



# SYNTHESIS, SPECTROSCOPIC, THERMAL AND KINETIC PARAMETERS STUDIES OF SOME NOVEL COORDINATION POLYMERS

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## ABSTRACT

The coordination polymers of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with newly synthesized adipoyl bis-nicotinamide ligand derived from adipoyl dichloride and nicotinamide have been synthesized by refluxing metal acetate and ligand in 1:1 stoichiometric ratio. These coordination polymers have been characterized by various instrumental techniques. Thermogravimetric analysis (TGA) has been used to determine thermal stability and some kinetic parameters of coordination polymers have been studied by using Sharp–Wentworth, Freeman–Carroll and Broido methods. The decomposition temperatures of the polymers were determined by half decomposition curve technique.

**Keywords:** Coordination polymers, Thermal studies, Kinetic parameters

## 1. Introduction

Coordination polymers having good thermal stability have enhanced the scope for development of some polymeric materials [1]. The coordination polymer  $\{[NiL][Co(NCS)_4]\}_n$  (where L = 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) have been studied for exhibiting good thermal stability[2]. The thermal stabilities and kinetic parameters of Coordination polymers of pimeloyl bis-2-

aminobenzothiazole with transition metal ions have been studied [3]. In the present paper we describe the synthesis, thermal and kinetic parameters studies of coordination polymers of ligand adipoyl bis-nicotinamide (ABNA) with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) metal ions.

## 2. Experimental

### 2.1 Materials:

All chemicals used were of analytical grade. Solvents were dried and distilled according to standard methods.

### Synthesis of ligand adipoyl bis-nicotinamide(ABNA)

Adipoyl bis-nicotinamide (ABNA) ligand have been synthesized by refluxing nicotinamide and adipoyl dichloride in 2:1 stoichiometric ratio in dry acetone medium[4]. The product was recrystallized to give ABNA(70%) yield, m.p found to be 218 OC (uncorrected).

### Synthesis of coordination polymers of ABNA ligand

Coordination polymers of adipoyl bis-nicotinamide have been synthesized by dissolving metal acetates and ligand in 1:1 mole ratio in dimethyl formamide. These newly synthesized coordination polymers were found to be insoluble in almost all organic solvents.

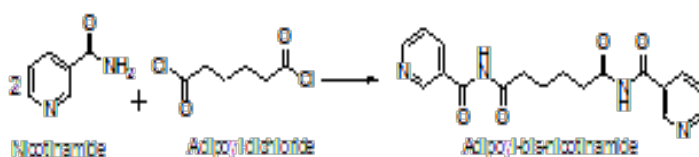


Fig. 1

### 3. Result and Discussion:

On the basis of analytical data obtained from various instrumental techniques the proposed structure of coordination polymers have been shown in Fig. (3). The elemental data of ligand and coordination polymers has been given in Table 1.

The IR spectral data of ligand and coordination polymers is presented in Table 2. The IR spectra of ligand exhibit strong bands at 1708.8  $\text{cm}^{-1}$  due to presence of C=O group which is shifted to 1691.6 -1699.0  $\text{cm}^{-1}$ . This suggests the involvement of C=O group in coordination. While the another C=O group frequency at 1686 and a sharp band at 3246.6  $\text{cm}^{-1}$ , assigned to -NH- group in the spectra of ligand are totally disappears in coordination polymers and new band is observed around 1625.7-1626.3  $\text{cm}^{-1}$ , due to formation of new C=N band as a result of enolization. This is further supported by the appearance of C-O band, which coordinated to metal ion around 1032.7-1098.3  $\text{cm}^{-1}$  in all coordination polymers. This indicates that bis-ligand undergoes tautomerism during polymerization. The unshifted band frequencies of both aliphatic and aromatic C=N shows no participation in chelation[5].

The electronic spectral data of coordination polymers of ABNA ligand has been given in Table 3. The observed positions of the absorption bands and their assigned transitions are in good agreement with the proposed probable structure for the coordination polymers[6,7]. The effective magnetic moment ( $\mu_{\text{eff}}$ ) values of all the coordination polymers are in good agreement with the expected high spin configurations. Since  $\{[\text{Zn}(\text{II})(\text{ABNA})]\}_n$  is a  $d^{10}$  system and hence is diamagnetic in nature, however, on the basis of elemental analysis, IR spectra and thermal decomposition data, its most probable geometry is suggested to be tetrahedral.

The dynamic (non-isothermal) thermogravimetric analysis of all the coordination polymers has been carried out from room temperature to 1200 $^{\circ}\text{C}$  in air atmosphere at 10 $^{\circ}\text{C min}^{-1}$  heating rate. In the present investigation Sharp-Wentworth, Freeman-Carroll and Briodo methods [8-10] have been used to determine the kinetic parameters of the coordination polymers and their linear plots are depicted in Figs. (4-6)

**Freeman-Carroll method:** In this method, following expression is used to evaluate various kinetic parameters:

$$\frac{\Delta \log dW/dt}{\Delta \log W_r} = (-E_a/2.303R) \frac{\Delta(1/T)}{\Delta \log W} + n$$

where  $dW/dt$  is the rate of change of weight with time,  $W_r = W_c - W$ , where  $W_c$  is the weight loss at completion of reaction or at a definite time  $t$ ,  $T$  is temperature,  $R$  is gas constant, and  $n$  is the order of reaction.

Hence, by plotting  $\frac{\Delta \log dW/dt}{\Delta \log W_r}$  versus  $\frac{\Delta(1/T)}{\Delta \log W}$

$n$  is obtained as an intercept on former axis and  $E_a$  is the slope of the line.

**Sharp-Wentworth method:** The following expression is used to evaluate activation energy:

$$\log\left(\frac{dc/dT}{1-c}\right) = \log(A/\beta) - (-E_a/2.303R) \times 1/T$$

where  $\beta$  is the linear heating rate,  $dT/dt$ .

Therefore, a linear plot of  $\log\left(\frac{dc/dT}{1-c}\right)$  versus  $1/T$  is obtained whose slope gives the value of  $E_a$ .

**Briodo method:** In this method following expression is used:  $\ln\left[\ln\frac{1}{y}\right] = \frac{-E_a}{R} \frac{1}{T} + \left[\frac{R}{E_a} \frac{A}{\beta} T^2 \max\right]$

Where,  $y$  is fraction of initial molecules not yet decomposed,  $y = (w_t - w_\alpha) / (w_0 - w_\alpha)$ ,  $w_0$  is the initial weight of the material and  $w_\alpha$  is the weight of the residue at the end of the degradation.  $T_{\text{max}}$  is the temperature of maximum reaction velocity. A plot of  $\ln(\ln 1/y)$  versus  $1/T$  yield a straight line. The slope is equal  $-E/2.303R$ .

The linear relationship confirmed that assumed order ( $n = 1$ ) is correct. In order to economize the space only representative TG curve of  $\{[\text{Ni}(\text{II})(\text{ABNA})(\text{H}_2\text{O})_2]\text{H}_2\text{O}\}_n$  has been shown in Fig. (2). Thermal activation energy data and kinetic parameters of ABNA coordination polymers at 10 $^{\circ}\text{C}$  is presented in Table 4. The thermogram of Ni(II)ABNA coordination polymer exhibit the mass loss upto 275 $^{\circ}\text{C}$ , which may be due to loss of one molecule of lattice and two coordinated water molecules. After 275-755 $^{\circ}\text{C}$ , a gradual mass loss is observed, due to decomposition of coordination polymer then it forms stable species. The end product obtained by the study of TGA and classical oxide method was nearly same [11].

**Table- 1- Elemental analysis of ligand and coordination polymers:**

Coordination polymers/Ligand	Emperical Formula	Formula weight	Carbon (%)		Hydrogen (%)		Nitrogen (%)	
			Cal	Obs	Cal	Obs	Cal	Obs
ABNA	C <sub>18</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub>	354.358	61.00	61.16	5.11	5.26	15.81	15.92
Mn-ABNA	Mn C <sub>18</sub> H <sub>24</sub> N <sub>4</sub> O <sub>7</sub>	463.288	46.66	46.73	5.22	5.41	12.09	12.13
Co-ABNA	CoC <sub>18</sub> H <sub>24</sub> N <sub>4</sub> O <sub>7</sub>	467.288	46.26	46.33	5.17	5.21	11.98	12.01
Ni-ABNA	NiC <sub>18</sub> H <sub>24</sub> N <sub>4</sub> O <sub>7</sub>	467.048	46.28	46.36	5.17	5.26	11.99	12.09
Cu-ABNA	CuC <sub>18</sub> H <sub>24</sub> N <sub>4</sub> O <sub>7</sub>	471.898	45.81	45.93	5.12	5.20	11.87	11.96
Zn-ABNA	ZnC <sub>18</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub>	419.748	51.50	51.63	4.32	4.48	13.34	13.47

**Table- 2- Infrared spectral studies of ligand and coordination polymers:**

Compound	-NH-	C= O	C= N (arom)	C=N (alph)	M-O	C-O	-CH <sub>2</sub>	H-O-H Coordinated water
ABNA	3246.6	1708.8	1580.9	---	---	----	2941.8	----
MnABNA	---	1694.7	1580.7	1626.3	520.9	1057.1	2948.9	823.7
CoABNA	----	1691.6	1580.8	1626.2	537.4	1049.4	2952.8	823.8
Ni-ABNA	----	1699.6	1580.8	1626.2	532.8	1098.3	2950.8	821.8
CuABNA	----	1697.3	1580.7	1625.7	543.7	1034.0	2945.7	816.8
Zn-ABNA	----	1699.0	1580.6	1625.9	524.7	1032.7	2949.5	---

**Table- 3- Electronic Spectral Studies of ABNA Coordination Polymers: :**

Coordination Polyme rs	Absorbance (kK)	Assignme nts	Stereochemi stry	Effective magnetic moment( $\mu_{\text{eff}}$ )
{[Mn(II)(ABNA)(H <sub>2</sub> O) <sub>2</sub> ](H <sub>2</sub> O) <sub>2</sub> }]n	23.40	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>2g</sub>	Octahedral	5.83
{[Co(II)(ABNA)(H <sub>2</sub> O) <sub>2</sub> ](H <sub>2</sub> O) <sub>2</sub> }]n	20.00 15.38	<sup>4</sup> T <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub> (P) <sup>4</sup> T <sub>1g</sub> → <sup>4</sup> A <sub>2g</sub>	Octahedral	4.21
{[Ni(II)(ABNA)](H <sub>2</sub> O) <sub>2</sub> }]n	24.69 14.18	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> (P) <sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> (F)	Octahedral	3.18
{[Cu(II)(ABNA)(H <sub>2</sub> O) <sub>2</sub> ](H <sub>2</sub> O) <sub>2</sub> }]n	16.52 14.08	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> E <sub>g</sub> <sup>2</sup> B <sub>1g</sub> → <sup>2</sup> B <sub>2g</sub>	Distorted Octahedral	2.02

**Table- 4- Data of thermogravimetric analysis of ABNA Coordination polymers:**

Coordination polymers	Activation energy (E <sub>a</sub> )/ kJ mol <sup>-1</sup>			Entropy change $\Delta$ (S)/J	Free energy Change $\Delta$ (F)/kJ	Frequency factor (Z)/S <sup>-1</sup>	Apparent entropy change (S <sup>*</sup> )/J	Order of Reaction (n)	Decomposition Temperature/ <sup>o</sup> C
	SW	FC	BR						
{[Mn(II)(ABNA)(H <sub>2</sub> O) <sub>2</sub> ](H <sub>2</sub> O) <sub>2</sub> }]n	15.01	14.11	16.60	-226.44	135.03	327.01	-202.81	1.07	341
{[Co(II)(ABNA)(H <sub>2</sub> O) <sub>2</sub> ](H <sub>2</sub> O) <sub>2</sub> }]n	10.51	12.97	14.57	-226.41	133.65	74.07	-215.41	1.09	360
{[Ni(II)(ABNA)(H <sub>2</sub> O) <sub>2</sub> ](H <sub>2</sub> O) <sub>2</sub> }]n	12.92	14.48	18.11	-229.96	145.11	98.41	-213.37	1.07	385
{[Cu(II)(ABNA)(H <sub>2</sub> O) <sub>2</sub> ](H <sub>2</sub> O) <sub>2</sub> }]n	13.80	14.92	17.04	-220.81	127.31	462.28	-199.58	1.01	316
{[Zn(II)(ABNA)]}n	24.37	21.67	25.10	-215.87	139.97	1529.70	-190.30	0.95	405

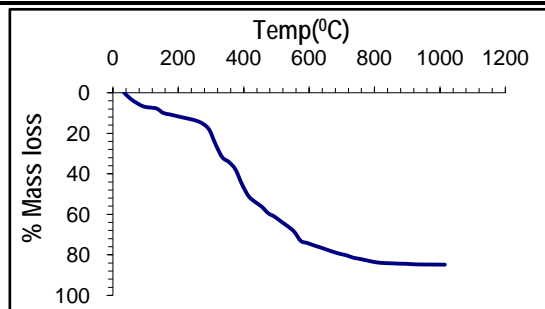


Fig.2 Thermogram of {[Ni(II)(ABNA)(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O}<sub>n</sub> Coordination Polymer y

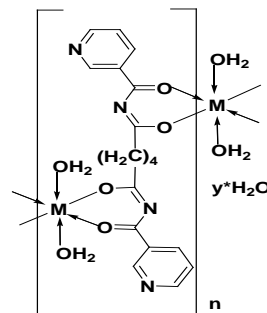


Fig. 3 Proposed structure of coordination Polymers \*H<sub>2</sub>O--lattice water. For all ABNA coordination polymers y=1

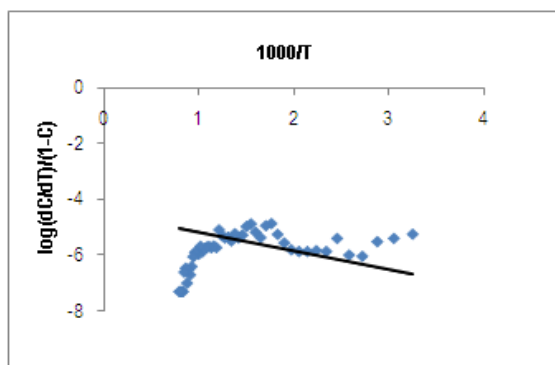


Fig. 4 Sharp Wentworth plot for activation energy of {[Ni(II)(ABNA)(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O}<sub>n</sub> Coordination polymer

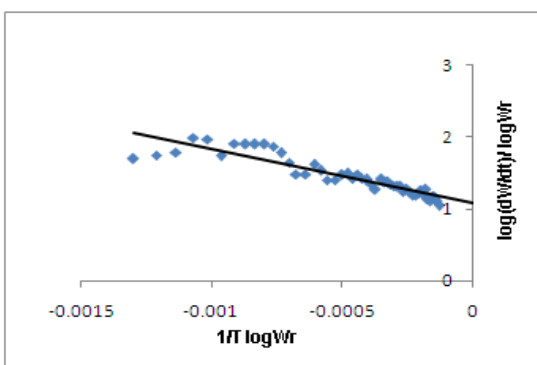


Fig. 5 Freeman-Carroll plot for activation energy of {[Ni(II)(ABNA)(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O}<sub>n</sub> Coordination polymer

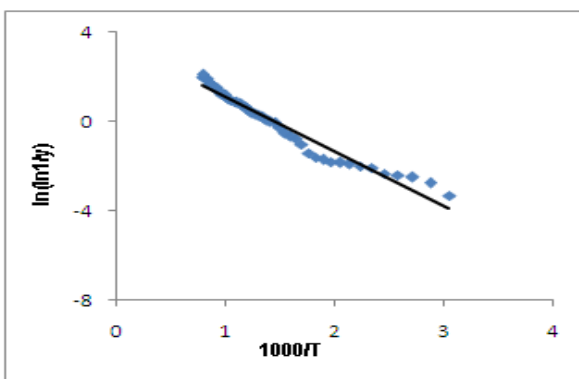


Fig. 6 Broido's plot for activation energy of {[Ni(II)(ABNA)(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O}<sub>n</sub> Coordination Polymer

#### 4. Conclusion

All the analytical data suggests octahedral geometry for Mn(II), Co(II) and Ni(II) ABNA coordination polymers, while Cu(II) and Zn(II) ABNA coordination polymers have distorted octahedral and tetrahedral geometry respectively. The coordination polymers have thermal stability in the order Zn(II) > Ni(II) > Co(II) > Mn(II) > Cu (II). The values of activation energy calculated by Sharp-Wentworth, Freeman-Carroll and Broido methods were in good agreement and the thermodynamic parameters obtained from Freeman-Carroll method were found to be similar, indicating the common reaction mode. Low values of frequency factor (*Z*) may be concluded that the decomposition of all the

coordination polymers can be classified as 'slow reaction'. Since these coordination polymers have high thermal stability they can be used as powder coating materials.

#### Acknowledgements

Authors are thankful to the Head of the Department of Chemistry, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur, India for providing the laboratory facility.

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