

Syntheses and characterization of fumaryl bis-2-aminobenzothiazole chelate polymers

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ABSTRACT

Chelate polymers of first row transition metal ions viz Mn (II), Co(II), Ni(II), Cu(II) and Zn(II) have been prepared with the ligand derived from fumaryl bis-2-aminobenzothiazole having equimolar stoichiometry of the cations and the ligands. The newly synthesized chelate polymers were characterized by elemental analyses, magnetic, infrared and reflectance spectra. The synthesized chelate polymers are coloured, amorphous, solid and highly insoluble in aqueous and common organic solvents. The structure of the chelate polymers has been assigned on the basis of spectral and magnetic studies.

Key words: Chelate polymers, Infrared spectroscopy, Magnetic measurements, Reflectance spectra.

INTRODUCTION

Polymers are important materials used in commodities such as tyres, textiles, thermosets, composites material, transportation industry, automotive, marine and aerospace. The demand for new materials with practical applications has been promoted research in the design and syntheses of chelate polymers, on account of its various applications¹⁻⁵. IR spectra have shown potential bidentate behaviour of ligands with different donor groups like nitrogen, oxygen and sulphur etc which could give complexes of varied coordination numbers and properties. The ligands derived from pri.diamines and 3, 6-dimethyl/diphenyl-4, 5-diazaocta-3, 5-diene-2, 7-dione and their complexes were stable upto 200°C; whereas 90% mass loss was recorded upto 552°C⁶.

A new macroacyclic amide ligand N,N'-bis(2-benzothiazolyl)2,6-pyridinedicarboxamide

formed by the condensation of 2,6-pyridinedicarbonyldichloride with 2-aminobenzothiazole and its complexes were found to be stable 700-800°C⁷.

We report here the preparation and characterization of fumaryl bis-2-aminobenzothiazole and its Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) chelate polymers.

EXPERIMENTAL

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

Preparation of bis-ligand

The bis-ligands were prepared by the condensation of acid dichloride (0.1m mol) with (0.2m mol) of 2-aminobenzothiazole and refluxing it in 100ml dry benzene for about 5-6h .The ligand

was then filtered and washed with hot benzene and then with hot alcohol. The resultant products were then dried and recrystallized.

Syntheses of Chelate Polymers

An equimolar quantity of bis ligand (0.1 mol) and metal acetate (0.1 mol) were dissolved separately in minimum quantity of DMF in hot condition. The hot solutions are then mixed and refluxed. The temperature of the reaction mixture was kept between 120-160°C. Polymers generally appeared after 24h heating in an oil bath. Syntheses of Fumaryl bis-2-aminobenzothiazole ligand (FBABT) is shown in Fig 1. Elemental analyses of the chelate polymers are given in Table 1.

RESULTS AND DISCUSSION

On the basis of C, H, N analyses, infrared spectra, magnetic data, reflectance spectra and thermal data, the proposed structure of chelate polymers have shown in fig. 2a & 2b.

Infra red spectral studies

Ligand shows moderately strong band near 3231 cm⁻¹ which may be assigned due to stretching vibration of a secondary amide -NH- group^{8,9,10}. The presence of band around 525-415 cm⁻¹ may be assigned to N→M bond¹¹. The IR spectra of ligand show a peak in the region of 2920-2853 cm⁻¹ that may be attributed to (-CH₂) stretching. The band

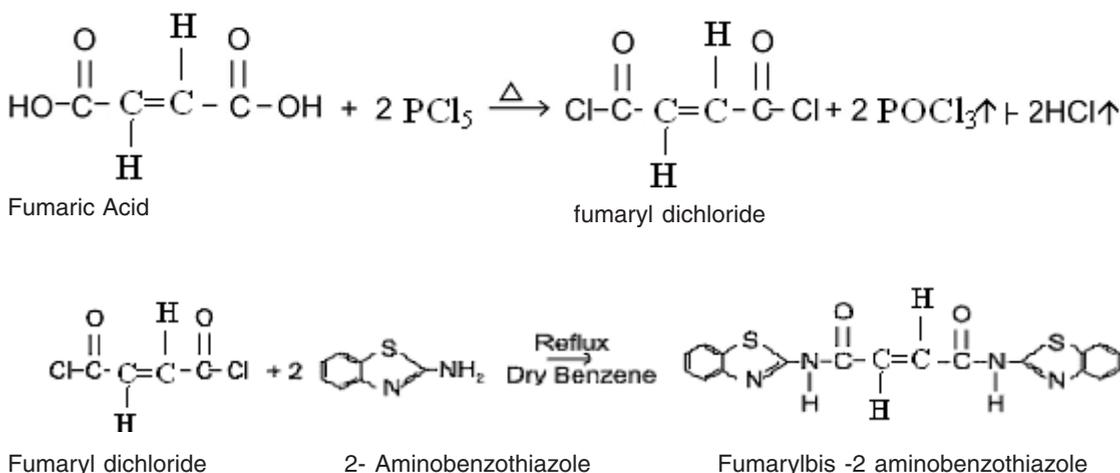
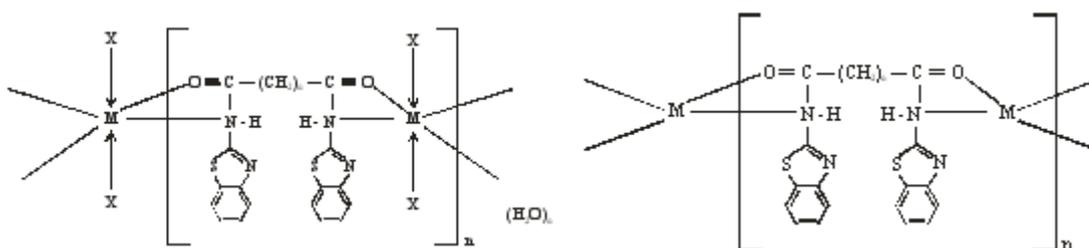


Fig. 1: Syntheses of Fumaryl bis-2-aminobenzothiazole Ligand (FBABT)



For $-(\text{CH}_2)_n$, $n = 2$ for Fumaric acid $M = \text{Mn(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}$ and Zn(II) . Fig: 2a $X =$ Coordinated Water, $X = 0$ in Co(II) . $(\text{H}_2\text{O})_n$ i.e lattice Water in case of $\text{Co(II)-FBABT}, \text{Ni(II)-FBABT}$

Fig 2b: In case of Mn(II)-FBABT, Cu (II)-FBABT, Zn (II)-FBABT

Table 1: Analyses of ligand its chelate polymers

Composition of Chelate Polymer	Empirical formula	Formula weight	% yield	% Loses Due to Decom- position	Decom- position Temp. Range °C	Decom- position Temp °C	Elemental Analyses Cal. (Found)				
							C	H	N	S	Metal
FBABT	$C_{18}H_{12}N_4O_2S_2$	380	72				56.84	3.15	14.73	16.84	-
[Mn(II)(FBABT)] n	$C_{18}H_{12}N_4O_2S_2Mn$	434.93	66	87	220-700	460	49.66 (49.62)	2.78 (2.71)	12.87 (12.83)	14.71 (14.69)	25.26 (25.2)
[Co(II)(FBABT)] n.(H ₂ O) ₂	$C_{18}H_{16}N_4O_{24}S_2Co$	466.8	68	88	120-690	375	46.27 (46.26)	2.57 (2.53)	11.9 (11.88)	13.71 (13.7)	25.24 (25.22)
[Ni(II)(FBABT)(H ₂ O) ₂]n(H ₂ O) ₂	$C_{18}H_{16}N_4O_6S_2Ni$	505.84	74	88	130-640	380	42.7 (42.68)	2.76 (2.74)	11.07 (11.05)	12.6 (12.5)	23.2 (23.19)
[Cu(II)(FBABT)] n	$C_{18}H_{12}N_4O_2S_2Cu$	443.546	79	89	210-740	475	48.69 (48.65)	2.7 (2.68)	12.62 (12.6)	14.42 (14.4)	28.65 (29.32)
[Zn(II)(FBABT)] n	$C_{18}H_{12}N_4O_2S_2Zn$	445.39	72	92	200-680	440	48.49 (48.47)	2.69 (2.67)	12.57 (12.54)	14.39 (14.32)	29.36 (29.32)

appearing in the region of 1700-1550 cm^{-1} in the ligand may be assigned to the C = O group¹², which gets lowered down in the chelate polymers confirming that the oxygen atom of the C = O group take part in coordination¹³. The C-N stretching band of primary amides appearing in the range of 1400-1350 cm^{-1} is found to be lowered in case of chelate polymers which supports the possibility of N→M bond. The C-S stretching vibration is observed in the region of 700-600 cm^{-1} , since there is no considerable change in the band frequencies of ligand and their chelate polymers, it gives an evidence that sulphur has not participated in bonding with the metal¹⁴. The new weak band appearing in the region of 670-618 cm^{-1} in the coordination polymers may be due to the formation of M-O bond¹⁵. Medium band appearing in the range of 820-750 cm^{-1} in case of few chelate polymers may be attributed to the presence of water of coordination¹⁶. The important IR spectra of ligands and its chelate polymers are given in Table: 2.

Electronic spectra and magnetic susceptibility of chelate polymers

In $[\text{Mn(II)}(\text{FBABT})]_n$ chelate polymer band appears at 6.18 kk may be assigned due to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_2$ (G) transition in octahedral field. The magnetic moment value also supported tetrahedral geometry of $[\text{Mn(II)}(\text{FBABT})]_n$ chelate polymer¹⁶. The band appearing in case of $[\text{Co(II)}(\text{FBABT})]_n(\text{H}_2\text{O})_2$ at 17.24 kk may be attributed to ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ (P) transition in tetrahedral field¹⁷. In $[\text{Ni(II)}(\text{FBABT})(\text{H}_2\text{O})_2]_n(\text{H}_2\text{O})_2$ chelate polymer the bands appear at 16.12 kk may be assigned due to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ transition in octahedral field¹⁷; respectively which is further supported by magnetic moment value. Zn(II) chelate polymer is diamagnetic in nature and has tetrahedral geometry. The electronic spectra and magnetic susceptibility of chelate polymers are given in Table: 3.

Thermogravimetric analyses of chelate polymers

Thermogram of Mn(II)(FBABT) Chelate polymer shows the absence of lattice and

Table 2: IR spectra of Ligand (FBABT) and its chelate polymers

Ligand & Chelate Polymers	C=O	CHN	NHH	HCH ₂	H-O-H	MHO	CHS	N→M
FBABT	1651	1469	3231	2921	-	-	625	-
$[\text{Mn(II)}(\text{FBABT})]_n$	1586	1447	3161	2920	-	652	625	485
$[\text{Co(II)}(\text{FBABT})]_n(\text{H}_2\text{O})_2$	1585	1450	3112	2920	-	653	624	482
$[\text{Ni(II)}(\text{FBABT})(\text{H}_2\text{O})_2]_n(\text{H}_2\text{O})_2$	1589	1459	3151	2920	802	654	627	475
$[\text{Cu(II)}(\text{FBABT})]_n$	1620	1462	3110	2924	-	650	627	489

Table: 3: The Electronic Spectra and Magnetic Susceptibility of Chelate Polymers

Chelate Polymer	Colour	$\mu_{\text{eff}}(\text{B.M})$ Spectra	Electronic	Assignments	Stereochemistry
$[\text{Mn(II)}(\text{FBABT})]_n$	Cream	6.18	27.7	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_2$ (G)	Octahedral
$[\text{Co(II)}(\text{FBABT})]_n(\text{H}_2\text{O})_2$	Purple	4.14	17.24	${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ (P)	Tetrahedral
$[\text{Ni(II)}(\text{FBABT})(\text{H}_2\text{O})_2]_n(\text{H}_2\text{O})_2$	Green	3.39	16.12	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$	Octahedral
$[\text{Cu(II)}(\text{FBABT})]_n$	Light Green	2.37	14.7	$d_{xy}, d_{yz} \rightarrow d_{x^2-y^2}$	Sq .Planar
$[\text{Zn(II)}(\text{FBABT})]_n$	Light Brown	diamagnetic			Tetrahedral

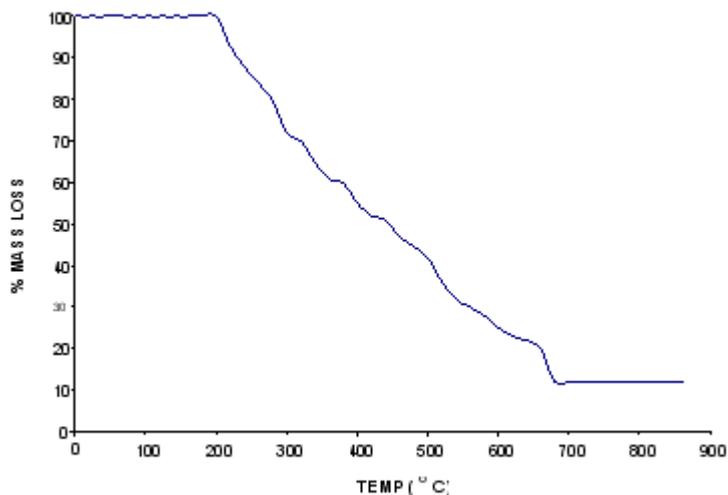


Fig. 3: TG curve for Zn(II) FB) ABT chelate polymer

coordinated water as no mass loss was observed upto 200°C. A gradual mass loss was seen from 220°C-700°C which may be due to the ligand attached to the metal ion and then no weight loss was observed after 700°C due to formation of stable metal oxide. In Co(II)(FBABT) Chelate polymer shows weight loss between 60°C to 100°C indicating presence of two lattice water molecules. Then a gradual weight loss was observed upto 690°C because of decomposition of ligand attached to the metal ion. In Ni(II)(FBABT) Chelate polymer shows weight loss between 80°C to 100°C & 110°C to 130°C indicating presence of two lattice water molecules two coordinated water molecules

respectively.. It then shows a gradual weight loss was observed upto 640°C because of decomposition of ligand attached to the metal ion .TG Curve of Cu(II)(FBABT) and Zn(II)(FBABT) shows no mass loss till 200°C It later shows a gradual decrease in mass between 210°C-740°C and 200°C to 680°C which may be due to the decomposition of ligand attached to the metal ion species; hereafter no further mass loss was observed indicating the formation of metal oxide. The decomposition temperatures of chelate polymers are given in Table 1. To economize the space only the TG curve of Zn(II) FBABT has been shown in Fig 3.

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