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Synthesis and Characterization of Sebacoyl Bis-P-Bromophenyl Urea Polymer

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ABSTRACT

New chelate polymers of sebacoyl bis-p-bromo phenyl urea with Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) have been synthesized. Characterisations of the ligand and its chelate polymers have been done by elemental analysis, infrared spectra, ^{1}H NMR spectra, reflectance spectra, magnetic susceptibility measurement and thermo gravimetric analysis. The thermal stability of chelate polymers has also determined. On the basis of instrumental analysis, it has been found that the interaction between ligand and metal ion takes place through oxygen and nitrogen.

Keywords: Thermo gravimetric studies, Chelate polymers, Sebacoyl bis-p-bromophenyl urea.

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INTRODUCTION

Development of new chelate polymers is of great interest owing to their potential applications [1-3]. During recent past, there has been an increasing interest in the synthesis of chelate polymers of transition metal ions with ligand containing carboxyl amide group, in which O and N as donor atoms. These polymers possesses thermal [4-5], catalytic and paramagnetic properties [6-7]. Properties are found to be effective in the formation of three dimensional open-framework materials [8], in the synthesis of coordination polymers which display anti-fungal biological activity [9] and designing supramolecular solid state architectures [10]. However, some other applications have been reported like ion exchanger [11], organometallic semiconductors [12], medicines [13] and sensors [14]. Due to the diverse coordinating behaviour of amide ligand and its important significance, this paper describes synthesis and characterisation of Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) chelate polymers derived from sebacoyl bis-p-bromophenyl urea and its metal acetate in dimethyl formamide media.

EXPERIMENTAL

Chemicals

All analytical reagent grade chemicals used were purified by standard method. Solvents were double distilled before used.

Instruments

Thermo gravimetric analysis was carried out on TGA/SDTA-851, METTLER TOLEDO at RSIC, Nagpur University, Nagpur, using Pt-Pt-Rh thermocouple from room temperature to 900^0C at a linear heating rate of 15^0C/min in air. Mass loss was recorded continuously on the recorder as a function of temperature. ^{1}H NMR spectra were obtained on a Brucker II-400 NMR spectrophotometer; using TMS as internal standard in CDCl3, Chemical shift were measured in ppm.

Synthesis of ligand and chelate polymers

Preparation of ligand and its chelate polymers were done on the basis of method reported earlier [15]. The elemental analyses and decomposition temperature of the ligand and its chelate polymers are given in Table- 1.

Table-1: Elemental and Thermal analyses of ligand and chelate polymers

Proposed composition of chelate polymers	Emperical formula	Formula weight	Yield %	Loss due to decomposition	Decomp. Temp. Range	Decomp. Temp. 0^0C	Elemental Analyses Calc. (found)				
							C	H	N	Br	M
SBPBPU (ligand)	$C_{24}H_{28}N_4O_4Br_2$	594.48	75	---	---	290	48.48 (48.40)	4.74 (4.71)	9.42 (9.35)	26.54 (26.48)	---
[M_n(II) (SBPBPU)]$_n$	$MnC_{24}H_{16}N_4O_4Br_2$	647.07	70	62.21	260-520	410	43.34 (43.26)	4.54 (4.47)	8.42 (8.30)	23.75 (24.29)	8.26 (8.21)
[Co(II) (SBPBPU)]$_n$	$CoC_{24}H_{16}N_4O_4Br_2$	651.06	60	63.41	270-510	420	44.27 (44.20)	4.33 (4.25)	8.62 (8.52)	24.26 (24.15)	9.05 (8.90)
{ [Ni(II) (SBPBPU)] (H_2O)}$_n$	$NiC_{24}H_{28}N_4O_8Br_2$	668.85	80	61.61	200-440	370	39.87 (39.79)	4.46 (4.38)	7.74 (7.66)	21.85 (21.72)	9.12 (8.05)
[Cu(II) (SBPBPU)]$_n$	$CuC_{24}H_{26}N_4O_4Br_2$	655.69	55	58.55	250-530	430	43.96 (43.82)	4.30 (4.21)	8.54 (8.47)	24.09 (23.90)	9.69 (9.58)
[Z_n(II) (SBPBPU)]$_n$	$ZnC_{24}\ H_{26}N_4O_4Br_2$	657.57	65	62.85	280-550	440	43.84 (43.75)	4.20 (3.96)	8.52 (8.43)	24.59 (23.85)	9.94 (9.82)

RESULTS AND DISCUSSION

Infrared Spectra

The infrared spectrum of the ligand SBPBPU shows a broad band at 3427 cm^{-1} which may be attributed to the N-H stretching frequency [16]. This band changes its position on coordination, indicating it participates in chelation. The above band merges with another band at around 3756 cm^{-1} may be due to H-OH of lattice water in Ni (II) polymeric chelate since only Ni (II) polymer in the present study has been found to contain lattice water. A sharp band observed at 1696 cm^{-1} may be assigned due to the C=O stretching vibrations [17]. It has been found that the band appears at 1696 cm^{-1} in ligand was disappeared in chelate polymers. It indicates that bis-ligand undergoes keto-enol tautomerism during polymerisation. A new band observed around 1528-1591cm^{-1} in chelate polymers. This clearly indicates that the (C=O) band disappeared due to formation of the C=N as a result of enolization [18].This is further supported by the presence of new band C-O in the range of 1102- 1199 cm^{-1} in chelate polymers.

The new bands appeared in the region 661-772 cm^{-1} in the chelate polymers may be attributed to the formation of the M-O bond [19], while the presence of band around 521- 580 cm^{-1} may be assigned to the M-N bond. The IR spectral data of the ligand and its chelate polymers have given in Table-2.

Table- 2: IR Spectral Assignments of SBPBPU ligand and its chelate polymers (cm^{-1})

SBPBPU	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Assignment
-	-	-	3756	-	-	Lattice (H-OH)
3427 (w)	3379 (w)	3287 (w)	3405 (s)	3432 (s)	3434 (s)	N-H
1696 (vs)	-	-	-	-	-	C = O
-	1560 (vs)	1528(s)	1569 (vs)	1591(vs)	1534 (vs)	C = N
2934 (w)	2925(w)	2924 (w)	2930 (w)	2946 (w)	2924 (w)	$-CH_2-$
-	668(w)	691 (w)	680 (w)	689 (w)	670 (w)	M – O
-	521 (vw)	560 (w)	550 (vw)	580 (w)	561 (w)	M – N

s- strong, vs – very strong, w – weak, vw – very weak

Electronic, Spectral and Magnetic Susceptibility of Chelate Polymers:

In {(Mn(II)(SBPBPU)}$_n$ polymer, band appears at 28.15 kK may be attributed to the $6A_1 \rightarrow 4E[D]$ transition in tetrahedral field [20] and in [Co(II)(SBPBPU)]n chelate polymer band appears at 14.63 kK may be assigned due to $^4A_2 \rightarrow {}^4T_1[P]$ transition in tetrahedral field [21]. In {[Ni (II)(SBPBPU)] (H$_2$O)]}$_n$ chelate polymer bands appear at 19.18 kK and 11.92 kK respectively may be attributed to $^3T_1 \rightarrow {}^1T_2$ and $^3T_1 \rightarrow {}^1E$ [22]. In [Cu (II) (SBPBPU)] $_n$ chelate polymer, band appears at 12.15 kK may be assigned to the dxz, dyz → $dx^2\text{-}y^2$ transition in square planar field. The magnetic moment value [23] also support the square planar geometry for Cu (II) chelate polymer. Zn (II) chelate polymer is diamagnetic in nature and is having tetrahedral geometry. The spectral and magnetic data are given in Table-3.

Table-3: Electronic Spectral and Magnetic Studies of Chelate Polymer

Chelate polymers	Colour	μ_{eff} (B.M.)	Electronic Spectra		Stereo chemistry
			Absorbance (kK)	Assignment	
[M$_n$(II) (SBPBPU)]$_n$	Light pink	5.85	28.15 18.52	$^6A_1 \rightarrow {}^4E$ (D) CT	Tetrahedral (high spin)
[Co(II) (SBPBPU)]$_n$	Pink	4.62	14.63 11.24	$^4A_2 \rightarrow {}^4T_1$ (P) CT	Tetrahedral (high spin)
{[Ni(II (SBPBPU)](H$_2$O)}$_n$	Light green	3.65	19.18 11.92	$^3T_1 \rightarrow {}^1T_2$ $^3A_1 \rightarrow {}^3E$	Tetrahedral (high spin)
[Cu(II) (SBPBPU)]$_n$	Blue	2.09	27.85 12.15	CT dxz, dyz → $dx^2 - y^2$	Square planar
[Zn (II) (SBPBPU)]$_n$	White	Diamagnetic	---	---	Tetrahedral

Thermo Gravimetric Analysis of Chelate Polymers:

The studies of thermal behaviour of all the chelate polymers provide information about their thermal stability and nature of degradation at different temperatures. According to Nikolaev et al. [24], water eliminated below 140-150^0 C may be considered as lattice water and water eliminated above 150-180^0 C may be considered as co-ordinated water. TG curves of Mn (II), Co (II), Cu (II) and Zn (II) chelate polymers showed the absence of coordinated and lattice water since no mass loss was observed up to 200^0 C.Then the gradual mass loss was seen upto 500^{0}C, which may be due to the decomposition of organic part of chelate polymers. Above 500^{0}C no mass loss observed due to the formation of stable metal oxide. The decomposition temperatures of these polymers were found to be 375^{0}C, 380^{0}C, 415^{0}C and 380^{0}C respectively. This favours the four coordinated geometry.

The chelate polymer of $\{[Ni (II) (SBPBPU)] (H_2O)\}_n$ shows a mass loss of 2.65 % up to 140^{0}C, due to the evolution of one lattice water [25]. A gradual mass loss was then observed between 200^{0}C to 450^{0}C due to decomposition of organic part of the polymer. After 450^{0}C no mass loss was observed due to formation stable metal oxide. The decomposition temperatures are given in Table-1. These newly synthesized chelate polymers have thermal stability in the following order.

Zn (II) > Cu (II) > Co (II) > Mn (II) > Ni (II).

NMR Studies of Ligand

The ^{1}H-NMR spectrum of ligand sebacoyl bis-p-bromo phenyl urea in acetone solvent along with complete assignments of signals for aliphatic and aromatic protons have shown in Fig. 3. The NMR spectral data of ligand is given in Table-4. The NMR signal around ∂ (chemical shift) 2.03-2.32 ppm is assigned to the over laps of ligand [26]. The aromatic protons of two phenyl groups are appeared at ∂ 7.48-7.63 ppm due to the presence of (-NHC=O) amide groups attached directly to benzene ring [27] and other resonance signal around ∂ 7.41-7.45 ppm is assigned due to two protons of benzene ring at which bromine attached [28]. The resonance weak signal around ∂ 5.58 ppm is assigned two protons of amide group (-NHC=O) [29].

Table 4: ^{1}HNMR Spectral Data of Ligand:

Observed Chemical Shift (δ) ppm	Nature of proton assigned	Expt. Chemical Shift (δ) ppm
2.03-2.3240	Methylene proton of $–CO-(CH_2)_n-CO$	1.4 – 2.4
5.58	Proton of Nitrogen of –C-NH-CO-	5.16
7.41-7.45	Aromatic Proton of Ar-H	7.41

Concluding Remarks

On the basis of elemental analyses, infrared spectra, electronic spectra, magnetic moment measurement and thermal analyses, the chelate polymers may be suggested to have high spin tetrahedral geometry for Mn (II), Co (II), Ni (II) and Zn (II) , while square planar geometry for Cu (II) polymer. Since these polymers are highly thermally stable, therefore these polymers may be used as powder coating materials. The structures of chelate polymers have shown in Fig. 1 and 2.

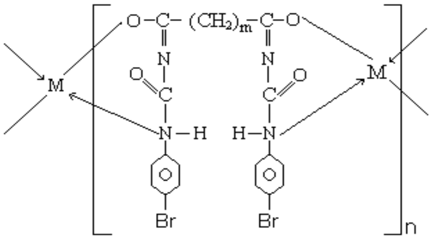
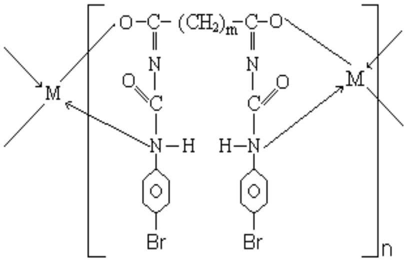


Fig. 1 **M = Mn (II), Co (II),Cu (II) and Zn (II)**

m = 8 (SBPBPU)



H_2O

Fig.2 **M= Ni (III),**
m = 8(SBPBPU)

Figure. 3: ^{1}H NMR of ligand (SBPBPU)

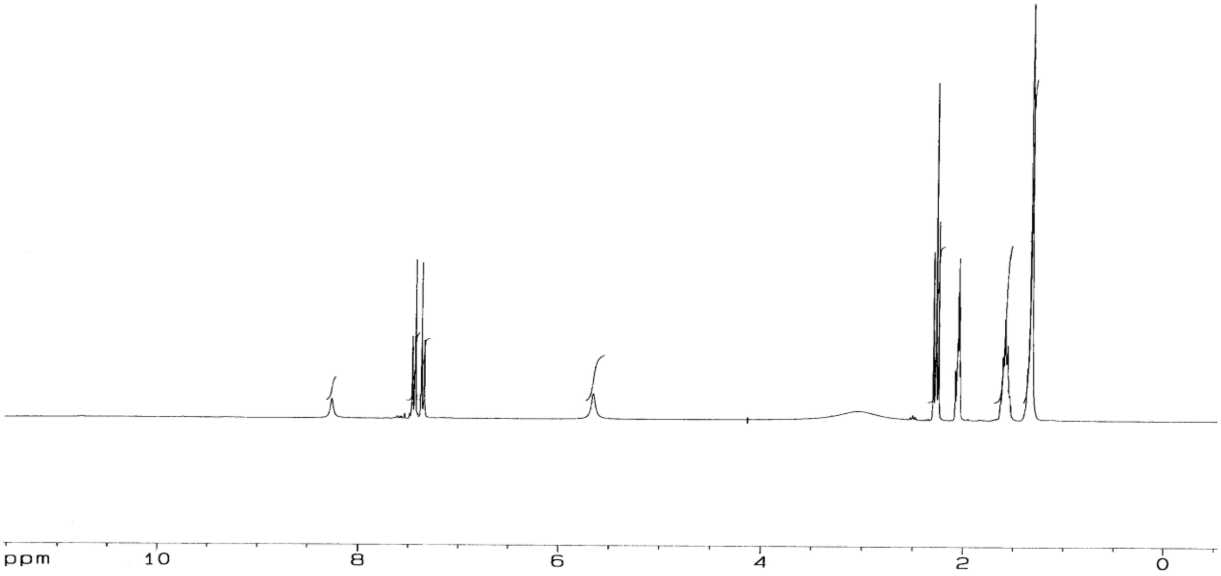
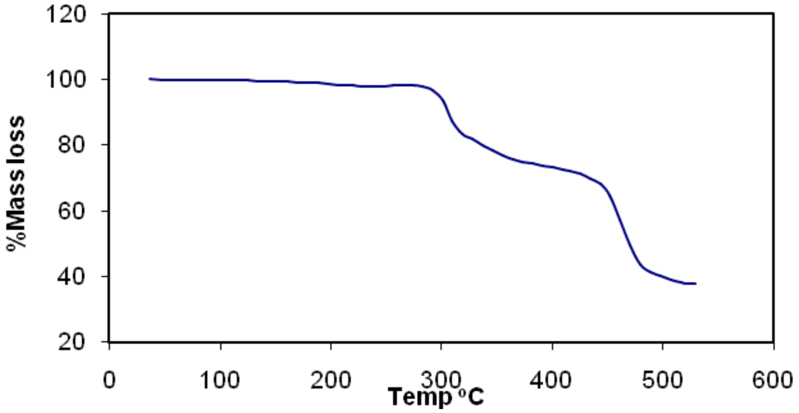


Figure-4. Thermo gram of [Mn(II)(SBPBPU)]$_n$ chelate polymer



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