



# THERMAL & SPECTROSCOPIC INVESTIGATIONS OF NOVEL SCHIFF BASE LIGAND [1-(2-HYDROXY-1-NAPHTHYL)ETHANONE-4-NITROBENZENAMINE] & THEIR METAL COMPLEXES

<sup>1</sup>Abdul Wajid, <sup>2</sup>N. R. Nahate, <sup>1</sup>C. A. Ladole

<sup>1</sup> Assistant Professor, Department of Chemistry, Shri Shivaji Arts, Commerce and Science College, Akot, Dist. Akola

<sup>2</sup> Assistant Professor, Department of Chemistry, Shri R. R. Lahoti Science College, Morshi  
wajidabdul871@gmail.com, nageshnahate@gmail.com, ladoleshekhar2@gmail.com

**Abstract—** Certain metal complexes exhibit different characteristic properties depending on the nature of the metal as well as the type of ligand. A novel schiff base ligand was prepared by condensation of [1-(2-Hydroxy-1-naphthyl)ethanone](HNET) and 4-Nitrobenzenamine(NBA). Its metal complexes of Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) was characterised and investigated by physical and spectral techniques, namely, elemental, electrical conductance, molecular weight, IR, electronic spectra, magnetic susceptibility measurements and thermogravimetric analysis.

Thermal properties and decomposition possibilities of all complexes are suggested. Detailed studies of the thermal properties of the complexes were investigated by thermogravimetric techniques. The interpretation of all thermal decomposition stages has been evaluated. The complexes are found to be colored and stable in air at room temperature.

**Index Terms—** azomethine linkage, decomposition possibilities, Spectral techniques, thermal studies.

## INTRODUCTION

From more than last one decade, there has been a dramatic growth of interest in inorganic complexes based materials that exhibit unusual properties [1]. Schiff bases derived from an amine and aldehyde/ketones are an important

class of ligands that coordinate to metal ion via azomethine nitrogen and have been studied extensively [2]. Schiff base complexes have been found to be important precursor for semi conducting materials [3, 4]. Various studies have shown that Schiff base derived from substituted acetophenone containing nitrogen/sulphur and/or oxygen as ligand atoms are of interest as simple structural models of more complicated biological systems application such as biochemical, analytical, industrial [5-6] and their metal complexes shown wide spectrum of antimicrobial agents. In the present paper, we report the synthesis and thermal studies of complexes derived from [1-(2-Hydroxy-1-naphthyl)ethanone](HNET) and 4-Nitrobenzenamine(NBA)

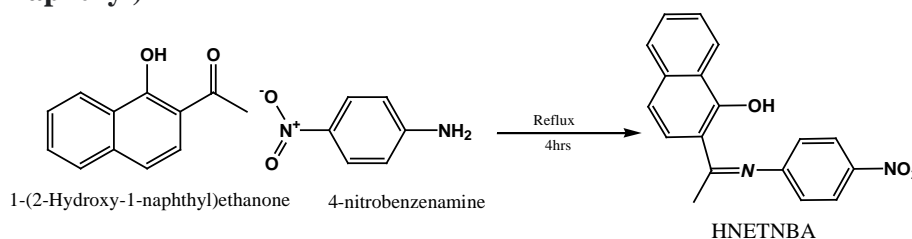
## MATERIALS AND METHOD

Manganese(II), cobalt(II), nickel(II), chromium(III), copper(II), zinc(II), and cadmium(II) acetate salts used were of Merck and BDH make. Organic solvents such as absolute ethanol, methanol, petroleum ether, dimethyl formamide (DMF) and dimethylsulfoxide (DMSO) were of AR grade from [1-(2-Hydroxy-1-naphthyl)ethanone] was prepared by known methods. The solvents were purified by standard methods. Elemental microanalysis was performed on a (C.H.N.) analyser from heraeus (Vario EL). IR spectra of the compounds were recorded on Perkin Elmer 842 spectrophotometer in the region 400-4000cm<sup>-1</sup>. <sup>1</sup>H-NMR spectrum of the ligand

was recorded in DMSO-d<sub>6</sub> on a Bruker DRX-300 FTNMR spectrometer. The diffuse reflectance spectra of the complexes were recorded on Varian Cary-5000 UV-visible spectrophotometer. The magnetic moment measurement were made on a Gouy balance at room temperature using [HgCo(SCN)<sub>4</sub>] as the calibrant.

### EXPERIMENTAL TECHNIQUE

#### Synthesis of Schiff base ligand [1-(2-Hydroxy-1-naphthyl)



**Fig.1** [1-(2-Hydroxy-1-naphthyl)ethanone-4Nitrobenzenamine] (HNETNBA)

#### Synthesis of Schiff base metal complexes

The Mn(II), Co(II), Ni(II), Cr(III), Cu(II), Zn(II) and Cd(II) complexes have been prepared by mixing the methanolic-ethanolic solution of corresponding metal acetates to the ethanolic solution of HNETNBA in 1 : 2 molar ratio. The precipitated complexes were recrystallized twice with ethanol, finally washed with petroleum ether (60– 80 °C), and dried under reduced pressure over anhydrous CaCl<sub>2</sub> in a dessicator.

**ethanone-4Nitrobenzenamine] (HNETNBA)**  
The experimental procedure involved mixing of [1-(2-Hydroxy-1-naphthyl)ethanone](HNET) 1 mmol (1.86gm) and 4-Nitrobenzenamine(NBA) 1 mmol (1.38g) dissolve in ethanol, dissolve in ethanol, mix in 250 ml round bottom flask. And the reaction mixture was refluxed on water bath for about 4 hour. Product is filtered and dry. Yellowish white solid obtained having melting point 175 °C.

### RESULTS AND DISCUSSION

The synthesized complexes are colored, stable and non-hygroscopic solids and are insoluble in water, ethanol and methanol but soluble in DMF and DMSO. The analytical data indicate 1:2 metal to ligand stoichiometry for all the complexes. All the complexes are found to be non-electrolytes [7-9]. The colors, magnetic susceptibilities as well as the percentage composition of the constituent elements are reported in Table 1.

**Table 1: Analytical Data of HNETNBA and its Complexes**

S.N.	Compounds	Color	Time of Reflux (hrs.)	Elemental analyses % found (calcd.)				
				M	C	H	N	Cl
1.	HNETNBA	Pale Yellow	4	--	54.21 (54.91)	4.24 (4.07)	3.22 (3.77)	--
2.	[Mn(HNETNBA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] (H <sub>2</sub> O)	Light Brown	9	14.98 (14.19)	52.12 (52.72)	3.60 (3.87)	3.52 (3.61)	--
3.	[Co(HNETNBA) <sub>2</sub> ]	Off Brown	5	15.59 (15.04)	52.46 (52.18)	3.95 (3.87)	3.41 (3.58)	--
4.	[Ni(HNETNBA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Pale Orange	5	15.12 (15.02)	52.48 (52.21)	3.98 (3.83)	3.45 (3.58)	--
5.	[Cr(HNETNBA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] (H <sub>2</sub> O) <sub>2</sub>	Apple Green	5	13.50 (13.53)	53.35 (53.12)	3.56 (3.90)	3.20 (3.64)	--
6.	[Cu(HNETNBA) <sub>2</sub> ](H <sub>2</sub> O)	Raven Song	8	16.28 (16.06)	51.42 (51.57)	3.86 (3.97)	3.42 (3.79)	--

7.	[Zn(HNETNBA) <sub>2</sub> ]	Pale Yellow	7	16.70 (16.45)	57.72 (57.33)	3.80 (3.77)	5.38 (3.52)	--
8.	[Cd(HNETNBA) <sub>2</sub> ] (H <sub>2</sub> O)	Yellow	7	25.13 (25.29)	45.72 (45.90)	3.56 (3.37)	3.00 (3.15)	--

**FT-IR (KBr, in cm<sup>-1</sup>)**

The characteristic infrared spectral assignment of ligand and its complexes have been reported in Table 2. The presence of broad band at 3587 cm<sup>-1</sup> in the infrared spectra may be due to the -OH group. All the above evidences were further supported by the emergence of new bands at 516-519 cm<sup>-1</sup> due to the metal-oxygen vibrations. These new bands were only observed in the spectra of the transition metal complexes only.

Selected IR spectral bands for the ligand and its complexes are given in Table 2. The IR spectrum of the free ligand is characterized mainly by the strong bands at 1698cm<sup>-1</sup>, 3587cm<sup>-1</sup>, and 1247 cm<sup>-1</sup> which are attributed to

the stretching frequencies of C=N (azomethine), O-H and C-O respectively[10]. The band at 1698 cm<sup>-1</sup> due to C=N stretching in the spectrum of the ligand shifts to lower wave numbers in all the metal complexes by 7-10 cm<sup>-1</sup> indicating that the azomethine nitrogen is co-ordinated to metal ion [11]. Further the IR spectra of the complexes of Co(II), Ni(II), Zn(II) and Cd(II) exhibit new bands at 519 and 459 cm<sup>-1</sup> and 516 and 443cm<sup>-1</sup> which may be assigned to M-O and M-N (terminal) stretching modes respectively [12]. IR spectra of the Schiff base showed a band at around 1610 cm<sup>-1</sup> assignable to azomethine group.

**Table 2: FT - IR spectral frequencies of selected metal complexes.**

Sr. No	Compounds	Assignment (cm <sup>-1</sup> )	Observed Value (cm <sup>-1</sup> )	Expected Value (cm <sup>-1</sup> )
1)	Ligand HNETNBA	V(C=N) V(O-H)/v(OH-N)H <sub>2</sub> O	1583.56 1211.30	1777-1600 1330-1063
2)	Co(II) HNETNBA	(C-O) (M-O) (M-N) (O-H) (O-CH <sub>3</sub> ) (Ar-C-H)	1251.80 530.42 426.27 3286.70 1749.44 3147.83	1330-1063 524-420 524-410 3600-3300 1725-1745 3200-3000
3)	Ni(II) HNETNBA	(C-O) (M-O) (M-N) (O-H) (O-CH <sub>3</sub> ) (Ar-C-H) (C=N)	1301 528.50 435.91 3307.92 1747.51 3147.83 1749.44	1330-1063 524-420 524-410 3600-3300 1725-1745 3200-3000 1777-1600
4)	Zn(II) HNETNBA	(C-O) (M-O) (M-N) (O-H) (O-CH <sub>3</sub> ) (Ar-C-H) (C=N)	1254 528.50 435.91 3307.92 1747.51 3147.83 1745.44	1330-1063 524-420 524-410 3600-3300 1725-1745 3200-3000 1777-1600

5)	Cd(II) HNETNBA	(C-O)	1312	1330-1063
		(M-O)	550.50	524-420
		(M-N)	435.91	524-410
		(O-H)	3307.92	3600-3300
		(O-CH <sub>3</sub> )	1747.51	1725-1745
		(Ar-C-H)	3005.50	3200-3000
		(C=N)	1749.44	1777-1600

### Thermal study and Magnetic study

The presence of water molecule suggested from IR spectra is confirmed by TG analysis [13]. Thermal decomposition results reveal that all the metal complexes decompose gradually. The TG curve of Mn(II) show stable plateau upto 62°C then weight loss is observed indicating the presence of one lattice water molecule [% wt loss obs./cal. 4.00:4.07]. The observed weight losses of Mn(II), Ni(II), Cr(III) complexes between 140-240°C corresponds to removal of three coordinated water molecule [% wt loss obs./calc. 12.10/12.21, 12.34/12.64, 11.25/11.79 ]. The observed magnetic moment of Mn(II), Ni(II) and Cr(III) complexes found to be 5.67, 3.1 and 4.81 B.M., indicating octahedral environment around central metal ion. Cu(II) and Zn(II) complex loss its weight upto 130 °C and 110 °C respectively corresponding to one lattice water [% wt loss obs./calc. 4.21/4.33, 4.60/4.51] and further upto 250 °C and 241°C corresponding to one coordinated water molecule [% wt loss obs./calc. 4.40/4.33, 4.50/4.51]. The TG curve of

Co(II) and Zn(II) complexes show stable plateau upto 77 °C and 80 °C respectively indicating absence of lattice water molecule from the metal complexes. The magnetic moment value of Cu(II) complex is found to be 1.78 B.M which is well within the expected range of square planar complexes. For Co(II) complex the magnetic moment value i.e. 2.44 B.M. is lower than those expected for square planar geometry. This lowering in magnetic moment value shows subnormal character of complex due to antiferromagnetic exchange [14]. The complexes of Zn(II) and Cd(II) were found to be diamagnetic, confirmed tetrahedral geometry. Complete decomposition of metal takes place in two steps. In the first step of decomposition in the temperature range 220-380 °C, indicate the decomposition of free part of ligand. In the second stage, major loss occurs between 410-600 °C, due to complete elimination of organic ligand molecule and subsequent slow oxidation. The remaining residue of the complexes at 600-710 °C corresponds to respective metal oxides [15].

**TABLE 3: Thermal decomposition data of the complexes of HNETNBA**

S.N.	Compound	DH (°C)	$\mu_{\text{eff}}$ (B.M.)	E (kJmol <sup>-1</sup> )		Z (S <sup>-1</sup> )	-ΔS (JK <sup>-1</sup> mol <sup>-1</sup> )	ΔF (kJ mol <sup>-1</sup> )	
				F-C	S-W				
1.	HNETNBA	260	---	5.50	4.35	85.20	229.45	110.52	
2.	[Mn(HNETNBA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](H <sub>2</sub> O)	410	5.67	17.50	15.10	225.44	240.12	310.25	
3.	[Co(HNETNBA) <sub>2</sub> ]	430	2.44	8.55	7.50	171.14	201.32	165.23	
4.	[Ni(HNETNBA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	380	3.1	5.25	3.35	156.11	226.30	123.65	
5.	[Cr(HNETNBA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](H <sub>2</sub> O) <sub>2</sub>	550	4.81	12.90	10.85	214.71	200.00	193.32	
6.	[Cu(HNETNBA) <sub>2</sub> ](H <sub>2</sub> O)	490	1.78	10.20	9.15	198.13	201.34	164.28	
7.	[Zn(HNETNBA) <sub>2</sub> ]	400	---	9.60	7.90	189.28	240.26	153.89	

8.	[Cd(HNETNBA) <sub>2</sub> ] (H <sub>2</sub> O)	420	---	16.05	14.65	226.69	211.89	269.60
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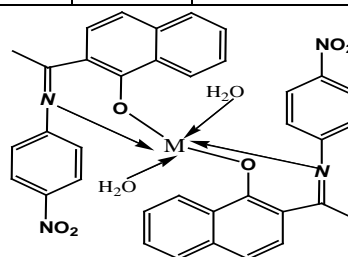
F-C = Freeman-Carroll, S-W =  
Sharp-Wentworth, DH - Half  
Decomposition temp.

Various kinetic and thermodynamic parameters such as activation energy ( $E$ ), half decomposition temperature (DH), frequency factor ( $Z$ ), entropy change ( $\Delta S$ ) and free energy change ( $\Delta F$ ) were calculated from TG data as shown in the Table 3. The kinetic parameter i.e. energy of activation has been calculated by Freeman–Carroll and sharp-Wentworth methods. Generally with decreasing the value of  $E$  the value of  $Z$  increase and the higher value of activation energy suggest the higher stability. Higher value of  $E$  (activation energy) and lower values of  $Z$  (frequency factor) favors the reaction to proceed slower than normal. The large negative values of entropy change and small  $Z$  suggest that the transition state is in highly ordered state than the individual reactants and the reactions are slower than normal.

Thermal stability of complexes follows the order Cr(III) > Cu(II) > Co(II) > Cd(II) > Mn(II) > Zn(II) > Ni(II).

## CONCLUSION

The coordination complexes of Mn(II), Co(II), Ni(II), Cr(III), Cu(II), Zn(II) and Cd(II) with new tridentate Schiff base ligand, *i.e.*, [1-(2-Hydroxy-1-naphthyl)ethanone-4-Nitrobenzamine] (HNETNBA), was synthesized and characterized. The ligands coordinated with the metal ions through N or O donors (ONO type). From the analysis it can be concluded that the complexes have an octahedral structures for [Mn(HNETNBA)(H<sub>2</sub>O)<sub>3</sub>](H<sub>2</sub>O), [Ni(HNETNBA)(H<sub>2</sub>O)<sub>3</sub>] and [Cr(HNETNBA)(H<sub>2</sub>O)<sub>3</sub>](H<sub>2</sub>O)<sub>2</sub>, square planar for [Co(HNETNBA)(H<sub>2</sub>O)], [Cu(HNETNBA)(H<sub>2</sub>O)](H<sub>2</sub>O) metal and tetrahedral structure for [Zn(HNETNBA)(H<sub>2</sub>O)] and [Cd(HNETNBA)(H<sub>2</sub>O)](H<sub>2</sub>O). The suggested geometrical structure is shown below:



Where, M = Mn(II), Co(II), Ni(II), Cr(III), Cu(II), Zn(II) and Cd(II)  
for Co(II), Cu(II), Zn(II) and Cd(II); H<sub>2</sub>O=0

## REFERENCES

- [1] Abdul Wajid, Naushad Zubair, Mohod Rahul B, Journal of Chemical and Pharmaceutical Research, vol. 5, no.4, pp.133-137, 2011.
- [2] Rahul. B. Mohod, Abdul Wajid, Am. J. Pharm. Tech. Res., vol. 3, no.2, pp. 752-758, 2012.
- [3] J. T. Makode, S. G. Bhadange, A. S. Aswar, Polish J. Chem., vol. 77, pp. 855–865, 2003.
- [4] B.N. Figgis and J. Lewis, Progress Inorg. Chem., vol. 6, pp. 192. 1965
- [5] S.R. Kelode, P. R. Mandlik, Int J Chem. Sci. & Tech; vol. 2, pp. 231-235, 2012
- [6] Rahangdale Murlidhar, Pethe Gaurav, Yaul Amit, Aswar Anand, RJPBCS, vo.2, no.3, pp.341-348, 2011.
- [7] M. A Hassaan, K Shehata. Synth. React. Inorg. Met-Org. Chem., 25(3), 815, 1993.
- [8] S. Konstantinovic, B. Radovanovic, J. Serb. Chem. Soc., vol. 68, pp. 641, 2003.
- [9] K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, 2<sup>nd</sup> ed, Wiley-Inter Science, 172, 1963.
- [10] S. Leela, K. Ramamurthi, G. Bhagavannarayana, Spectrochim. Acta, vol. A74, pp. 78, 2009.
- [11] K. Nakamoto, "Infrared and Raman spectra of Inorganic and Coordination Compounds", 4<sup>th</sup> ed., John Wiley and Sons, 1986.
- [12] M. Ashraf., K. Mahmood, A. Wajid. Chem. Process, vol. 10, pp.1-7, 2011
- [13] G. G. Mohamed, M. M. Omar Ahmed and M. Hindy, Turk J Chem., vol. 30, pp. 361 – 382, 2006.
- [14] Samik Gupta et al, Polyhedron vol. 27, pp. 2519, 2008.
- [15] D. T. Masram, K. P. Kariya and N. S. Bhawe. High Performance Polymers, vol. 8, pp.1004-1016, 2010.