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Synthesis, Characterization, Magnetic and Thermal Analysis of Chelate Polymers Derived from adipyl bis-p-tolylcarbamide

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Abstract **- In the present article we describe synthesis and characterization of some chelate polymers of adipyl bis-p-tolylcarbamide (ADBPU) with first transition series metal ions such as Mn (II), Co (II), Ni (II), Cu (II) and Zn (II). The structure and composition resulting chelate polymers is confirmed by elemental analysis, reflectance spectra and FTIR studies. Further the thermal analysis and kinetic parameters were analyzed by Sharp-Wentworth and Freeman-Carroll methods.**

Index Terms **- Chelate polymers, Freeman-Carroll methods, FTIR, Sharp-Wentworth, Thermal studies.**

I.INTRODUCTION

Polymers are basic materials used in goods such as textiles, tires, and packaging (e.g., film and containers). Also, polymers, particularly thermosets, in applications they are generally used as composite materials. In the transportation market, including automotive, marine, and aerospace. Today most of these markets are mature, and it is predicted that future growth will be small. There are several more polymer uses however, this may be less evident, but it has tremendous potential and includes challenges for new technology and growth into the 21st century. The demand for practical applications of new materials has been research in chelate polymers, design and synthesis has been promoted, because of their diverse uses [1-4]. Chelate polymers of a number of bis (biuret) with transition metals have been reported by [5]. Gandhi and co-workers reported chelate polymers of hydroxamic acid with high thermal stability [6]. Tadavi et al. prepared series of transition metal complexes with Mn (III), Co(II), Ni(II) and Cu(II) and studied thermal stability [7]. Chaudhary reported thermal decomposition studies of some metal chelate polymers and morphological behaviour of a particular ligand with various metal ions at heating rate 5 °C min-1 under nitrogen atmosphere. We found out only TG, DTG and DTA investigation of metal chelate polymers at heating rate 5 °C min 1. The thermogravimetric data, the dehydration of water and degradation of organic ligands were invoked to monitor in order to evaluate decomposing temperature [8]. Various studies have been reported on thermal stability, synthesis, morphological and applications of transition metal organic coordination polymers with derivative of dicarboxylic [9-13].

Coordination polymer of divalent transition metal with chelating ligand is an interesting topic in the branch of coordination chemistry due to its specific properties and high thermal stability than ordinary complexes. Literature survey reveals that the synthesis of transition metal coordination polymers with chelating ligand was based on stability [14-15]. Herein, we have reported thermal study of three novel coordination polymers of d10 divalent transition metals. The aim of current work was to describe the comparative thermal behaviors by using TG–DTG and DTA techniques under multiple heating rates. Also, we have evaluated thermal decomposition kinetics and thermodynamic parameters including activation energy, order of reaction by Sharp-Wentworth and Freeman-Carroll method.

II. EXPERIMENTAL

A. CHEMICALS

All the chemicals used were AR grade. The solvents used were doubled-distilled before use.

B. INSTRUMENTS

Carbon, hydrogen, and nitrogen content were examined on an EA 1108 Carlo Erba elemental analyzer from CDRI Lucknow (India). FTIR spectra of ligand and chelate polymers were recorded at the Regional Sophisticated Instrumentation Centre, Nagpur India, on a Bruker IFS 66V spectrometer (Germany), using the KBr pellet in the range of 400–4000 cm-1. Reflectance spectra of the chelate polymers in solid state were recorded on a single-beam Karl-Zeiss Jena, Specord M-400 spectrophotometer in the range 250–600 nm.

Finely powdered magnesium oxide was used as a reference material. Magnetic susceptibility of the chelate polymers was determined by Gouy's method at room temperature using mercury tetrathiocyanato cobaltate (II) as the standard. Thermogravimetric analysis was carried out at RSIC; RTM Nagpur University, Nagpur, India on an TGA/SDTA-851, Mettler Toledo. The thermocouple used was Pt-Pt-Rh with a temperature range of 20°C–1000°C at a heating rate of 15°C/min. A 12-mg sample was used in the thermal analyses, which were carried out in an air atmosphere. Mass loss was recorded continuously on the recorder.

C. SYNTHESIS OF LIGAND

In a oven dried round bottom flask a quantity of 30 g (2 m mol) of finely powdered of adipyl bis-p-tolylcarbamide was taken and 50ml sodium dried benzene was applied. The corresponding acid chloride was then added to it while the benzene–tolyl carbamide was slowly swirled. Afterward it was fitted with fully dry Leibag water condenser with anhydrous CaCl2 filled in guard tube. The reaction begins immediately with the HCl gas evolution. On a water bath, the reaction mixture was then refluxed and vigoursly shaken. The products obtained after 4-5 h was filtered, washed with hot benzene and kept in an oven at 100 0C as shown in figure-1

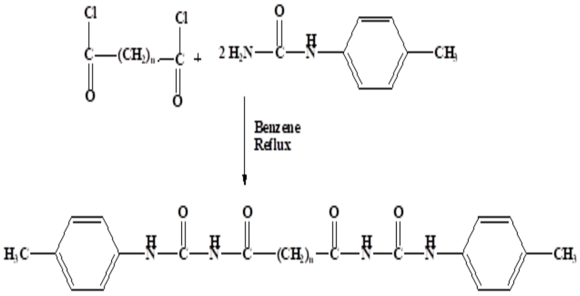


Figure-1 Synthesis of ligand

D. SYNTHESIS OF CHELATE POLYMERS

Three chelate polymers were coordinated in the present work. Coordination polymers were synthesized separately by dissolving metal acetate (10 m mol) and ligand (5 m mol) (figure- 2) in 25 ml of hot dimethylformamide. Metal acetate and bis-ligand solutions were purified in hot conditions and the mixture was refluxed in an oil bath. The temperature of the reaction mixture was maintained at 120–140 °C. Afterward 20–24 h the coordination polymers emerge out. The products obtained were filtered, thoroughly washed with hot dimethylformamide, dimethyl sulfoxide, and alcohol was used to expel the unresponsive reactant, if any present. Finally, the polymers were dried. Repeated washing with hot DMF and ethanol has determined the purity of products. At room temperature, the polymers obtained were stable. They were characterized by elemental analysis, IR spectroscopy, diffuse reflectance and magnetic measurements were defined by synthesized coordination polymers to allocate the geometry.

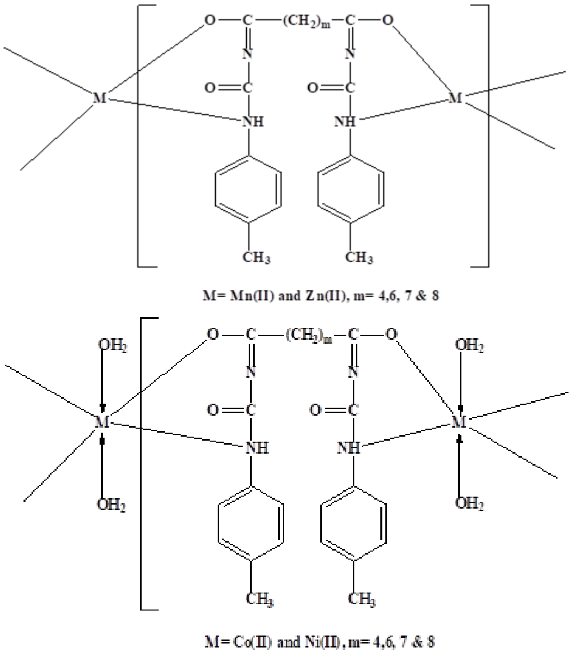


Figure-2 Synthesis scheme of chelate polymer.

III. RESULTS AND DISCUSSION

Based on elemental analyses, infrared spectra, reflectance spectra, and thermal studies, the proposed structures of these chelate polymers were determined, which are shown in Figure 2. The analytical data on the chelate polymers adipyl bis-p-tolylcarbamide

(ADBPU) are given in Table I. The presence of water of crystallization as well as water of coordination was ascertained on the basis of the thermal studies.

A. ELEMENTAL ANALYSIS

The synthesized chelate polymer was analyzed for carbon, hydrogen, nitrogen and sulphur at Indian Institute of Technology, Mumbai. The results are presented in Table 1. The elemental analysis data are in good agreement with the theoretical (calculated) data. The elemental analysis data were used to assign empirical formula and empirical weight to chelate polymer.

Table 1. Elemental analysis Chelate polymers.

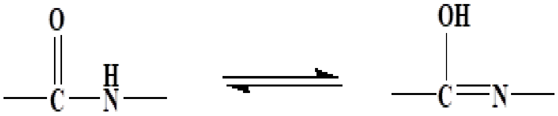
Proposed Polymeric Unit	Elemental Analysis							
	Theoretical				Experimental			
	% C	% H	% N	% M	% C	% H	% N	% M
$[Mn(II)(ADBPU)]_n$	57.06	5.18	13.12	11.90	57.02	5.23	12.09	11.85
$[Co(II)(ADBPU)\ (H_2O)_2]_n$	52.38	45.56	11.11	11.78	52.49	5.61	11.13	11.70
$[Ni(II)(\ ADBPU(H_2O)_2)]_n$	52.60	5.65	11.15	11.70	52.52	5.62	11.14	11.67
$[Zn(II)(\ ADBPU)]_n$	55.60	5.01	11.85	13.82	57.77	5.11	11.82	13.80

B. INFRARED SPECTRAL STUDIES

The infrared spectra of the chelate polymers were nearly identical (Figure 3). The frequencies of some significant bands of the free ligand and of the chelate polymers are reported in Table 2.

IR bands observed at 3225 cm-1 in the ligand may be assigned to the N-H stretching frequency [16]. At 1688 cm-1 sharp band of C=O stretching is observed. The medium band shown at 2959 cm-1 assigned to aromatic CH3 group. Medium band obtained in the range 1493 cm-1 might be due to C-N group.

It has been found that bis-ligand shows keto-enol tautomerism during polymerization as follows.



This has been proved by the fact by that the band observed at 1691cm1 due to C=O stretching mode in case of ligand disappears and new band is observed around 1556-1559 cm-1 in polymers clearly indicated that the C=O band disappears due to the formation of C=N as a result of enolization [17]. This is further supported by the appearance of C-O band around 1100 cm-1 in case of polymers. The weak bands appearing at 613-620 cm-1 in polymers are assigned due to the M-O bond interaction. While the presence of band around 450-520 cm-1 can be assigned to the M-N bond.

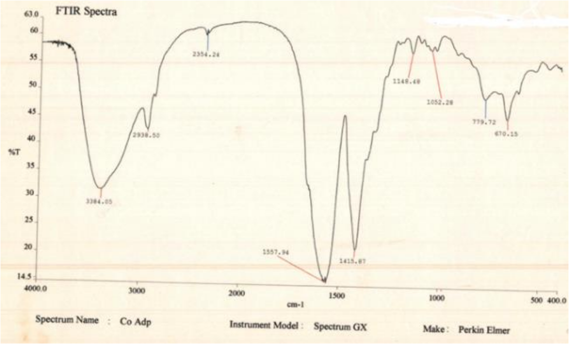


Figure 3 IR spectra of Co-ADBPU chelate polymer.

Table 2 IR spectral assignments of the ligand and chelate polymers (cm-1)

Chelate polymers	H-O-H	-NH-	C=O-	-C=N-	C-O	M-O	M←N	(Aromatic) CH_3
ADBPU Ligand	--	3225 (b)	1688 (s)	-	-	-	-	2959
$[Mn\ (II)(ADBPU)]_n$	--	3435 (b)	-	1559	1135	620	520	2922
$[Co\ (II)(ADBPU)(H_2O)_2]_n$	779 (w)	3384 (b)	-	1557	1148	670	451	2938
$[Ni\ (II)(ADBPU)\ (H_2O)_2]_n$	781 (w)	3422 (b)	-	1570	1144	618	510	2922
$[Zn\ (II)(ADBPU)]_n$	--	3445 (b)	-	1536	1150	613	450	2950

C. ELECTRONIC SPECTRAL STUDIES AND MAGNETIC SUSCEPTIBILITY DATA OF CHELATE POLYMERS

A band appeared at 21.40 kK in the [Mn (II)(ADBPU)] *n* chelate polymer that could be allocated in a tetrahedral field due to the the $^6A_{1g}$ → AE(G)transition. The tetrahedral geometry of the [Mn (II)(ADBPU)] *n* chelate polymer was also supported by the magnetic moment value. The bands that appeared at 23.80 and 11.59 kK in the [Co (II)(ADBPU) $(H_2O)_2$] (H_2O)] *n* chelate polymer can be due to the $^4T_1g \rightarrow {}^4T_1g$ (P) and $^4T_1g \rightarrow {}^4A_2g$ transition in the octahedral field [18]. The octahedral geometry was further supported by the magnetic moment value. The bands that appeared at 17.97 and 27.85 kK in the [Ni (II)(ADBPU) $(H_2O)_2$] *n* chelate polymer, may be assigned to the $^3A_2g \rightarrow {}^3T^1g$ (F) and $^3A_2g \rightarrow {}^3T_1g$ (P) transitions, respectively, in octahedral field [19], which was further supported by the magnetic moment value. Because [Zn (II)(ADBPU)] *n* is a d^{10} system, it is diamagnetic. Still, the results of elemental analyses, an infrared spectrum, and thermal decomposition analysis suggested that its most probable geometry was tetrahedral. The electronic spectral (Figure 4) and magnetic susceptibility data of the chelate polymers are given in the Table-3.

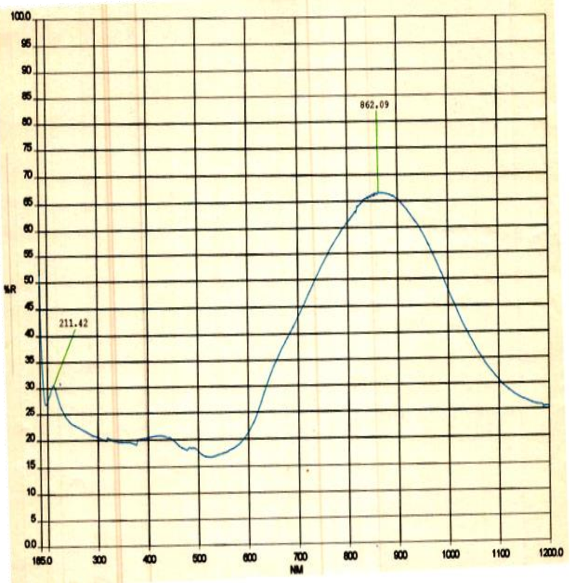


Figure 4 Reflectance spectra of Cobalt-ADBPU chelate polymer

Table 3 Electronic spectral and magnetic susceptibility data of chelate polymers.

Chelate polymers	Colour	μ_{ef} (B. M.)	Electronic spectra		Stereochemistry
			Absorbance (kK)	Assignments	
[Mn (II)(ADBPU)] $_n$	Light pink	5.88	30.94	$^6A_1$-^4E(G)	Tetrahedral
[Co (II)(ADBPU) $(H_2O)_2$] $_n$	Pink	4.50	16.48	$^4A_2$-$^4T_1$(P)	Octahedral
[Ni (II)(ADBPU) $(H_2O)_2$] n	Green	3.28	8.67	$^3T_1$-$^3T_1$(P)	Octahedral
[Zn (II) ADBPU)] $_n$	White	Diamagnetic	-	-	Tetrahedral

D. THERMOGRAVIMETRIC STUDIES OF ADBPU CHELATE POLYMERS

Sharp-Wentworth [19] and Freeman-Carroll [20] methods were employed to determine the kinetic parameters of chelate polymers with the help of thermogravimetric curves. The application of Freeman-Carroll method is that the parameters of temperature and time can be varied at the same time the order of reaction and activation energy can be calculated by same experiment.

FREEMAN-CARROLL METHOD

The following expression is utilized to determine various kinetic parameters.

$$[\Delta \log(dw/dt)]/\Delta \log W_r = (-E/2.303R).\ \Delta(1/T)/\Delta \log W_r + n$$

This show that a plot of

log (dCw/dt)/log Wr against Δ(1/T)/Δ log Wr will give an intercept on the y-axis at x=0 which is equal to the value of n (order of reaction) and a slope m= -Ea/2.303R.

Where, dw/dt=rate of change of mass with time.

Wr = Wc-W

Wc=weight loss at completion of reaction.

W=fraction of weight loss at time t.

Ea=energy of activation

n=order of reaction.

SHARP-WENTWORTH METHOD

The following expression is used to evaluate the energy of activation by this method.

$\log[(dc/dT)/(1-c)] = \log(A/\beta) - [Ea/2.303R].1/T$

Where,

dc/dT=rate of change of fraction of weight with change in temperature

β=linear heating rate dT/dt.

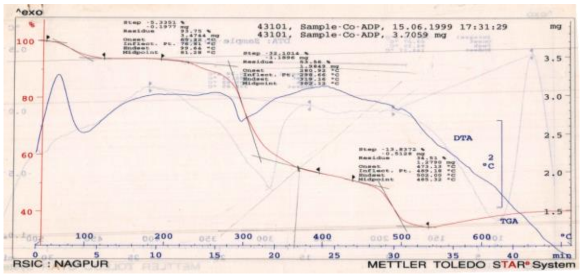


Figure 5 Thermogravimetric curve of Co-ADBPU chelate polymer

Table 4 Thermal data of ADBPU chelate polymers

Chelate polymers	% Loss due to coordinated water	% Loss due to Decomposition	Decomposition Range (°C)	Decomposition Temperature (°C)
[Mn (II)(ADBPU)] $_n$	--	69.00	260-600	313
[Co (II) (ADBPU ($H_2O)_2$] $_n$	7.11	73.38	220-504	340
[Ni (II)(ADBPU) ($H_2O)_2$] n	7.63	70.88	180-560	333
[Zn (II)(ADBPU)] n	--	62.48	240-580	380

The presence of water of crystallization has been confirmed based on TGA and DTA analysis; the findings obtained for these polymers are presented in table-. The representative thermal degradation curves for Co-ADBPU polymer shown in figure- 5.

The percentage mass loss corresponding to coordinated water molecules was considered at about 210 °C. Beyond this a gradual mass loss is observed up to 680 °C, which can be attributed to decomposition of chelate polymers. The curve in most cases does not show any sharp transition but a gradual decomposition, which is characteristic feature of these compounds. Co (II)-ADBPU and Ni (II)-ADBPU chelate polymers show absence of lattice water whereas; there is presence of two molecules of coordinated water. Thus, TG analysis, IR spectra, electronic spectra and magnetic moment value supported octahedral geometry for Co (II)-ADBPU and Ni (II)-ADBPU chelates polymers. However, Mn (II) and Zn (II) polymers are tetrahedral in nature due to absence of water of coordination. Different stages involved in thermogram for the chelate polymers are tabulated in table 4.

E. EVALUATION OF KINETIC PARAMETERS

The kinetic parameters determined by Sharp-Wentworth and Freeman-Carroll methods are given in table-5. A representative sharp-Wentworth plot, thermal activation energy plot and Freeman-Carroll of Co (II) ADBPU are shown in (Figure 6-8). Thermodynamic parameters have been calculated on the basis of thermal activation energy.

The evaluation of TGA data and from the nature of thermograms, the thermal decomposition can be explained by considering monomeric unit of the polymer. On the basis of decomposition temperature data given in table- 4, the order of thermal stability of chelate polymers are found to be Zn> Co > Ni > Mn.

Table 5 Kinetic parameters of ADBPU chelate polymers.

Chelate polymers	Activation energy Ea (kJ/mol)		Entropy change ΔS (JK^{-1})	Free energy change ΔF (JK^{-1})	Frequency factor Z (S^{-1})	Apparent entropy change S* (JK^{-1})	Order of reaction (n)	Decomposition temperature (°C)
	SW	FC						
[Mn (II)(ADBPU)]$_n$	14.05	14.53	-260.14	153.18	16.93	-227.05	0.89	310
[Co (II)(ADBPU) ($H_2O)_2$] n	21.64	26.15	-269.86	159.19	7.26	-234.5	0.6	360
[Ni (II)(ADBPU) ($H_2O)_2$)]$_n$	20.95	20.37	-271.94	143.56	10.64	-231.18	0.73	390
[Zn (II)(ADBPU)]$_n$	30.70	34.38	-262.51	169.05	6.57	-235.32	0.53	371

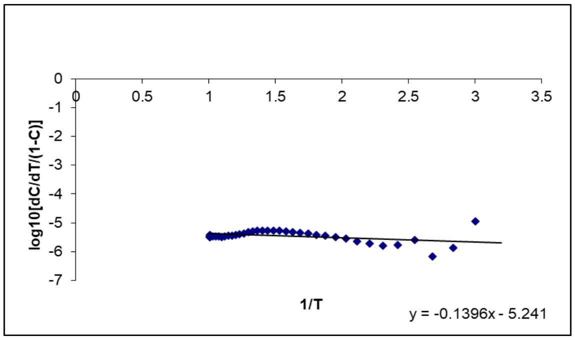


Figure 6 Sharp-Wentworth plot of Co (II) ADBPU polymer

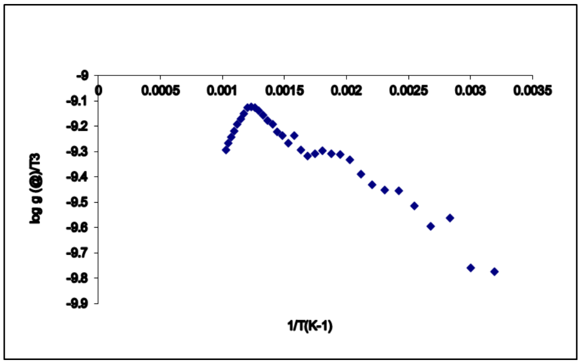


Figure 7 Thermal activation energy plot of Co (II) ADBPU polymer

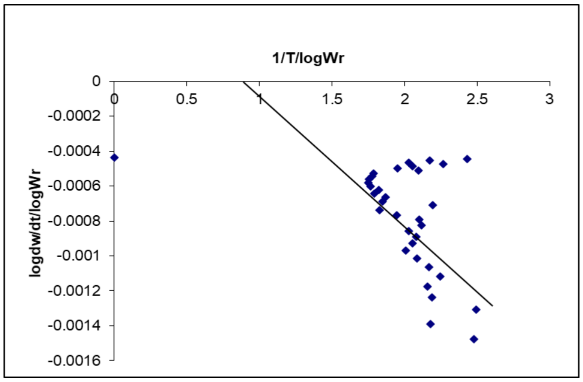


Figure 8 Freeman-Carroll plot of Co (II) ADBPU polymer

IV. CONCLUSIONS

In the current study of thermal decomposition of some metal chelate polymer compounds and of a particular ligand with different metal ions under nitrogen atmosphere at heating rate 10 °C min-1. Comparative studies were reported from the point of view. In almost all the organic solvents, newly synthesized chelate polymers are colored and insoluble. TG, DTA, CHN and IR spectroscopy have confirmed the existence of number of lattice and coordinated water. The chelate polymer compounds are found to be thermally stable on the basis of TG/DTA analysis, but Ni (II) was somewhat highly thermally stable compared to other chelate polymer compounds. The thermal stability of chelate polymers follows the order: Ni (II)>Mn(II)>Zn(II)>Co(II).

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