Asian Journal of Chemistry Vol. 11, No. 4 (1999), 1251–1258

Synthetic, Structural and Thermal Studies of Some Coordination Polymers of Sebacyl Bis-Biuret with First Transition Series Metals

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Some new polymeric chelates have been synthesized by combining sebacyl bis-biuret with metals of first transition series, *viz.*, Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). These were characterized with the help of elemental analysis, infrared and reflectance spectral and magnetic studies. A detailed thermal study was carried out and thermal stability compared. Freeman-Carrol and Sharp-Wentworth methods have been used to calculate the activation energy and order of reaction. Thermodynamic parameters have been calculated, using the data of Freeman-Carrol method. The results obtained have been suitably discussed.

INTRODUCTION

Polymeric chelates are fast becoming important due to their thermal stability and other practical applications. Lot of work has been reported from our laboratories on the synthesis, characterization and thermal properties of several coordination polymers[1,2]. Vensco-Szmocsanyl and Szilagri have reported thermal behaviour of coordination polymers including ionic polyesters[3]. The present paper describes a detailed study on the synthesis, characterization, structural and thermal degradation of polymeric chelates of sebacyl bis-biurets with metals of first transition series, *viz.*, Mn(II), Co(II), Ni(II), Cu(II) and Zn(II).

The Freeman-Carrol[4] and Sharp-Wentworth[5] methods have been used to evaluate various kinetic parameters for these coordination polymers with the help of non-isothermal TG pattern of coordination polymers. Sestal has compared experimental and analytical errors in these and other methods of analysis[6]. The advantage of Freeman-Carrol method is that in one single step by keeping dT/dt constant, both the order of reaction and the energy of activation can be calculated.

Theoretical considerations

Freeman-Carrol method (FC): The following expression is used to evaluate various kinetic parameters by this method:

$$\frac{\Delta \log(dw/dt)}{\Delta \log(w_r)} = \frac{-E_a}{2.303R} \frac{\Delta(1/T)}{\Delta \log(w_r)} + n \qquad \ldots (1)$$

A plot between $[\Delta \log (dw/dt)]/[\Delta \log (w_r)]$ against $[\Delta(1/T)]/[\Delta \log (w_r)]$ will give on y-axis (x = 0) an intercept for the value of n, the order of reaction and the slope $m = -E_a/2.303R$. In the above equation, $w_r = w_c - w$, where w_c is the weight loss at the completion or at a definite time, w is the total weight loss up to time t, T is the temperature.

Sharp-Wentworth method (SW): The expression to evaluate the activation energy is as follows:

$$\frac{\log (dc/dt)}{(1-c)} = \log (A/\beta) - \frac{E_a}{2.303}(1/T) \qquad \ldots (2)$$

where dc/dT is the fraction of mass loss with time t, T is temperature and rate $\beta = dT/dt$.

EXPERIMENTAL

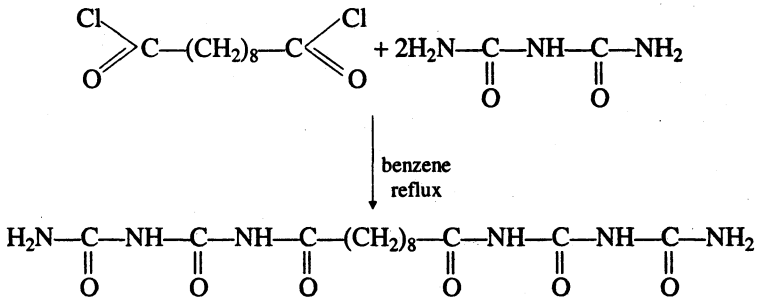
All the chemicals used were of AR grade.

C, H, N contents were analysed on EA 1108 elemental analyser Carlo Erbus instrument. FTIR were recorded on a Nicholet Magna IR 550 series 2, USA using KBr technique in the wavelength range 4000–400 cm^{-1} at RSIC, Nagpur. Reflectance spectra were recorded on a single beam Karl-Zeiss Jena, Specord M-400 spectrophotometer in the range 250–600 nm. Magnetic susceptibility of the polymeric chelate was determined by Gouy's method.

The non-isothermal TG measurements of Mn(II), Ni(II) and Zn(II) coordination polymers were carried out using a thermobalance fabricated at the Department of Chemistry, Nagpur University, Nagpur. A copper-constantan thermocouple with a temperature range of 0°–600°C was used as a temperature indicator. All the measurements were made at a linear heating rate of 4 deg min^{-1} in air. Mass loss was recorded at a regular interval of 20°C. Co(II) and Cu(II) coordination polymers were analysed at RSIC, Nagpur using Pt-PtRh thermocouple from 0°–1000°C at a linear heating rate of 10 deg min^{-1} in air. Mass loss was recorded continuously on the recorder.

Preparation of ligand

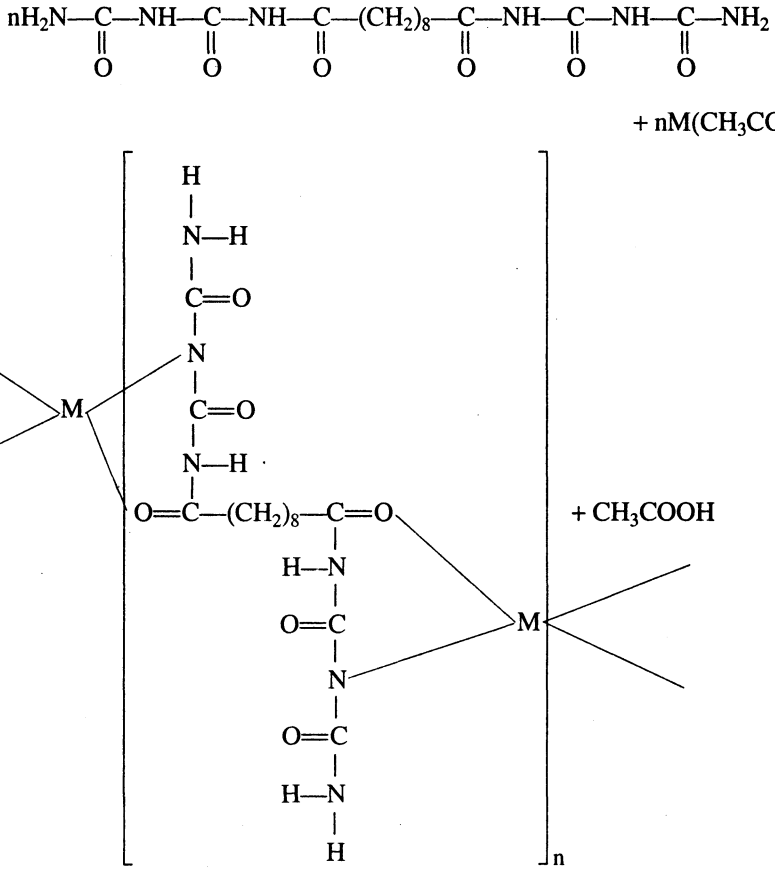
The ligand was synthesized by condensation of biuret with sebacyl chloride in aprotic medium.



The ligand thus formed was recrystallized, dried and characterized with elemental analysis and IR spectral studies.

Preparation of coordination polymers

The coordination polymers were synthesized by the reaction between equimolar quantities of bis-ligands and metal acetates in minimum amount of DMF. The reaction mixture was heated in an oil bath at 120°C for 24 h. The following reaction produces the solid coordination polymers which were filtered and washed with hot DMF and alcohol to remove unreacted ligand and metal acetates. Then they were dried and characterized.



RESULTS AND DISCUSSIONS

The composition of the polymeric unit was elucidated on the basis of a detailed study of elemental analysis of polymers, IR and reflectance spectral and magnetic studies. The presence of water of crystallization was ascertained on the basis of TG studies.

The polychelates are found to be insoluble in all common organic solvents. The elemental analysis data are presented in Table-1.

The infrared spectrum of the ligand shows a broad peak in the region 3400 cm^{-1} attributed to $—NH_2$ group[7] which does not shift its position in the

polymers indicating its non-participation in chelation. This band merges with another band due to lattice water in Co(II) polymeric chelate. A medium band in the region 2880–2854 cm^{-1} of the ligand is assigned to —NH (imino) group[8]. In the polymeric chelate, it shows a slight shifting toward the lower frequency region. This insignificant shift is because of the presence of other non-coordinated —NH groups present in the ligand. A careful examination of IR spectra however reveals that the intensity of —NH bands in the polymeric chelates is reduced compared to ligands[9] as only one of the rings, to give rise to —N—M covalent bond in the region 540–440 cm^{-1}.

TABLE-1
ELEMENTAL ANALYSIS OF POLYMERIC CHELATES

Polymeric unit	Colour	% found (calcd.)			
		C	H	N	M
$[Mn(SEBB)]_n$	Dark Brown	39.46 (39.34)	5.70 (5.60)	19.07 (19.67)	12.44 (12.84)
$\{[Co(SEBB)(H_2O)_2]H_2O\}_n$	Pink	36.55 (35.98)	5.72 (6.04)	17.99 (17.98)	13.95 (12.61)
$[Ni(SEBB)(H_2O)_2]_n$	Light green	35.85 (35.90)	5.65 (5.13)	17.50 (17.95)	12.63 (12.50)
$[Cu(SEBB)]_n$	Brown	38.65 (38.56)	5.61 (5.50)	19.18 (19.28)	13.08 (14.58)
$[Zn(SEBB)]_n$	White	38.69 (38.44)	5.50 (5.49)	19.12 (19.22)	14.74 (14.94)

TABLE-2
IMPORTANT IR-BANDS (cm^{-1}) OF THE LIGAND AND POLYMERIC CHELATES

SEBB	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Assignments
—	—	3540	—	—	—	—H—OH lattice water
3400	3375	3415	3380	3431	3432	$—NH_2$
2854	2855	2854	2856	2855	2851	—NH
1690	1683	1661	1685	1614	1620	—C=O at —C=O → M
—	—	784	795	—	—	—H—OH coodinated water
—	624	611	600	555	560	—O—M
—	520	540	440	458	490	—N—M

The band in the region 1780–1550 cm^{-1} in ligands is attributed to (—C=O) groups[10, 11]. It is shifted towards lower frequency region in the polymeric chelate. This indicates the delocalization of the electronic charge of (—C=O) into the chelate ring[12, 13]. However, again due to the presence of non-chelated (—C=O) groups, the effect is somewhat less prominent. A coordinate bond —C=O → M is formed[14, 15]. This is further confirmed by the presence of a new

band in the region 625–480 cm^{-1} in the polymeric chelates which may be due to O → M band[16, 17]. Important IR bands (cm^{-1}) are tabulated in Table-2.

Magnetic susceptibility studies

The magnetic susceptibility value of Mn(II) polychelate is 6.11 BM which is consistent with the high spin tetrahedral configuration[18]. The Co(II) polymeric chelate shows a magnetic moment of 5.08 BM indicative of high spin octahedral stereochemistry[19]. And for a Cu(II) polymer, the magnetic moment is 2.40 BM showing a square planar geometry. Zn(II) polymeric chelate is found to be diamagnetic due to filled *d*-orbitals. The stereochemistry of the polymeric chelates is further supported by electronic spectral studies.

Electronic spectral studies

Mn(II) polymeric chelate shows one band in the region 21.44 kk corresponding to $^6A_1 \rightarrow {}^4E(G)$ d-d transition. The other band at 15.63 kk is of charge transfer transition. The spacial arrangement of the ligand molecule around the Mn(II) is tetrahdral.

Electronic spectra of Co(II) polymeric chelate exhibit two d-d transition bands in the region 18.86 kk and 14.43 kk which may be reasonably assigned to $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ and $^4T_{1g} \rightarrow {}^4A_{2g}$ respectively and are consistent with reported observations for octahedral geometry around Co(II) ion.

In case of Ni(II) polymeric chelate, bands at 22.74 kk and 15.87 kk can be attributed to $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ in octahedral field.

Cu(II) polymeric chelate shows one d-d transition band at 14.08 kk due to $d_{xy}, d_{xz} \rightarrow d_{x^2} - d_{y^2}$ transition suggestive of its square planarity[20].

TABLE-3
MAGNETIC AND ELECTRONIC SPECTRAL DATA OF POLYCHELATES

Polymer	Absorbance (kk)	Assignments	Effective magnetic moment (BM)	Stereochemistry
Mn-SEBB	21.74	$^6A_1 \rightarrow {}^4E(G)$	6.11	Tetrahedral
	15.63	C.T.		(h.s.)
Co-SEBB	18.86	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$	5.08	Octahedral
	14.43	$^4T_{1g} \rightarrow {}^4A_{2g}$		(h.s.)
Ni-SEBB	22.74	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	4.38	Octahedral
	15.87	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$		(h.s.)
Cu-SEBB	20.00	C.T.	2.40	Sq. planar
	14.70	$d_{xy}, d_{xz} \rightarrow d_{x^2}-d_{y^2}$		

Since Zn(II) is a d^{10} system, the reflectance data are of very little importance. From TGA data, its most probable geometry is suggested to be tetrahedral.

Table-3 shows the magnetic and electronic spectral data of the polymeric chelates.

Thermogravimetric analysis

The Mn(II), Cu(II) and Zn(II) coordination polymers do not show presence of lattice or coordinated water. Decomposition ranges of these polymers are 240–370, 340–480 and 290–510°C while decomposition temperatures are 320, 290 and 430°C respectively.

In case of Co(II) coordination polymer, the thermogram shows a mass loss between 100 and 130°C corresponding to one molecule of lattice water. Then there is another loss observed between 130 and 210°C, attributed to two molecules of coordinated water. After this a gradual degradation of organic part of the polymer takes place between 250 and 510°C. Decomposition temperature is found to be 400°C.

On the other hand, the loss of water in Ni(II) coordination polymer is between 110 and 220°C corresponding to two molecules of coordinated water. Decomposition range is from 220 to 510°C while decomposition temperature is 330°C. The thermal stabilities of SEBB coordination polymers were found to be in the order:

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

A representative TG curve of Co(II) coordination polymer is shown in Fig. 1.

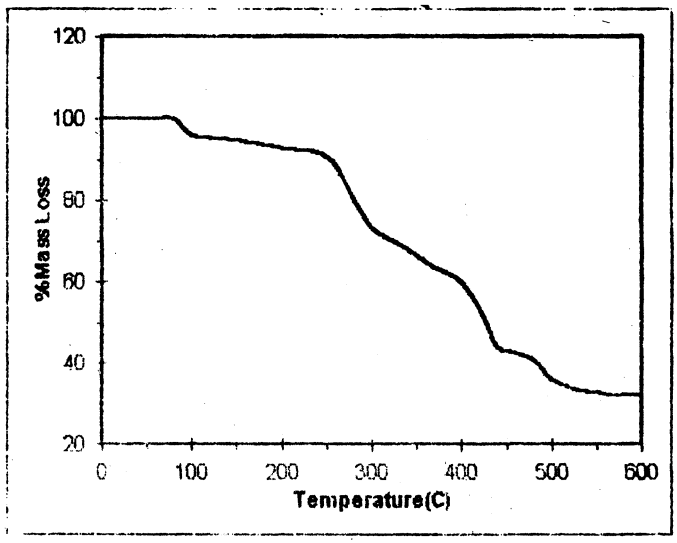


Fig. 1 Thermogram of Co-SEBB Polymer

Kinetic parameters

By applying the Freeman-Carrol and Sharp-Wentworth methods to the thermogravimetric data, activation energy and order of reaction have been calculated. These values are given in Table-1. Representative plots of Freeman-Carrol and Sharp-Wentworth of Co(II) SEBB coordination polymer is shown in Figure 2.

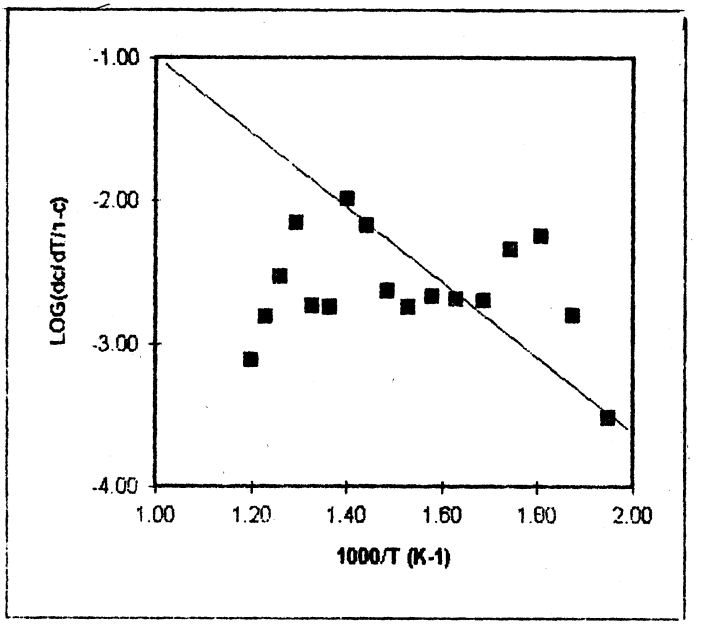


Fig. 2 Sharp-Wentworth Plot of Co-SEBB Polymer

TABLE-4
ACTIVATION ENERGY AND DECOMPOSITION TEMPERATURE OF COORDINATION POLYMERS

Polymer	Decomposition temperature (°C)	Activation energy (kJ^{-1})	
		FC	SW
$[Mn(SEBB)]_n$	320	52.92	43.04
$\{[Co(SEBB)(H_2O)_2]H_2O\}_n$	400	25.50	49.73
$[Ni(SEBB)(H_2O)_2]_n$	330	23.91	42.08
$[Cu(SEBB)]_n$	390	73.85	68.01
$[Zn(SEBB)]_n$	430	31.08	71.05

Thermodynamic parameters have been calculated on the basis of thermal activation energy. These values are presented in Table-5.

These calculations were done with the help of a computer program to have minimal human error. From the data given in Table-5, it can be seen that thermodyanamic parameters are comparable. The similarity of the thermodyanamic parameters indicates a common mode of reaction. It can be further observed that Z values are comparatively lower. From this it can only be concluded that decomposition of coordination polymers is a slow reaction. Also it is observed that the decomposition of the polychelates are frequently found not to obey first order kinetics perfectly consistent with the observations of Jacobs and Tompkins[21] and of Coats and Redfern[22].

TABLE-5
THERMODYANAMIC PARAMTERS OF SEBB COORDINATION POLYMERS

Polymeric unit	Entropy change ΔS (J)	Free energy ΔF (kJ)	Frequency factor Z (s^{-1})	Apparent Entropy change S^* (J)	Order of reaction n
$[Mn(SEBB)]_n$	164.65	117.33	1.70×10^3	–188.49	1.05
$\{[Co(SEBB)(H_2O)_2]H_2O\}_n$	162.23	137.19	1.04×10^2	–174.85	0.9
$[Ni(SEBB)(H_2O)_2]_n$	163.11	159.70	1.59×10^2	–245.36	0.8
$[Cu(SEBB)]_n$	154.37	193.29	7.46×10^2	–196.37	0.89
$[Zn(SEBB)]_n$	110.81	219.18	1.62×10^2	–236.28	0.6

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(*Received*: 26 February 1999; *Accepted*: 13 July 1999) AJC-1780