

SPECTRAL, MAGNETIC AND THERMAL STUDIES OF SOME CHELATE POLYMERS

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ABSTRACT

The present paper describes the synthesis and structural features of some chelate polymers of Azeloyl bis p-tolyl carbamide (AZBPU) with first transition series metal ions viz. Mn(II), Co(II), Ni(II) and Zn(II). The resulting chelate polymers have been characterized on the basis of elemental analysis, electronics spectral and magnetic susceptibility studies. The nature of bonding has been discussed on the basis of IR spectral data. To ascertain their thermal stability a detailed thermal studies was carried out by Freeman-Carroll and Sharp-Wentworth methods

Keywords: Spectral, Magnetic and Thermal studies, Chelate, Polymer.

INTRODUCTION

One of the most exciting areas in the field of chemistry, chemical engineering and material science is the preparation, characterization and applications of polymer. The growing importance of polymers have been truly a standing to the point that it is difficult to imagine our life without polymers.

Coordination polymers of polyvinyl butyrol borate with bis-acetyl acetato titanium dibutoxide are reported¹, to be used as spray anticorrosion primers.

Coordination polymers are also used as superconductors². A method is reported for the preparation of polymer magnets from coordination compounds with polysiloxane³. Anticorrosive layers on Cu and Cu alloys (especially printed circuit boards) are reported to be prepared by treatment of same with alcoholic solutions of heterocyclic nitrogen compounds and copper and zinc salts of accelerators such as 2-mercaptobenzimidazole. This is followed by heat treatment⁴.

In the present case the chelate polymers of first row transition metal ions viz. Mn(II), Co(II), Ni(II) and Zn(II) with Azeloyl bis p-tolyl carbamide (AZBPU) have been synthesized and were characterized.

EXPERIMENTAL

Analytical reagent grade chemicals were used for synthesis purpose. All chemicals and solvents were purified by standard methods.

Preparation of ligand

A quantity of 30.0 mg (2 m mol) of finely powdered p-tolyl carbamide was taken in a oven dried round bottom flask and 50 ml of sodium dried benzene was added. Then 22.5 g (1 m mol) of Azeloyl chloride was added into the flask with constant stirring. It was then fitted with a perfectly dry Liebig water condensor with calcium chloride guard tube. The reaction starts immediately with evolution of HCl gas. The reaction mixture was then refluxed on a water bath and shaken vigorously. The product obtained after 3-4 hrs. were filtered, washed with hot benzene to remove unreacted p-tolyl carbamide and acid dichloride if any and were then purified by absolute alcohol and dried in oven at 100°C.

Synthesis of chelate polymers

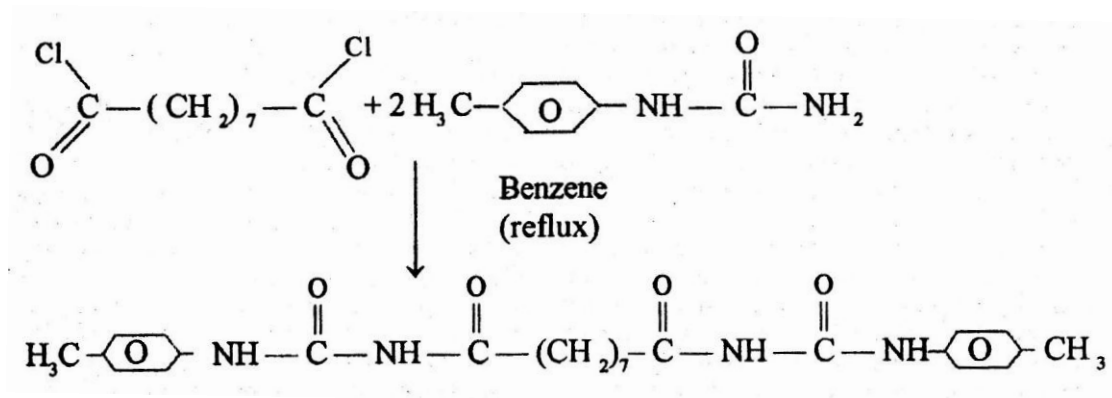
A quantity of 4.52 g (0.1 m mol) of ligand and 2g (0.1 m mol) of metal acetate were dissolved separately in minimum quantity of DMF in hot condition. The hot solution were then mixed and

Table-1 : Thermal data of AZBPU chelate polymers

Chelate polymers	% loss due to coordinated water	% loss due to decomposition	Decomposition range (°C)	Decomposition temp (°C)
[Mn(AZBPU)] _n		66.35	260-600	275
[Co(AZBPU)(H ₂ O) ₂] _n	6.18 (6.59)	75.44	240-580	440
[Ni(AZBPU)(H ₂ O)] _n	6.36 (7.15)	66.35	200-580	320
[Zn(AZBPU)] _n		62.68	200-600	445

Table-2 : Kinetic parameters of AZBPU chelate polymers

Chelate polymers	Activation Energy		Entropy change ΔS (J)	Free energy change ΔF (KJ)	Frequency factor Z Z(S ⁻¹)	Apparent entropy change S* (J)	Order of reaction (n)
	FC	SW					
Mn-AZBPU	22.45	21.45	-264.23	147.43	8.70	-232.03	0.72
Co-AZBPU	30.61	29.90	-283.66	164.78	5.53	-237.29	0.58
Ni-AZBPU	21.62	21.92	-273.10	129.45	8.51	-232.87	0.74
Zn-AZBPU	42.54	43.52	-266.62	173.89	6.05	-237.31	0.45



refluxed for 6-8 hrs. at about 132-140 °C. The product formed were cooled, filtered and washed 2-3 times with hot DMF to remove any unreacted metal acetate and ligand. The product thus obtained were found to be insoluble in almost all organic solvents. It is then dried in oven at 100 °C to remove any moisture content.

RESULTS AND DISCUSSION

Electronic spectra and magnetic studies-

A band appearing around 20.40 kK in the chelate polymer of Mn(II) may be assigned due to ${}^6\text{A}_1 \rightarrow {}^4\text{E}$ (G) transition in tetrahedral field⁵. The magnetic moment value also support

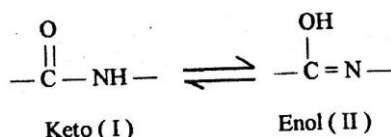
Band appears at 12.66 kK in case of Co(II) polymer may be attributed to ${}^4T_{1g} \rightarrow {}^4A_{2g}$ transition in octahedral field⁶ which is also supported by magnetic moment value.

In case of Ni(II) polymer, the bands appearing at 18.69 kK and 27.42 kK were assigned to ${}^4A_{1g} \rightarrow {}^3T_{1g}(P)$ transition in octahedral field⁷. Zn(II) polymer is diamagnetic in nature and having tetrahedral geometry.

Infrared spectral studies

Infrared bands observed around 3229 cm^{-1} in ligand has been assigned due to N-H stretching frequency⁸. The sharp band of C=O stretching⁹ is observed at 1697 cm^{-1} . The medium band observed at 2926 cm^{-1} have been assigned due to aromatic $-\text{CH}_3$ group frequency¹⁰. Medium band observed in the range between $1316\text{--}1408\text{ cm}^{-1}$ may be assigned due to C-N group frequency¹¹.

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



This has been proved by the fact the band observed at 1697 cm^{-1} due to C=O stretching mode in case of ligand disappears and new band is observed around $1535\text{--}1558\text{ cm}^{-1}$ in polymers which clearly indicates that the C=O band disappears due to formation of C=N as a result of enolization¹². This is further supported by the appearance of C—O band around 1100 cm^{-1} in case of polymers.

The weak band appearing at $615\text{--}460\text{ cm}^{-1}$ in polymers are assigned due to M—O bond interaction¹³ while the presence of band around $680\text{ to }660\text{ cm}^{-1}$ may be assigned to M—N bond.

Medium band appearing in the region $820\text{--}760\text{ cm}^{-1}$ in case of Co(II) and Ni(II) polymers is due to the presence of water of co-ordination¹⁴.

On the basis of results obtained from elemental analysis, infrared spectra, magnetic and thermal studies the tentative structures for these polymers are given in Fig. 1.

Thermal studies

Freeman-Carroll¹⁵ and Sharp-Wentworth¹⁶ methods have been used to determine the kinetic parameters of the chelate polymers with the help

of dynamic TG curves. The usefulness of Freeman - Carroll method is that the parameters of temperature and time can be varied and at the same time the order of reaction or energy of activation can be determined by same experiment

Freeman-Carroll method- The following expression is used to evaluate various kinetic parameters

$$\frac{\Delta \log(dC_w/dt)}{\Delta \log(W_r)} = - \frac{E_a}{2.30 \text{ BR}} - \frac{\Delta \left(\frac{1}{T} \right)}{A \log W_r} + n$$

This shows that a plot of

$$\frac{\Delta \log(dC_w/dt)}{\Delta \log(W_r)} \text{ against } \frac{\Delta \left(\frac{1}{T} \right)}{\Delta \log W_r}$$

will give an intercept of the y axis at $x = 0$ which is equal to the value of n (the order of reaction)

and a slope $m = - \frac{E_a}{2.30 \text{ BR}}$

In the expression given to above $W_r = W_c - C_w$, where W_c is the weight loss at the completion of the reaction or at definite time. C_w is the total weight loss up to time t , dC_w/dt the weight loss up to time t , dC_w/dt the weight loss with time t , and T the temperature.

Sharp-Wentworth method- The following expression is used to evaluate the activation energy by this method,

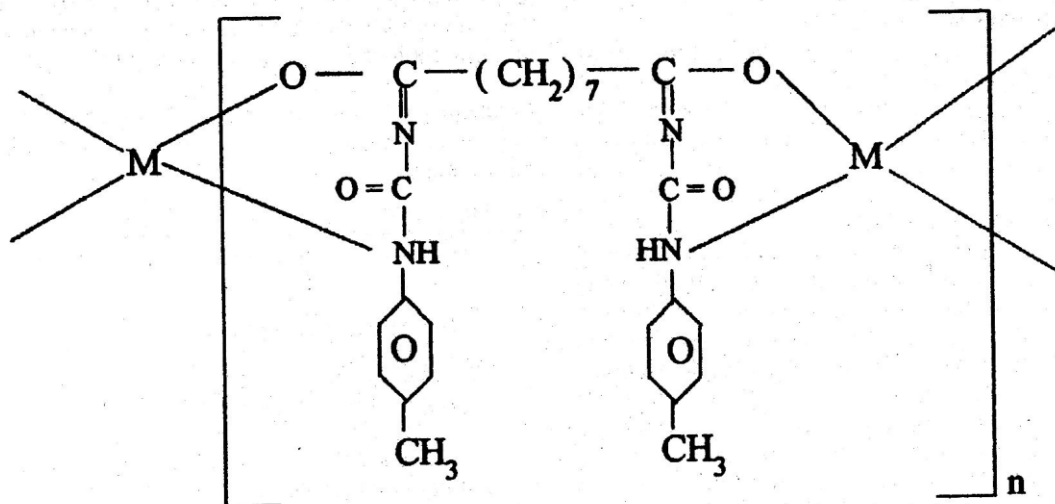
$$\frac{\log(dC_w/dt)}{1 - C_w} = \log(A/\beta) - \frac{E_a}{2.30 \text{ BR}} - \frac{1}{T}$$

Where dC_w/dt is the fraction of mass loss with time t , T the temperature and $\beta = dT/dt$

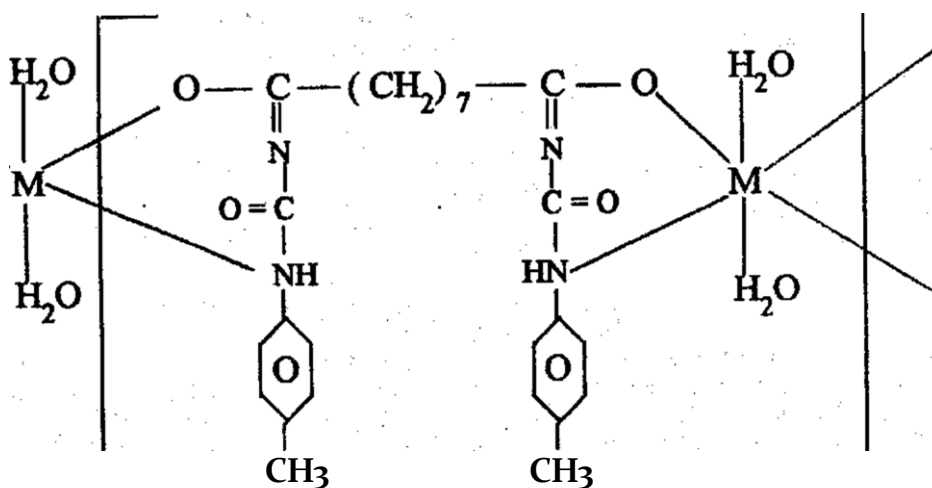
The presence of water of crystallisation was ascertained on the basis of TGA and DTA studies the result obtained for different polymers are summarised below. Representative thermal degradation curves for Co-AZBPU has been shown in Fig. 2.

i) TG analysis of $[\text{Mn}(\text{AZBPU})]_n$

The TG curve of Mn(II) chelate polymer shows absence of both lattice water and coordinated water, as no weight loss is observed up to 250°C . This polymer shows gradual mass loss between $260\text{--}600^\circ\text{C}$ with the formation of stable species.



$M = \text{Mn (II) and Zn (II)}$



$M = \text{Co (II) and Ni (II)}$

Fig. 1. Proposed structure of chelate polymer

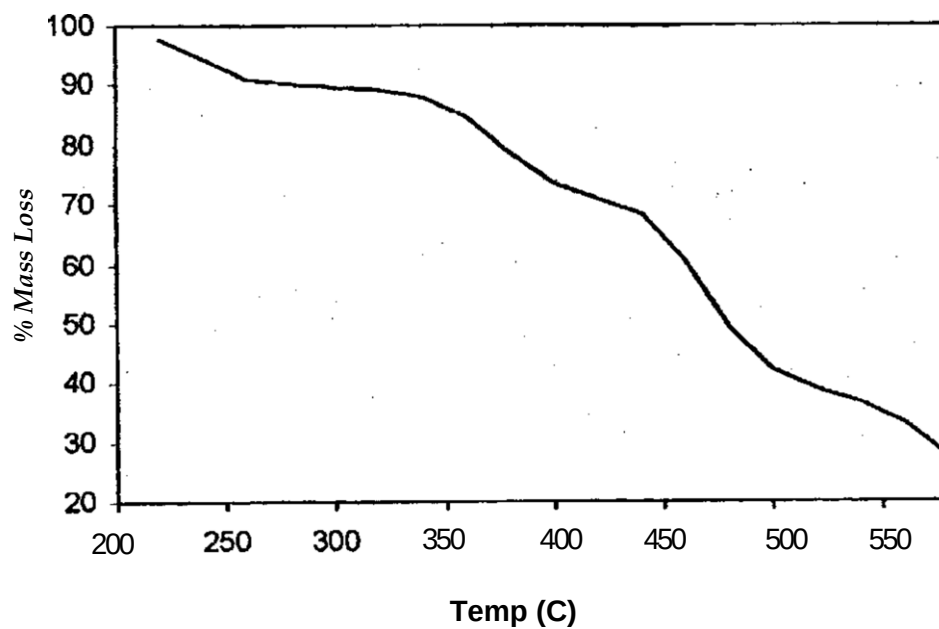


Fig. 2. Thermogram of Co(II) AZBPU chelate polymer

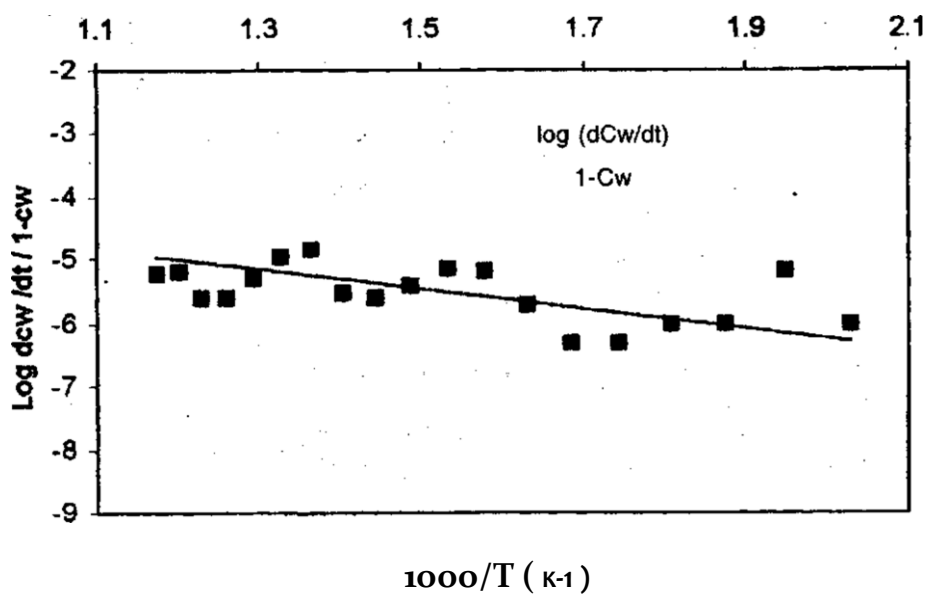


Fig. 3. Sharpe-Wentworth plot of Co(II) AZBPU chelate polymer

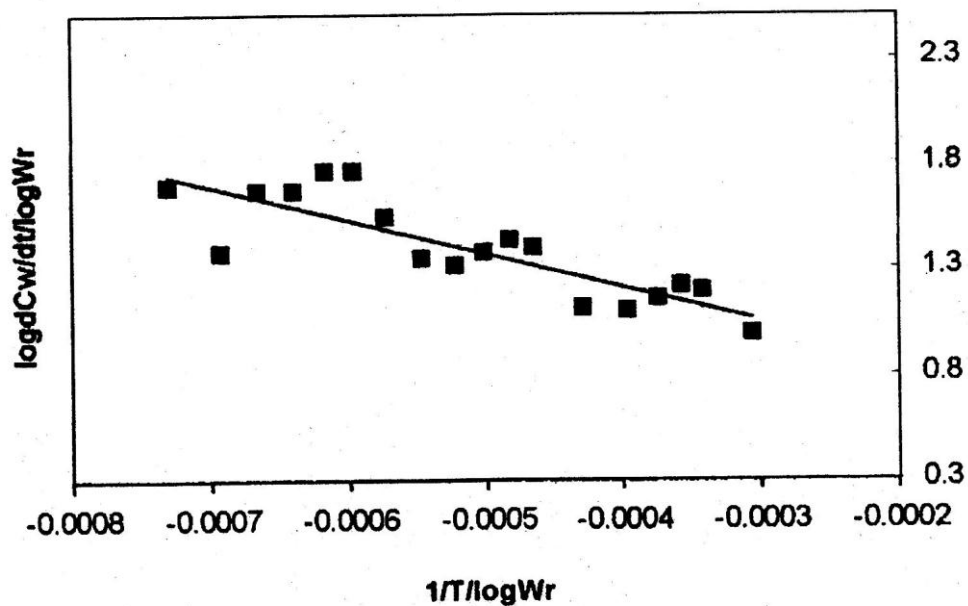


Fig. 4. Thermal activation energy plot of Co(II) AZBPU chelate polymer

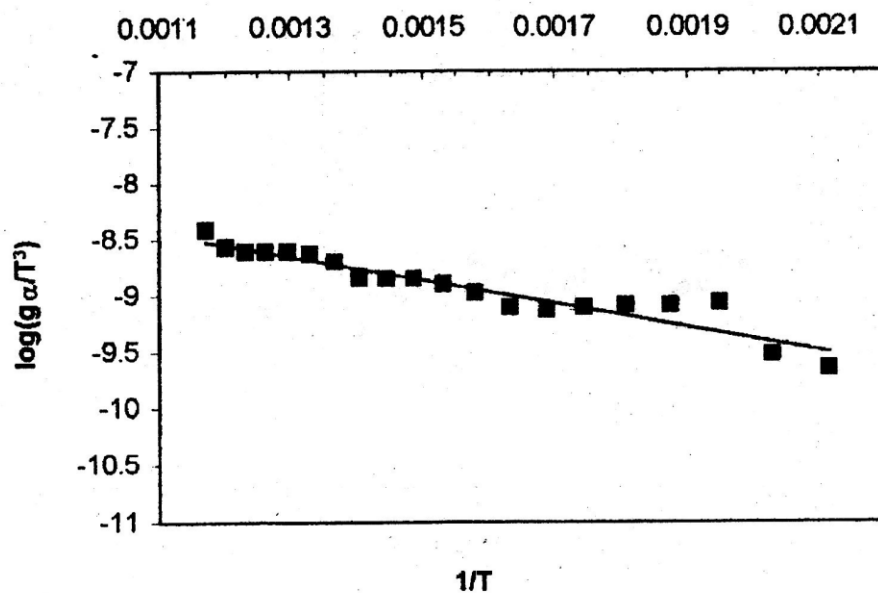


Fig. 5. Freeman-Carroll plot of Co(II) AZBPU chelate polymer

ii) TG analysis of [Co(AZBPU) (H₂O)₂]_n

The percentage mass loss corresponding to lattice water and considered near 130°C and 210°C respectively. The TG curve of Co(II) polymer shows that there is a loss of two molecules of coordinated water between 180°C to 210°C. After this a gradual mass loss is observed from 240°C to 580°C which can be attributed to the degradation of organic part of ligand and than it forms stable species. The curve do not show any sharp transition but a gradual decomposition.

iii) TG analysis of [Ni(AZBPU) (H₂O)₂]_n

The TG curve of Ni(II) chelate polymer show that there is an absence of lattice water since no weight loss is observed up to 160°C and after this, loss in weight is observed from 170°C to 190°C which will be corresponds to two molecules of water of coordination. After that a gradual mass loss was observed up to 580°C with the formation of stable species, since no weight loss is observed after 580°C.

iv) TG analysis of [Zn(AZBPU)]_n

The Zn(II) chelate polymer is stable upto 190°C, since no weight, loss is observed upto 190°C, indicating absence of water of coordination as well as lattice water and thus support the tetrahedral geometry of Zn(II) chelate polymer.

Various steps involved in thermograms for the polychelates are give in Table 1 taking in to account % mass loss and decomposition temperature.

The kinetic parameters calculated by Freeman-Carroll and Sharpe-Wentworth method are given in Table 2. A representative Sharpe-Wentworth plot, Thermal activation energy plot and Freeman-Carroll plot of Co(AZBPU) polymer are given (Figure 3, 4 and 5). 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 1, the order of thermal stability of metal chelates are found to be Zn > Co > Ni > Mn.

The values of thermodynamic parameters are nearly the same for each polychelate. This similarity indicate that the basic steps involved are similar in the thermal degradation of polychelates. The low value of frequency factor (Z) indicate that the decomposition reaction of the polychelate can be classified as a slow reaction¹⁷. The negative value of AS indicates that the activated complex has more ordered structure than the reactant, and the reaction are slower than normal. It is observed that the degradation of polymer is a complex process as noted from the non integer order of reaction¹⁸.

Good straight line plots are obtained using both the methods since as the calculations and plotting is done on computer, the selection of points for drawing a straight line was considered to be more correct, instead of manual drawing since all the standard deviation were taken in to consideration. Hence, probability of error is definitely reduced.

In Freeman-Carroll method very few abnormal points must be disregarded to get a clear picture of the curve. Similarly in Sharpe-Wentworth method, straight line plot have some points either in the beginning or at the end which do not fall on the straight line. This is expected, since the decomposition of polychelates is know not to follow first order kinetics perfectly as observed by Jacobs and Tompkins¹⁹ and by Coats and Redfern²⁰

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