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SYNTHESIS, CHARACTERIZATION AND THERMAL ANALYSIS OF CHELATE POLYMERS OF SUBERYL BIS-P-BROMOPHENYLUREA WITH SOME TRANSITION METAL IONS

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ABSTRACT
Thermal decomposition studies of chelate polymers synthesized using metal acetate of Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) with suberoyl bis-p-bromophenyl urea were carried out by thermogravimetric analysis (TGA). The kinetic parameters (activation energy, entropy change and free energy change and frequency factor) were determined on the basis of TG curve and using data of the Freeman-Carroll and Sharp Wentworth methods. TGA detect the water molecules associated with the polymers either coordinated or crystalline. It suggests tetrahedral geometry for Mn(II), Co(II), and Zn(II) while octahedral geometry for Ni (II) and Cu (II) chelate polymers supported by elemental analyses, spectral and magnetic studies. On the basis of all instrumentation techniques it has been observed that the polymeric unit has M: L composition 1:1 and it was found that chelate polymer is highly thermally stable. Due to high thermal stability and insolubility they can be used as powder coating materials.

Key Words: *Thermogravimetric Studies, Chelate Polymers, Suberoyl Bis-P-Bromophenyl Urea*

INTRODUCTION
Since past few years, we have been engaged in the synthesis of organometallic complexes synthesized from transition metal ions with organic ligands, characterized by good thermal stability (Garg *et al.*, 2004) which might be used as surface coating materials (Yakuanoglu and Yoo, 2006) electrical semiconductors (Kaya and Chlhaoglu, 2008) for separation and determination of trace and toxic metal (Sharma, 2001) and catalyst (Venkatachalam *et al.*, 2005). Masoud *et al.,* (2006) reported the thermal properties of transition metal mureoxide complexes and calculated thermodynamic parameters of the decomposition steps (Masoud *et al.*, 2006). Earlier workers have reported polymeric chelates of a number of bis-biurets with metals of the first transition series from our laboratories (Gurnule, 2003).

This study is focused on the synthesis and characterization of some new chelate polymers of Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) with suberoyl bis-p-bromophenylurea as ligand in dimethyl formamide solvent.

MATERIALS AND METHODS
Materials
All Analytical Reagent Grade (Merck) chemicals and double distilled solvents were used for the preparation of ligand and chelate polymers.
Instruments
Reflectance spectra of chelate polymer 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 sophisticated instrumentation centre for Applied Research Testing, Vallabh Vidya Nagar, Anand Gujrat (SICART). FTIR spectra were recorded on Nicolet magna. R 550 series 2, spectrophotometer, USA, using KBr Technique in the range 400-4000 cm-[1] at Regional Sophisticated Instrumentation Centre, Lucknow. Bromine contents were analyzed at National Chemical Laboratory, Pune. C, H, N element contents were analyzed on E. A. 1108 Carlo Erba instruments. Thermo gravimetric analysis was carried out on TGA/SDTA-851, METTLER TOLEDO at RSIC, Nagpur University, Nagpur, using pt-pt-Rh thermocouple from 40 ^{0}C to 900 ^{0}C at a linear heating rate of 15^{0}C/min in air. Mass loss was recorded

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continuously on the recorder as a function of temperature. Magnetic susceptibilities of the chelate polymers were determined by Gouy's method and metal contents were estimated by Classical oxide method using platinum crucible.

Synthesis of Ligand and Chelate Polymers[1]

Preparation of –p-bromophenyl Urea: A quantity of (0.2 m mol) of finely powdered p- bromoaniline dissolved in a mixture of 100 ml glacial acetic acid and 200 ml distilled water at 35^0C. The solution of sodium cynate (NaCNO), (0.2 m. mol) in 100 ml distilled water at 35^0C, added gradually with constant stirring. Solid obtained was filtered and re-crystallized from 90% aqueous ethanol.

Preparation of Subaroyl dichloride: Subaroyl dichloride was prepared by the reaction of (0.1 m. mol) dry Subaric 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 SO_2, HCl and un-reacted $SOCl_2$, reaction mixture was then refluxed under reduced pressure for about 30 min.

Preparation of ligand (SUPBPU): The ligand subaroyl bis-p-bromophenyl urea was prepared by the condensation of subaroyl dichloride (0.1 m. mol) with p-bromophenyl 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-bromophenyl urea and was crystallized from DMF and dried at 100^0C and characterized by elemental analyses IR and ^{1}H NMR studies.

Synthesis of chelate 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 (70^0-80^0C). Both the solution 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 135^0C to 145^0C. The colour products obtained were filtered, washed thoroughly first with hot DMF and then with ethanol and acetone to remove untreated reactants if any and finally dried in oven. All the polymers formed are found to be insoluble in water and almost all organic solvents. Hence normal method of characterization such as ^{1}H NMR and electronic spectra in solution cannot be applied.

RESULTS AND DISCUSSION

Thermal Analysis of Chelate Polymers

The study of the thermal behavior of all the chelate polymers in air provides information about its thermal stability and nature of degradation of product at various temperatures.

The TG curves for [Mn(II) (SUPBPU)], [Co(II) (SUPPBPU)] and [Zn(II) (SUPBPU)] chelate polymers shows no mass loss observed up to 250 ^{0}C, which indicates absence of lattice as well as coordinated water. A gradual mass loss was observed between 250 ^{0}C- 530 ^{0}C may be due to the decomposition of organic species, thus suggested the tetrahedral geometry for these polymers and their decomposition temperatures are 375 ^{0}C, 380 ^{0}C and 425 ^{0}C respectively.

In the thermogram of $\{[Ni (II) (SUPBPU)] (H_2O)_2\}_n$ chelate polymer mass loss of 5.5 % between the temperature range of 100 ^{0}C to 220 ^{0}C corresponds to two coordinated water molecules (Nikolayev, 1969). A gradual mass loss between 220^{0}C to 450^{0}C represents degradation of organic part of the polymer corresponding to 47% mass loss from the polymer against calculated 48.5%. After 450 ^{0}C no mass loss was observed, indicates stable species formation and thus supports the octahedral geometry (Bonde, 2006).

In the TG curve of $\{[Cu (II) (SUPBPU)] (H_2O)_2\}_n$ chelate polymer no mass loss observed up to 120 ^{0}C indicates absence of water of hydration, then rapid thermal degradation observed up to 210 ^{0}C corresponding to 5.8 % mass loss, indicates presence of two molecules of coordinated water. From 210 ^{0}C a slow degradation observed up to 550 ^{0}C, which represents decomposition of organic species of chelate polymer. After that no change in mass observed indicates stable metal oxide formation. It suggests the octahedral geometry supported by spectral and magnetic studies (Lange *et al.*, 2004).

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The thermal activation energy has been calculated by using Freeman-Carroll (1958) and Sharp-Wentworth methods (1969). The thermodynamic parameters such as entropy change, free energy change, apparent entropy, frequency factor (z) and order of reaction (n) have been calculated using transition state theory. All these values are nearly same for each chelate polymer, which indicates similar type of reaction mode in all chelate polymers. The negative values of entropy change indicate that the activated complex has more ordered structure than the reactants and reactions are slow. Fig. 1 shows the representative thermogram of $\{[Ni (II) (SUPBPU)] (H_2O)_2\}_n$ chelate polymer. The important thermal data is given in the Table-1.

Electronic, Spectral and Magnetic Studies of Chelate Polymers

The electronic spectra of $[(Mn(II)(SUPBPU)]_n$ chelate polymer which shows one weak d-d transition at 23.42 kK may be assigned to the transition $^6A_1 \rightarrow {}^4E$ [D] and band appears at 17.27 kK may be due to charge transfer in tetrahedral field. The [Co (II) (SUPBPU)]$_n$ chelate polymer shows d-d transition at 15.72kK which is assigned to $^4A_2 \rightarrow {}^4T_1$ [P] transition indicates tetrahedral geometry (Omer, 2008). The spectra of $\{[Ni(II)(SUPBPU)](H_2O)_2\}_n$ chelate polymer exhibit two bands at about 21.27 kK and 12.12 kK which can be assigned to $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transitions respectively. These bands are in good agreement in octahedral field (Omer, 2008). In [Cu (II)(SUPBPU)$_n$] chelate polymer, bands appear at 12.85 kK and 18.93 kK which can be assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transition in octahedral field (Distorted). The magnetic moment values also support the octahedral geometry of Cu(II) chelate polymer (Khalid, 2008). Zn (II) chelate polymer is diamagnetic in nature and is having tetrahedral geometry. The spectral and magnetic data is given in Table-2.
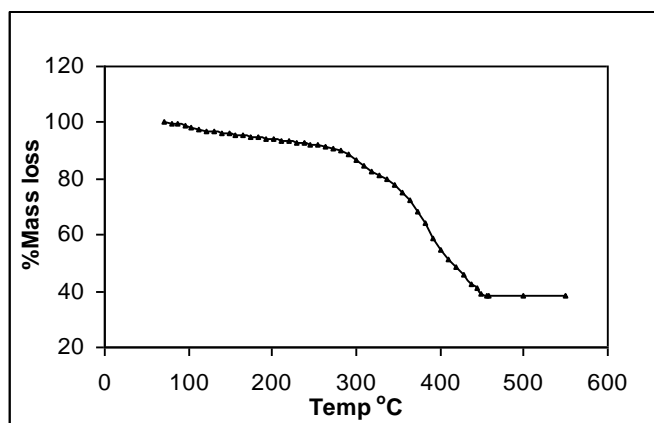
Figure 1: Thermogram of [Ni (II) (SUPBPU) (H$_2$O) $_2$] $_n$ Chelate Polymer

Table 1: Kinetic parameters of SUPBPU chelate polymers

Chelate Polymers	Activation energy (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)	Decom. Temp. ^0C
	SW	FC						
[Mn(II) (SUPBPU)]$_n$	25.23	24.68	-230.63	174.13	15.14	-228.81	0.73	375
[Co(II) (SUPBPU)]$_n$	21.95	22.49	-245.34	184.88	18.72	-227.10	0.75	380
[Ni(II) (SUPBPU)(H$_2$0)$_2$]$_n$	19.84	20.50	-290.37	189.79	12.19	-229.73	0.87	310
[Cu(II) (SUPBPU)(H$_2$0)$_2$]$_n$	19.17	19.35	-286.96	216.78	07.19	-235.49	0.93	415
[Zn(II) (SUPBPU)]$_n$	22.46	23.78	-250.48	198.61	19.12	-227.48	0.77	425

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

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Table 2: Electronic Spectral and Magnetic studies of chelate polymer

Chelate polymers	μ_{eff} (B.M.)	Electronic Spectra Absorbance (kK)	Assignment	Stereo chemistry
$[M_n(II) (SUPBPU)]_n$	5.79	23.42 17.27	$^6A_1 \to {^4E}$ (D) CT	Tetrahedral (high spin)
$[Co(II) (SUPBPU)]_n$	4.38	15.72 28.27	$^4A_2 \to {^4T_1}$ (P) CT	Tetrahedral (high spin)
$\{[Ni(II) (SUPBPU)](H_2O)_2\}_n$	3.70	21.27 12.12	$^3A_{2g1} \to {^3T_{1g}}(P)$ $^3A_{2g} \to {^3T_{1g}}(F)$	Octahedral (high spin)
$[Cu(II) (SUPBPU) (H_2O)_2]_n$	1.78	12.85 18.93	$^2B_{1g} \to {^2A_{1g}}$ $^2B_{1g} \to {^3E_g}$	Distorted Octahedral
$[Zn (II) (SUPBPU)]_n$	Diamagnetic	---	---	Tetrahedral

Infrared Studies of Chelate Polymers
In ligand SUPBPU, the IR bands observed at 3432 cm-1 and 1656 cm-1 have been assigned to stretching vibration of ((N-H) and ((C=0) of amide groups respectively (Patel *et al.*, 2012) . In all these chelate polymers, ((N-H) bands appeared in the region 3410-3431 cm-1. The band appears at 1656 cm-1 in ligand disappears in chelate polymers because bis-ligand undergoes keto-enol tautomerism.

Table 3: IR Spectral assignments of SUPBPU ligand and its chelate polymers cm^{-1}

SUPBPU	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Assignment
-	-	-	-	-	-	Lattice (H-O-H)
-	-	-	770(w)	728(w)	-	Coord. (H-O-H)
3432 (m)	3410 (b)	3427 (b)	3423 (b)	3431 (b)	3415 (b)	N-H
1656 (m)	-	-	-	-	-	C = O
-	1588 (s)	1585 (s)	1581 (s)	1591 (s)	1549 (s)	C = N
-	1196 (w)	1205 (w)	1135 (w)	1181 (w)	1206 (w)	C – O
2940 (w)	2932 (m)	2934 (m)	2936 (m)	2933 (m)	2928 (m)	-CH$_2$-
-	667 (w)	669 (w)	676 (w)	622 (w)	698 (w)	M – O
-	529 (w)	540 (w)	590 (w)	476 (w)	541 (w)	M – N

A new band observed around 1549-1591 cm-1 in chelate polymers may be due to formation of the C=N bond as a result of enolization, this is further supported by the presence of new band C-O in the range of 1135-1206 cm-1 in the chelate polymers. The new weak band appears in the region 622-698 cm-1 in the chelate polymers is attributed to the formation of Metal-Oxygen bond (Zhou *et al.*, 2006), while the presence of band around 476-590cm-1 may be assigned to M-N bond (Metal-Nitrogen interaction). The IR spectral data of the ligand and chelate polymers have given in Table-3.

Conclusion
On the basis of the results obtained from elemental analyses, infrared spectra, magnetic moment and thermal analyses, these newly synthesized chelate polymers of transition metal ions viz. Mn(II), Co(II) and Zn(II) are tetrahedral in nature, where as Cu(II) and Ni(II) chelate polymer are six coordinated in nature and all these polymers have thermal stability in the following order Zn(II) > Cu(II) > Co(II) > Mn(II) > Ni(II). Since all these polymers are highly insoluble in almost all organic solvents and have high thermal stability, they can be used as high thermally stable materials.

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