schiff base ligand was synthesized by condensation of o-vanillin with 8-aminoquinoline in 1:1 molar ratio. The Schiff base metal complex of Ni (II) was prepared using the metal salt and ligand in 1:2 ratio. The ligand was characterized by elemental analysis, UV-Visible, IR, NMR and mass spectra. The metal complex was characterized by using elemental analysis, magnetic susceptibility, UV-Visible, IR spectra and XRD studies. It was also characterized by thermo-gravimetric analysis. The composition of the Schiff base ligand and the metal complex was established by elemental analysis which indicated a metal: ligand ratio of 1:2. Magnetic, thermal and spectral studies indicated that ligand behaved as bidentate coordinating through phenolic oxygen and azomethine nitrogen and formed octahedral metal complex. The metal complex revealed its general formula as $[ML_2(H_2O)_2]$ where $M=Ni(II)$ and $L=deprotonated\ Schiff\ base\ ligand$.

KEYWORDS : Synthesis, Schiff base ligand, transition metal complexes, spectral characterization, thermal and XRD studies.

INTRODUCTION

Schiff bases derived from aromatic aldehydes and amines have a wide variety of applications in various fields like biological, inorganic and analytical chemistry. Schiff bases can be synthesized by relatively simple procedures enabling us to design compounds which are structurally similar to some substances of biological origin [1-5].

It is well known that N and O atoms play a key role in the co-ordination of metals at the active sites of many metallic-biomolecules [4]. Schiff bases form stable metal complexes with many transition metals. They have been widely studied because they have various properties like antibacterial, antifungal, anticancer, herbicidal, analytical etc. They find wide applications as catalysts in many synthetic and biological reactions. Besides, they can undergo bonding with metal ions in a variety of ways and the resulting compounds show varied activities. 8-aminoquinoline and o-vanillin are especially known for their antibacterial and antifungal activities and are thus used as synthetic precursors in pharmaceuticals. In continuation of earlier work, a Schiff base derived from 8-aminoquinoline and o-vanillin was used to synthesize its Ni(II) complex. Considering the distinct biological activities of these compounds herein put forth an account of the synthesis and characterization of ligand and its complex. [6-9].

2. EXPERIMENTAL:

2.1 Apparatus:

An UV-VIS-NIR-3600 recording spectrophotometer (Shimadzu, Japan) was used for the UV spectrum scanning and determination experiments. Bruker, Germany Model 3000 Hyperion Microscope with Vertex 80FTIR system range $400-4000\text{ cm}^{-1}$ (KBr discs) at SAIF, IIT, Bombay was used for IR spectral characterization of the Schiff base ligand and metal complexes. The thermogravimetric analysis of ligand and metal complexes was performed on Perkin-Elmer Diamond TG at SAIF, IIT, and Bombay. X-Ray powder

diffraction of metal complexes was scanned on X-Ray Diffractometer Ultima IV of Rigaku Corporation Japan, at Instrumentation centre of PAH Solapur University, Solapur.

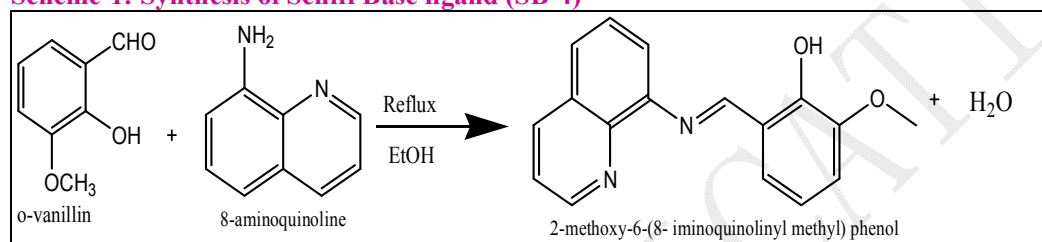
2.2 Reagents:

Sigma- Aldrich o-vanillin, 8-aminoquinoline, and Standard Qualigens (SQ) hydrated Nickel (II) chloride was used for synthesis. The solvents ethanol, DMSO etc. was used.

2.3 Synthesis of Schiff base ligand (SB-4)

20 mmol (3.04g) of o-vanillin is dissolved in absolute ethanol. Then it was added dropwise into 20mmol (2.88g) of ethanolic solution of 8-aminoquinoline. The mixture was refluxed for 2 hours then cooled and filtered [10-15]. Intense red colored crystals of Schiff base SB-4 were formed (yield 89%, 5.0 g). The crystals were washed with cold ethanol and anhydrous diethyl ether and dried over anhydrous CaCl₂. The synthesis of Schiff base ligand (SB-4) is shown in Scheme-1

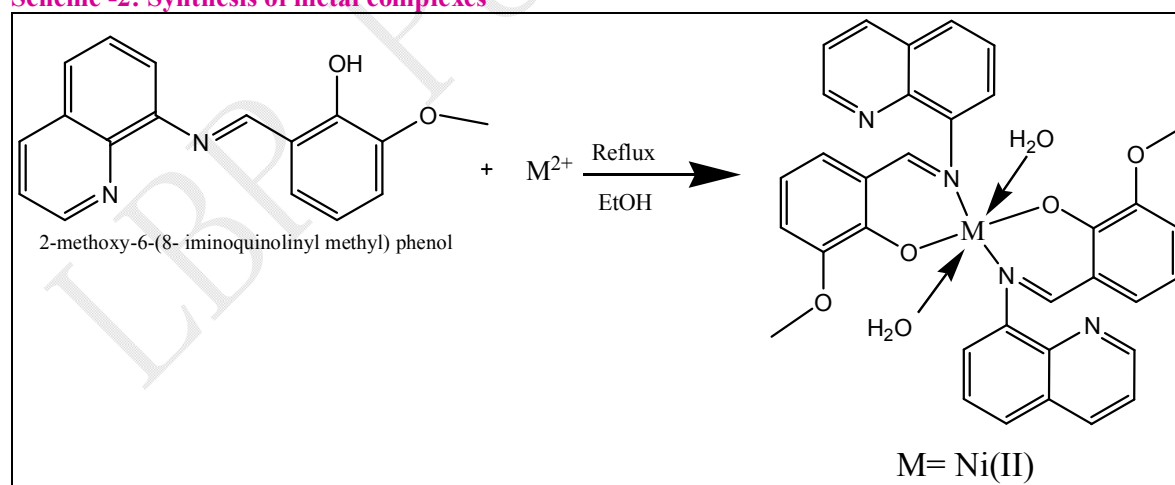
Scheme-1: Synthesis of Schiff Base ligand (SB-4)



2.4 Synthesis of Schiff base transition metal complex:

20 mmol of Schiff base (SB-4) was dissolved in ethanol (30ml) and added to 10 mmol ethanolic solution (20ml) of metal (II) chloride salt. The metal-ligand molar ratio taken was 1:2. The mixture was refluxed for 3 hours. On cooling, a crystalline metal complex was obtained. It was filtered, recrystallized from ethanol and dried in desiccator over anhydrous CaCl₂. The Ni(II) metal complex of Schiff base (SB-4) were prepared by above general method using salts NiCl₂.6H₂O. The preparation of metal complex is shown in Scheme -2.

Scheme -2: Synthesis of metal complexes



Schiff base (SB-4) and its Ni (II) complex synthesized were stable at room temperature and soluble in common solvents like DMSO, methanol etc.[16-21] The synthesized ligand and the metal complexes were characterized by elemental analysis. The geometry of the synthesized compounds has been elucidated on the basis of their elemental and spectral studies.

3. RESULTS AND DISCUSSION:

3.1 Analytical and Physicochemical data:

The stoichiometry of ligand and their metal complex was confirmed by the elemental analysis. The analytical and physicochemical data of Schiff base (SB-4) and its metal complex was found in good agreement with the proposed structure of ligand and the metal complex. The data being listed in Table-1

Table-1: Analytical and Physicochemical data of Schiff base (SB-4) and its metal complex

Comp.	Molecular formula	M. p. (°C)	Mol. Weight	Color	% Observed (Theoretical)			
					C%	H%	N%	M%
SB-4	C ₁₇ H ₁₄ O ₂ N ₂	103	278	Red	72.91 (73.38)	4.87 (5.03)	9.98 (10.07)	-
SB-4-Ni	C ₃₄ H ₂₆ O ₄ N ₄ Ni.(H ₂ O) ₂	>350	648.69	Dark Green	62.38 (62.89)	4.79 (4.62)	8.91 (8.63)	8.90 (9.04)

3.2 UV Spectral Analysis:

The UV spectrum of Schiff base ligand SB-4 is exhibiting two intense bands at 241 nm and 346 nm which can be assigned respectively to $\pi \rightarrow \pi^*$ transition within aromatic moiety and $n \rightarrow \pi^*$ transition of azomethine group of ligand. In the spectra of complex, the bands due to azomethine group are shifted to higher frequency indicating that azomethine nitrogen atom is involved in coordination to the metal ion.

In the present investigation, the electronic spectra of Ni(II) complex exhibited three bands associated with d-d transitions at 1066 nm, 677 nm and 433 nm assignable to transitions ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) respectively. These observed d-d transitions for metal complex are consistent with octahedral geometry of Ni(II) metal complexes of Schiff base ligand [12-22]. The UV spectra of Schiff base SB-4 and its metal complex are represented in Figure-1.

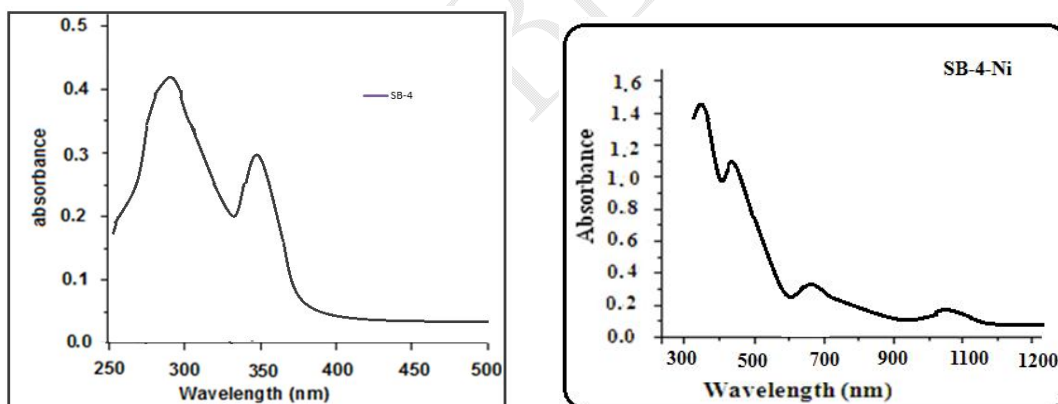


Figure-1: The UV spectra Schiff base and metal complex

3.3 Magnetic Susceptibility and molar conductance studies of complex:

The magnetic moments obtained at room temperature for the metal complex indicated Paramagnetism. The Ni(II) complex showed magnetic moment of 2.90 BM. This value of magnetic moment is within the range of 2.7 to 3.3 BM, reported for octahedral Ni(II) complex thereby suggesting octahedral geometry for Ni(II) complex under study [22-25].

The solution conductivity of the Ni(II) metal complex was determined by measuring their molar conductance values in DMSO as solvent at the concentration of 1×10^{-3} M. The observed solution conductivity $32.41 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ revealed its non-electrolytic nature.

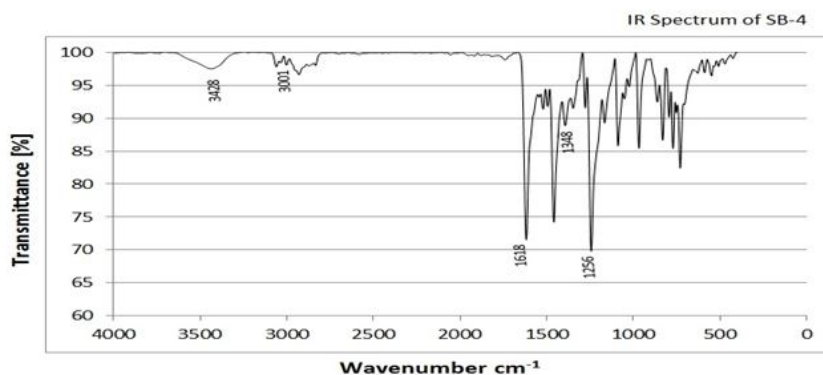
3.4 FTIR Spectral Analysis:

The IR spectra of complexes are compared with those of ligand in order to determine the coordination sites that may be involved in chelation. The prominent FTIR data with the assignments of bond frequencies of Schiff base ligand (SB-4) and its Co(II),Ni(II) and Cu(II) metal complexes are presented in Table-2 and FTIR spectra of these compounds are represented in Figure-2.

Table-2: FTIR Spectral data (cm⁻¹) of Schiff base ligand and its metal complex

Assignments	SB-4	SB-4-Ni
ν (Hydrogen bonded O-H)	3428	-
ν (Coordinated water)	-	3328
ν (C=N)	1618	1605
ν (Ar-O)	1244	1269
ν (C-N)	1348	1380
ν (O-CH ₃)	3001	3003
ν (H ₂ O rocking)	-	833
ν (M-O)	-	558
ν (M-N)	-	429

The broad peak observed at 3328 cm⁻¹ in the IR spectra of Schiff base ligand assigned to ν (O-H), was found to be disappeared in all the complexes, thereby indicating deprotonation and formation of metal-oxygen bond. This is further supported by the shifting of phenolic ν (Ar-O) towards higher frequency, indicating the coordination of phenolate oxygen to metal ion. The ν (C=N) vibration of the Schiff base ligand (SB-4) occurs at 1618 cm⁻¹, which is shifted to a lower frequency of the complexes, indicating the involvement of azomethine nitrogen in chelation with the metal ion. The observed increase in magnitude of ν (C-N) on complexation may be attributed to increase in double bond character of aryl azomethine C-N bond. It is due to π electron delocalization from the metal ion to the nitrogen atom and resonance interaction with the benzene ring. However the stretching frequencies of Methoxy O-CH₃ bonds for ligand and complexes are almost same, indicating the nonparticipation of methoxy oxygen in coordination. The new bands in IR spectra of complexes at 549 cm⁻¹ and 434 cm⁻¹ are ascribed to ν (M-O) and ν (M-N) vibrations respectively. In the IR spectra of complex appearance of a new broad band at 3330 cm⁻¹ corresponding to the stretching frequency of ν (O-H) of H₂O indicated the presence of coordinated water. It is further confirmed by the appearance of non-ligand band in complex at 833 cm⁻¹ assignable to rocking mode of water. Presence of two molecules of coordinated water in molecules of metal complexes is further confirmed by their thermogravimetric analysis. From the above observations, it can be concluded that the ligand behaves as bidentate coordinating through deprotonated phenolic oxygen and azomethine nitrogen [20-33].



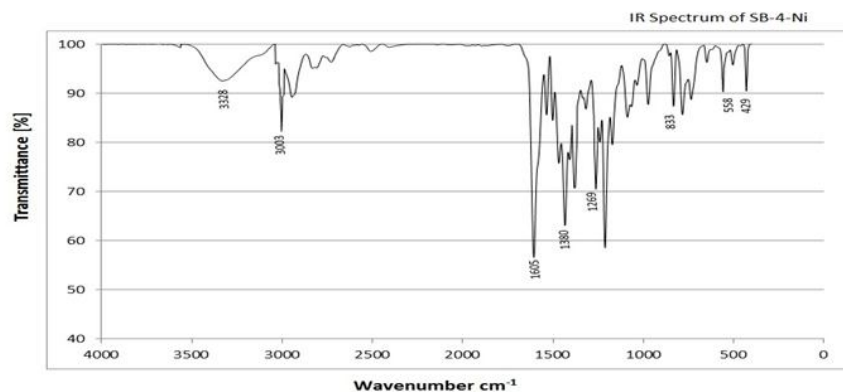


Figure-2: FTIR spectra of Schiff base-4 and its metal complex

3.5 Thermal decomposition studies of metal complex:

Thermal decomposition studies of metal complex have been undertaken to know the presence or absence of coordinated water molecules. Thermal decomposition data of metal complexes of Schiff base -4 is reported in Table-3. The thermograms of complexes are shown in Figure-3

Table-3 : Thermal data of metal complex

Complex	Temperature (°C)	Loss of molecule	Percentage weight loss	
			Calculated	Observed
SB-4 Ni	180°C-240°C	2H ₂ O	5.54	5.71
	240°C-560°C	Org. moiety	85.40	83.56
	>560°C	NiO	11.51	11.42

In case of Ni(II) complex observed weight loss of 5.71% between temperature range 180°C-240°C indicated the presence of two molecules of coordinated water (calculated 5.54%). The anhydrous compound further decomposed rapidly between 240°C-560°C with 83.56% weight loss corresponding to decomposition of organic moiety of the complex (calculated 85.40%) leading to the formation of 11.42% stable residue of nickel oxide (calculated 11.51%) above 560°C. The complex is found to follow two step decomposition patterns. In the first step there is loss of two molecules of coordinated water and in the second step there is oxidative decomposition of organic part of the ligand leading to the formation of stable residue of metal oxide. Thermal studies supported the octahedral structure of the metal complex indicating presence of two coordinated water molecules [15-25].

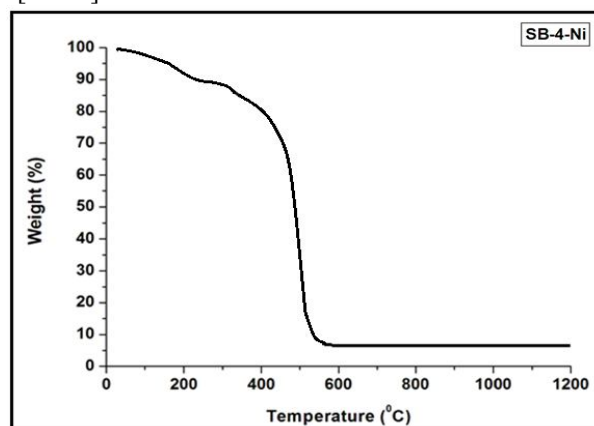


Figure-3 : Thermogram of metal complex

3.8X-Ray diffraction study of metal complex:

The Ni(II) metal complex of Schiff base ligand SB-4 showed sharp peaks in its diffractogram (Figure-6) indicating sharp crystalline nature of metal complex. The observed interplanar d-spacing values of the metal complex have been found to be in good agreement with their observed values (Table-3). Further, indexed data of the metal complex indicated $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$ which clearly support the orthorhombic crystal system with primitive (P) Bravais type for metal complex[30-33].

Table-3: X-Ray Diffraction Data of Metal Complex SB-4-Ni

Pos. [$^\circ 2\theta$.]	Height [cts]	FWHM [$^\circ 2\theta$.]	d-spacing [\AA]	Rel. Int. [%]
6.6708	135.25	0.3149	13.25070	4.62
8.3589	2928.68	0.3149	10.57808	100.00
9.4080	2839.90	0.3149	9.40070	96.97
10.6421	109.05	0.3149	8.31318	3.72
12.5963	1387.30	0.3149	7.02752	47.37
15.4062	540.75	0.3149	5.75155	18.46
16.9456	528.72	0.3149	5.23238	18.05
18.0330	595.12	0.3149	4.91923	20.32
20.7346	676.70	0.3936	4.28399	23.11
23.8699	1301.61	0.3149	3.72791	44.44
25.4185	41.33	0.4723	3.50420	1.41
30.2417	146.38	0.3936	2.95541	5.00
31.3782	587.61	0.3149	2.85092	20.06
32.8422	162.73	0.3149	2.72710	5.56
34.6129	56.27	0.3149	2.59154	1.92
35.6244	41.01	0.3149	2.52024	1.40
36.4929	225.84	0.3149	2.46223	7.71
39.4991	32.79	0.3149	2.28149	1.12
41.1038	97.29	0.3149	2.19606	3.32
41.8817	50.53	0.4723	2.15705	1.73
44.0182	47.84	0.4723	2.05718	1.63
49.0712	30.26	0.4723	1.85652	1.03
56.1487	25.56	0.4723	1.63814	0.87
59.1899	20.90	0.3840	1.55973	0.71

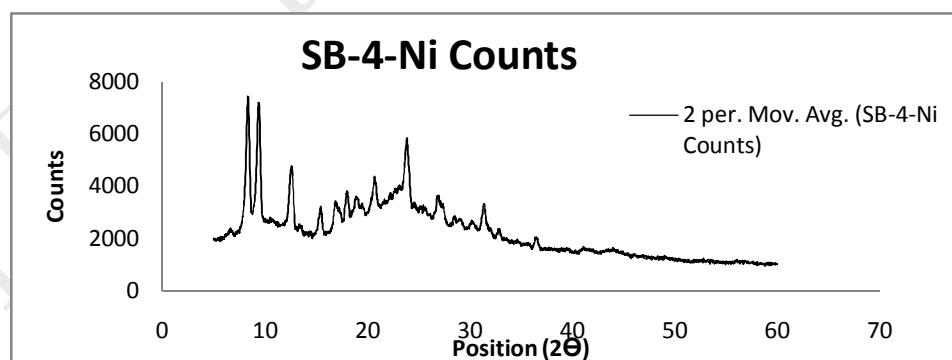


Figure 6: X-Ray Diffractogram of Metal Complex SB-4-Ni

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REFERENCES:

- [1] G. Y. Nagesh, U. D. Mahadev, B. H. M. Mruthyunjayswamy, *Int. J. Pharm. Sci. Rev.*, 31(1) (2015) 190-197.
- [2] P. Rajavel, M.S.S.C. Anitha, *European J. of Chemistry*,5(3) (2008) 620.
- [3] E.A. Keskioglu, B.G. Hamuraw, *Spectrochimica Acta Part A*,70(3) (2008) 634
- [4] C. Aladin, Ibrahim Yilmaj, Alabibe Ozman and Misir Ahmedizade, *Trans. Met.Chem.* 27 (2002) 171.
- [5] M. B. Fugu, N.P. Ndahi, B.B. Paul and A.N. Mustapha, *J. Chemical and Pharmaceutical Research*, 5(4) (2013) 2.
- [6] A.H. Manikshete, M.M. Awatade, S.K. Sarsamkar, M.R. Asabe, *International J. of Engg. Sci. Invention* Vol. 4, Issue 1 (2015) 22.
- [7] RojiJahan, *International Journal of Multidisciplinary Research and Development*, Vol.2, Issue:7, (2015) 472-473.
- [8] Sanjit Nayak, Patrick Gamez, Bojan Kozlevcar, Andrej Pevec, Olivier Roubeau, Stefanie Dehnen, Jan Reedjik, *Polyhedron* 29 (2010) 2291.
- [9] E.V. Shekhar, K.N. Jayaveera and S. Srihari *J. of Chemical and Pharmaceutical Research*, 4(12) (2012) 5121.
- [10] J. Bassett, R. C. Denny, G. H. Jeffery and J. Mendham, *'Vogel's Text Book of Quantitative Inorganic Analysis*, ELBS Longman, England P 849-868 (1985).
- [11] M. C. Day (Jr) and Selbin J., *'Theoretical Inorganic Chemistry'*, 2nd Edition. Affil. East West Press, New Delhi P 483-486 (1971).
- [12] D. A. Skoog, *"Principles of Instrumental Analysis"* 3rd International Edition, Holt Saunders College Publisher, New York P 344-346, 484, 713-726 (1968).
- [13] Earnshaw, *'Introduction to Magneto chemistry'* U. S. Ed. Academic press Inc. New York (1968).
- [14] K. Burger, *"Coordination Chemistry Experimental Methods"*, First Edition, East West Press New Delhi, P 215 (1972).
- [15] R.M. Silverstein, G.C. Bassler and T.C. Norris "Spectrometric Identification of Compounds" John Wiley and Sons, 4th edition. (1981).
- [16] K. Nakamoto *Infrared and Raman Spectra of Inorganic coordination compounds*, 5th ed., John Wiley and Sons. New York, (1998).
- [17] D.T. Sakhare, T.K. Chondhekar, S.G. Shankarwar and A.G. Shankarwar, *Pelagia Research Library, Advances in Applied Science Research*, 6(6) (2015) 10.
- [18] Masoumeh Orojloo, FereshTech Nourian Raziyeen Arabahmadi, Saeid Amani, *Quimica Nova*, Vol. 38, No.9, Sao Paulo Nov. (2015).
- [19] K. Siddappa and Nabiya Sultana Mayana, Hindawi Publishing Corporation *Bioinorganic Chemistry and Applications*, Volume 2014, Article ID 483282.
- [20] W.W. Wendladt, *'Thermal methods of analysis'* Heyden Philadelphia (1977).
- [21] K. Miyokawa and H. Wakida, *Thermo Chimica Acta* 21 (1991) 182.
- [22] R. Selwin Joseyphus; C. Shiju; J. Joseph; C. Justin; Dhanaraj and K.C. Bright *Der Pharma Chimica* 7(6) (2015) 265.
- [23] W. Kemp, *'Organic Spectroscopy'* McMillan Press Ltd. 2nd Edition (1991).
- [24] E.F. Bowersand, L.R. Jeffries, *J. Clin. Patho.* 8 (1995) 58.
- [25] Srinivasan Durairaj, Sangeetha, Srinivasan, P. Lakshmana Perumalasamy, *Elect. J. of Biol.*,5 (1) (2009) 5.
- [26] B. Rizwana, Santha Lakshmi S. *International J. ChemTech Research*, Vol.4, No.1, (2012) 464.
- [27] A.A. Osowale and S.A. Balogun, *Eur. J. Applied Sciences* 4(1) (2012) 06.
- [28] Bao-dui Wang Zheng-Yin Yang et al., *J. Photochem. Photobiol. A*, 194 (2008) 49.
- [29] Houghton Peter et al., *Methods*, 42 (2007) 377.
- [30] M. M. Lubran *Ann Clin. Lab.Sci.* 19 (1989) 114.

- [31] Devajani Chakraborty, Barakha Shah *International Journal of Pharmacy and Pharmaceutical Sciences* Vol.3 (2011) 192.
- [32] V. L. Borde, S. G. Shankarwar, C. D. Thakur, A. G. Shankarwar, *Advances in applied science and research*, (2014) 5(6), 229-235.
- [33] S. A. Deodware, S. H. Gaikwad, U. B. Chanshetti, D. J. Sathe, *Der Pharma Chemica* (2015), 7(7), 365-372.