

SYNTHESIS, SPECTRAL AND THERMAL STUDIES OF COORDINATION POLYMERS OF SEBACOYL BIS-P-CHLOROPHENYL UREA

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ABSTRACT

The coordination polymers of a new bis ligand, sebacoyl bis-p-chlorophenyl urea with Mn(II),Co(II),Ni(II),Cu(II) and Zn(II) metal ions have been synthesized and characterized by elemental analyses, spectral, magnetic and thermal studies. Various kinetic and thermodynamic parameters such as entropy change, free energy change, apparent entropy, frequency factor and order of reaction have also been evaluated and values obtained are comparable. Tentative structure for coordination complexes has been assigned on the basis of above analyses. All the coordination polymers except Cu (II) coordination polymer are found to have tetrahedral geometry and are thermally stable.

Keywords: Coordination polymers, Sebacoyl bis-p-chlorophenyl urea, Thermodynamic and Kinetic parameters, Electronic spectra.

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INTRODUCTION

Extensive work in recent years have provided evidence that the synthesis and characterization of coordination polymers continue to receive considerable interest owing to the fact that this research has unearthed wide assortment of applications ranging from catalyst¹ to enormous acceptance in material sciences, such as powder surface coating materials², metal extractants and radio therapeutic³, and in antimicrobial⁴, anticancer⁵, antitubercular⁶, antimalarial⁷, antileishmanial⁸, and antifungal activities⁹. Some sulphur and nitrogen containing ligands and their complexes have been found to be important precursor for semi-conducting materials¹⁰.

Coordination polymers of bis ligand with transition metals have been reported by earlier workers from our laboratories¹¹. A survey of literature however, reveals that the coordination polymers of sebacoyl bis-p-chlorophenyl urea with first transition series metal ions are yet to be studied. In the present study the synthesis and characterization of some coordination polymers of Mn(II),Co(II),Ni(II),Cu(II) and Zn(II) with SEPCPU have been reported.

EXPERIMENTAL

Materials

All the chemicals used were of A R grade (Merck). Solvents used were purified by the usual method before their use.

Instruments

Carbon, hydrogen, nitrogen, analysis were obtained from micro-analytical unit CDRI Lucknow, India. Chlorine contents were analysed at NCL Pune, India. The IR spectra were recorded in KBr pellets on Perkin-Elmer spectrum RXI spectrophotometer from CDRI Lucknow, India. The reflectance spectra in the solid state were recorded on UV-VIS-NIR spectrophotometer in the range of 180-1200 nm using magnesium oxide as reference material at SICART, Vallabh Vidya Nagar Anand, Gujrat, India. The

magnetic measurements were carried out by Gouy's method at room temperature using Hg [Co(NCS)₄] as a standard. The metal contents in each polymer were determined by classical oxide method¹². Thermogravimetric analysis was carried out on a TGA\SDTA-851, METTLER TOLEDO in air with 15⁰ min⁻¹ heating rates at RSIC, Nagpur.

Synthesis of ligand

Preparation of -p-chlorophenyl Urea

A quantity of (0.2 m mol) of finely powdered p- chloroaniline was dissolved in a mixture of 100 ml glacial acetic acid and 200 ml distilled water at 35⁰C. The solution of sodium cyanate (0.2 m. mol) in 100 ml distilled water at 35⁰C, was added gradually with constant stirring. Solid obtained was filtered and re-crystallized from 90% aqueous ethanol. Melting point of the product (p-chlorophenyl urea) was 238⁰C.

Preparation of Sebacyl dichloride

Sebacyl dichloride was prepared by the reaction of (0.1 m. mol) dry Sebacic acid and (0.25 m. mol) double distilled thionyl chloride placed in a 100 ml dry R.B. flask fitted with a perfectly dry liebig water condenser, provided with calcium chloride guard tube. The reaction mixture was then refluxed on a water bath till clear solution was obtained. To remove SO₂, HCl and un-reacted SOCl₂, reaction mixture was then refluxed under reduced pressure for about 30 minutes.

Preparation of ligand (SEPCPU)

The ligand sebacyl bis-p-chlorophenyl urea was prepared by the condensation of sebacyl dichloride (0.1 m. mol) with p-chlorophenyl urea (0.2 m. mol) in sodium-dried benzene for about 5 hrs. A white shiny crystals of ligand obtained was filtered and washed with hot ethanol to remove unreacted p-chlorophenyl urea and was crystallized from DMF and dried at 100⁰ C and characterized by elemental analyses, IR and ¹H NMR studies (fig.-1). Results are given in the Table-1.

Synthesis of coordination polymers

The coordination polymers were synthesized by dissolving (0.1 m. mol) of ligand and (0.1 m. mol) of metal acetate separately in a minimum quantity (20–30 ml) of hot DMF (70⁰-80⁰ C). Both the solutions were then filtered and mixed in hot conditions. The reaction mixture was refluxed on an oil bath for 5 to 6 hrs and the temperature was maintained at 135⁰C to 145⁰C. The colour products obtained were filtered, washed thoroughly first with hot DMF and then with ethanol and acetone to remove unreacted reactants if any and finally dried in oven. All the polymers formed are found to be insoluble in water and in almost all organic solvents. Hence normal method of characterization such as ¹H NMR and electronic spectra in solution cannot be applied.

RESULTS AND DISCUSSION

IR Studies

The infrared spectrum of the ligand SEPCPU shows a broad band at 3425cm⁻¹, which may be assigned to the stretching vibration of the NH-group¹³. The sharp band appears at 1656 cm⁻¹, which may be due to the C=O stretching vibrations¹⁴.

The band observed at 1656 cm⁻¹ in ligand disappears in coordination polymers, as a result of enolization. This has been supported by the fact that, bands observed at 1656 cm⁻¹ in the SEPCPU ligand due to the C=O stretching mode is shifted towards lower frequencies i.e., 1527-1600 cm⁻¹ in coordination polymers, which clearly indicates that the C=O band disappeared due to the formation of the C=N bond as a result of enolization and metal coordination.

The new weak band appears in the region 668-688 cm⁻¹ in the coordination polymers may be due to the formation of the M–O bond (Metal Oxygen)¹⁵. While the presence of weak band in the range 460-580 cm⁻¹ may be assigned to the M–N bond (Metal Nitrogen). The important IR spectral data of the coordination polymers are given in the Table-2.

Electronic spectral and magnetic susceptibility of the coordination polymers

In [Mn (II) SEPCPU]_n coordination polymer band appears at 28.01 and 27.02 kK may be assigned to ⁶A₁→⁴E(D) transition in tetrahedral field¹⁶. In [Co (II) SEPCPU]_n coordination polymer bands appear at 13.65 kK may be assigned to the ⁴A₂→⁴T₁ (P) transition in tetrahedral field¹⁶. The band appears at 19.14 kK and 11.93 kK in [Ni (II) SEPCPU]_n coordination polymer may be assigned to ³T₁ →¹T₂ and ³T₁ →¹E

transitions in tetrahedral field respectively. This is further supported by magnetic moment value (3.2 BM)¹⁶.

In [Cu(II)SEPCPU]_n coordination polymer bands appear at 12.10 kK and 10.52 kK may be assigned to $dyz, dxy \rightarrow dx^2-y^2$ transition in square planer field¹⁶. The magnetic moment values also support the square planer geometry for [Cu (II) SEPCPU] n coordination polymer. The coordination polymer [Zn (II) SEPCPU] n is diamagnetic in nature and has tetrahedral geometry. Electronic spectral and magnetic susceptibility data are given in Table-3.

Thermal behavior and kinetics of decomposition of the coordination polymers

The study of the thermal behaviour of all the coordination polymers in air provides information about its thermal stability and nature of decomposition of products at different temperature. The Freeman-Carroll and Sharp-Wentworth methods are used to evaluate the kinetic parameters¹⁷⁻¹⁸. In Freeman-Carroll method the expression used is-

$$\frac{\Delta \log \left(\frac{dc_w}{dt} \right)}{\Delta \log W_r} = - \frac{E_a}{2.303R} \cdot \frac{\Delta \left(\frac{1}{T} \right)}{\Delta \log W_r} + n \quad (1)$$

Hence, a plot of $\Delta \log (dc_w/dt) / \Delta \log W_r$ Vs $\Delta(1/T) / \Delta \log W_r$ should give a straight line and on Y axis (X = 0) an intercept equal to the value of n (order of reaction) and slope $m = -E_a / 2.303R$. In the expression (i) $W_r = W_c - W$, W_c is the weight loss at the completion of the reaction or at the definite time, W is the total weight loss up to time t, dc_w/dt is the fraction of weight loss with time t and T is the temperature.

While in Sharp- Wentworth method the expression used is -

$$\log \left(\frac{dc_w/dt}{1-c_w} \right) = \log \left(\frac{A}{\beta} \right) - \left(\frac{E_a}{2.303R} \right) \cdot \frac{1}{T} \quad (2)$$

In the expression (ii) dc_w / dt is the fraction of weight loss with time t, T is the temperature and $\beta = \frac{dT}{dt}$. In

the present investigation the TG curves of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) coordination polymers show common mode of decomposition and no loss due to lattice water as well as water of coordination. The decomposition temperature of the coordination polymers is 400, 410, 360, 320 and 440 °C respectively. All the polymers start degradation after 220 °C because of the decomposition of organic species. (Fig.3, 4, 5 and 6 are the representative plots of Ni (II) SEPCPU coordination polymer). From decomposition temperature data it is concluded that the thermal stability of coordination polymers is in the order Zn (II) > Co (II) > Mn (II) > Ni (II) > Cu (II). The thermal activation energy and kinetic parameters have been evaluated by using thermal decomposition data and are given in the Table-4.

Table-1: Elemental, IR and ¹H NMR analyses data of ligand

Ligand	Elemental Analysis: Calculated (Found)			
	C	H	N	Cl
SEPCPU	56.16(55.81)	5.41 (5.56)	11.15 (11.05)	14.54 (14.00)
Empirical formula C ₂₄ H ₂₈ N ₄ O ₄ Cl ₂	IR Spectral Data (Cm ⁻¹)			
	-NH-(3425)	-CH ₂ -(2935)		C=O(1656)
	¹ H NMR Spectral data			
	Obs. chem. shift (δ) ppm	Expt. chem. shift (δ) ppm	Nature of proton assigned	
	2.00 – 2.27	1.4 – 2.4	Methylene proton of –CO-(CH ₂) _n -CO	
	5.68	5.16	Proton of nitrogen of –C-NH-CO	
7.18 – 7.48	7.41	Aromatic Proton of Ar – H		

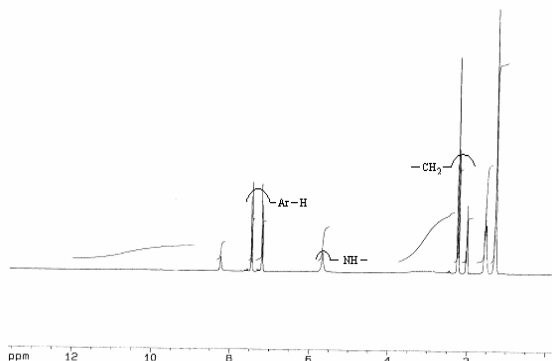


Fig.1: ¹H NMR Spectra of SEPCPU Ligand

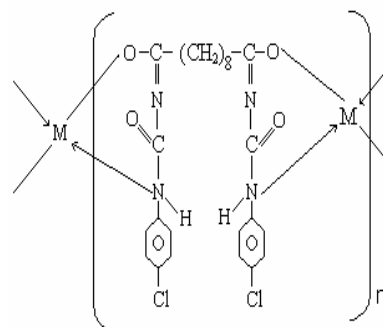


Fig.-2: Structure

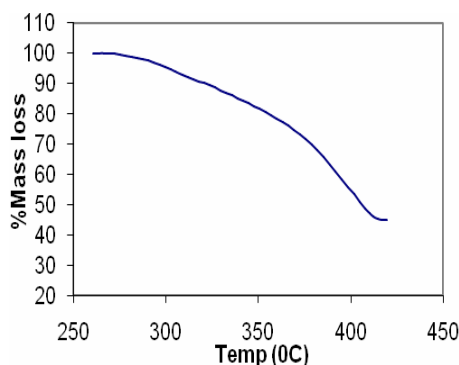


Fig.-3: TG Curve of Ni(II)SEPCPU Coordination polymer

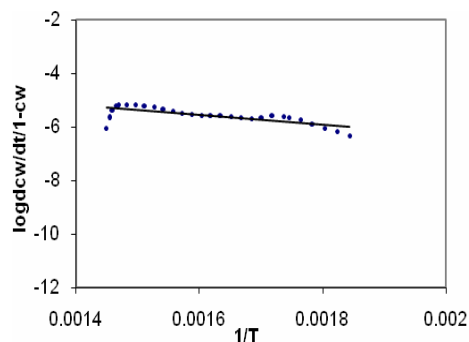


Fig.- 4: Sharp Went-worth plot of Ni(II)SEPCPU coordination polymer

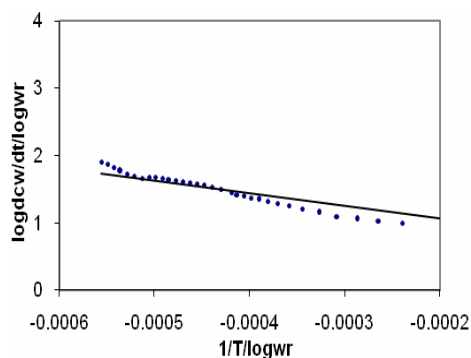


Fig.-5: Thermal activation energy plot of Ni(II)SEPCPU coordination polymer

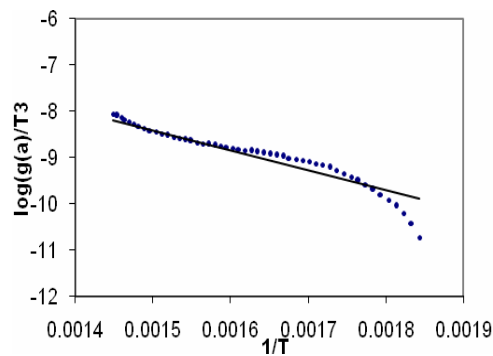


Fig.-6: Freeman Carroll plot of Ni(II)SEPCPU coordination polymer

CONCLUSION

On the basis of results obtained from various instrumental techniques, the coordination polymers may be suggested to have tetrahedral geometry for Mn(II), Co(II), Ni(II) and Zn(II), and square planar geometry for Cu(II) coordination polymers. All the coordination polymers are thermally stable and insoluble in

almost all organic solvents and hence they can be used as highly thermally stable powder coating materials. Structure is shown in Fig.- 2.

Table-2: IR Spectral assignment of coordination polymers (Cm⁻¹)

Coordination polymers	-NH-	-CH ₂ -	=C=N	-O-M	N→M
[Mn(II)(SEPCPU)] _n	3300 (w)	2925 (s)	1558 (s)	668 (m)	489(w)
[Co(II)(SEPCPU)] _n	3427(w)	2924(m)	1527 (s)	688 (w)	480(w)
[Ni(II)(SEPCPU)] _n	3405(b)	2929 (m)	1568(s)	678 (w)	500(w)
[Cu(II)(SEPCPU)] _n	3357 (b)	2922 (m)	1587(s)	681(w)	487 (w)
[Zn(II)(SEPCPU)] _n	3428(b)	2924 (m)	1600 (s)	680(w)	460 (w)

s – strong, vs – very strong, w – weak, b – broad, m – medium

Table – 3: Electronic spectral and magnetic susceptibility data of coordination polymers

Coordination polymer	Colour	μ _{ef} (B.M.)	Electronic spectra		
			Absorbance (kK)	Assignment	Stereochemistry
[Mn(II)(SEPCPU)] _n	Light pink	5.04	28.01,27.02	⁶ A ₁ → 4E(D)	Tetrahedral(High spin)
[Co(II)(SEPCPU)] _n	Pink	3.7	13.65	⁴ A ₂ → 4T ₁ (P)	Tetrahedral(High spin)
[Ni(II)(SEPCPU)] _n	Light green	3.2	19.94, 11.13	³ T ₁ → ¹ T ₂ ³ T ₁ → ¹ E	Tetrahedral(High spin)
[Cu(II)(SEPCPU)] _n	Blue	2.2	12.10, 10.52	dyz, dxy → dx ² y ²	Square planar
[Zn(II)(SEPCPU)] _n	White	diamagnetic	-	-	Tetrahedral

Table – 4: Thermal decomposition data of SEPCPU coordination polymers

Coordination polymer	Activation energy Ea(KJ/mole)		Entropy change (ΔS) JK ⁻¹	Free energy change (ΔF) KJ	Frequency factor (Z) Sec ⁻¹	Apparent Entropy Change (S*) JK ⁻¹	Order of reaction (n)	Decomposition temp. °C
	SW	FC						
[Mn(II)(SEPCPU)] _n	30.36	31.85	-243.66	195.09	18.16	-227.61	0.95	400
[Co(II)(SEPCPU)] _n	32.13	31.82	-260.41	209.83	19.32	-227.22	0.90	410
[Ni(II)(SEPCPU)] _n	33.85	35.52	-181.48	149.56	27.19	-223.03	0.96	360
[Cu(II)(SEPCPU)] _n	27.44	31.28	-240.11	171.03	19.34	-226.04	0.77	320
[Zn(II)(SEPCPU)] _n	23.96	26.31	-203.49	170.23	16.45	-228.91	1.00	440

FC: Freeman – Carroll Method SW: Sharp – Wentworth Method

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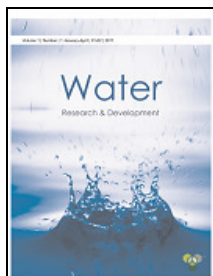
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