X-RAY DIFFRACTION STUDIES OF SOME CHELATE POLYMERS OF ADIPIC ACID

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ABSTRACT

Chelate polymers of Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) have been prepared with the ligand derived from adipyl bis-2-aminobenzothiazole having equimolar stochiometry of the cations and the ligands. In the present communication, a detailed study of X-Ray diffraction have been undertaken. The synthesized chelate polymers are coloured, amorphous, solid and highly insoluble in aqueous and common organic solvents. On the basis of X-Ray diffraction data, an orthorhombic crystal system has been proposed for the chelate polymers. The diffraction data were also used to index the compounds and for determination of various parameters.

Key words: X-Ray diffraction studies, Chelate polymers, Adipic acid.

INTRODUCTION

X-Ray powder diffraction (XRD), is an instrumental technique that is used to identify crystalline materials[1]. Most of the literature survey reveals that transition metal complexes generally crystallize with octahedral, tetrahedral or square planer geometry[2]. Most of the transition metal complexes are synthesized for their analytical and commercial application[3-10]. But the systematic study on determination of lattice parameters are the short comings for synthesizing and characterizing Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) complexes of adipyl bis-2-aminobenzothiazole. It is also interesting to note that the above chelate polymers also exhibit good thermal stability. X-Ray diffractometry is an important technique for structure determination because; it is non-destructive, non-contrast, fast and sensitive one. XRD however does not provide the quantitative compositional data obtained by the electron microprobe of the textural and qualitative compositional data obtained by SEM. The objective of an X-Ray diffraction measurement is to determine the dimensions

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and shape of unit cell and to identify the detailed structure of the molecule. To achieve this objective, we must be able to mathematically express the nature of the measured interference pattern in terms of the position of the various atoms within the crystal[11].

EXPERIMENTAL

All the chemicals used were AR Grade (Merck). The solvents used were double distilled before used. The powders were characterized by X-Ray diffraction (XRD) using Cu-Kα_1 radiation PAN analytical X-Ray diffractometer, at 40KVand 30mA in the range 20< 2θ >60 degree with step size of 0.02 degree 2θ and scanning speed of 0.5 degree 2θ per minute.

Syntheses of chelate polymers

Chelate polymers of ABABT with Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) have been prepared by dissolving metal acetate (0.01M) separately in minimum amount of DMF and were added to a solution of adipyl bis-2-aminobenzothiazole (0.01M) in (25 mL) DMF[12]. The reaction mixtures were heated in an oil bath at 120ºC temperature. The chelate polymers were formed after 8 hrs of constant heating in an oil bath. The chelate polymers obtained were filtered, washed thoroughly with hot DMF and then dried. These newly synthesized chelate polymers were found to be insoluble in almost all organic solvents such as alcohol, acetone, chloroform, carbon tetrachloride, dimethyl formamide, dioxin, diethyl sulphoxide etc. The purity of these chelate polymers was ascertained by repeated washings as recrystallzation was not possible. The final product appeared as amorphous powder. These newly synthesized chelate polymers were stable at room temperature.

RESULTS AND DISCUSSION

A good quality X-Ray diffractograms of chelate polymers indicates semi crystallinity as well as amorphous nature of complexes. All the reflection has been indexed for h, k, l values using methods reported in the literature[13]. The 'd' values of reflection were obtained using Bragg's equation (n λ = 2d sin θ). All the chelate polymers except the amorphous complexes are found to be orthorhombic crystal. These values of sin 2θ for each peak have been calculated with the help of cell parameters and corresponding h, k, l, values. The lattice constants a, b and c for each unit cell have been found out and are given in Tables 1-3.
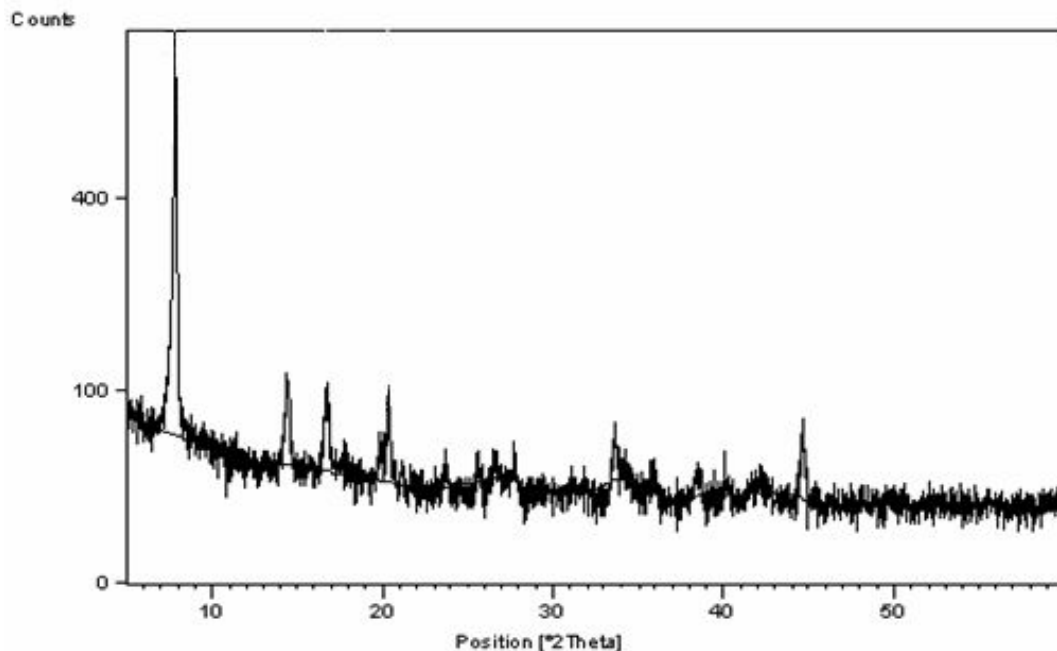
Fig. 1   :   X-Ray diffraction data of [Mn (II) (ABABT)] $_n$ chelate polymer

Table 1

d observed	d calculated	I/Io (%)	h	k	l
11.2347	11.2347	100	1	0	0
5.3063	5.3063	8.43	0	4	0
4.38372	4.38372	4.13	0	0	4

Type of crystal system: Orthorhombic; Lattice parameters; a = 11.23471Å; b = 21.2252Å; c = 17.5348Å, Volume of unit cell = 4181.33029(Å)^3.
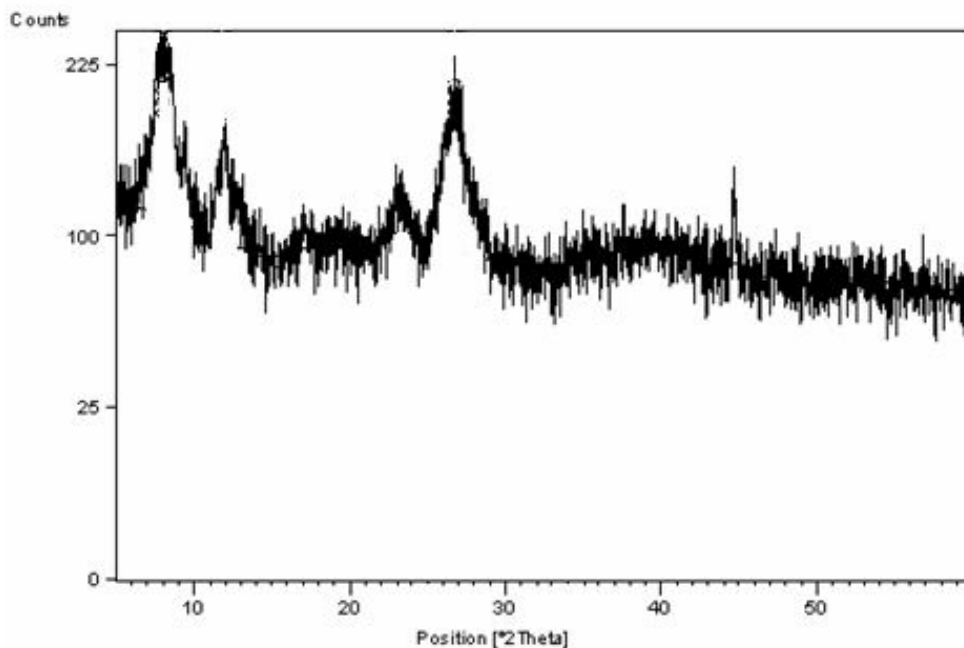
Fig. 2 : X-Ray diffraction data of [Cu(II) (ABABT)]ₙ chelate polymer

Table 2

d observed	d calculated	I/Io (%)	h	k	l
11.0200	11.0201	100	1	0	0
7.4587	7.4586	44.0	0	3	0
3.3258	3.3258	88.9	0	0	5

Type of crystal system-Orthorhombic; Lattice parameters; a = 11.0200 Å; b = 22.3671 Å; c = 16.8290 Å, Volume of unit cell = 4335.22818(Å)^3.
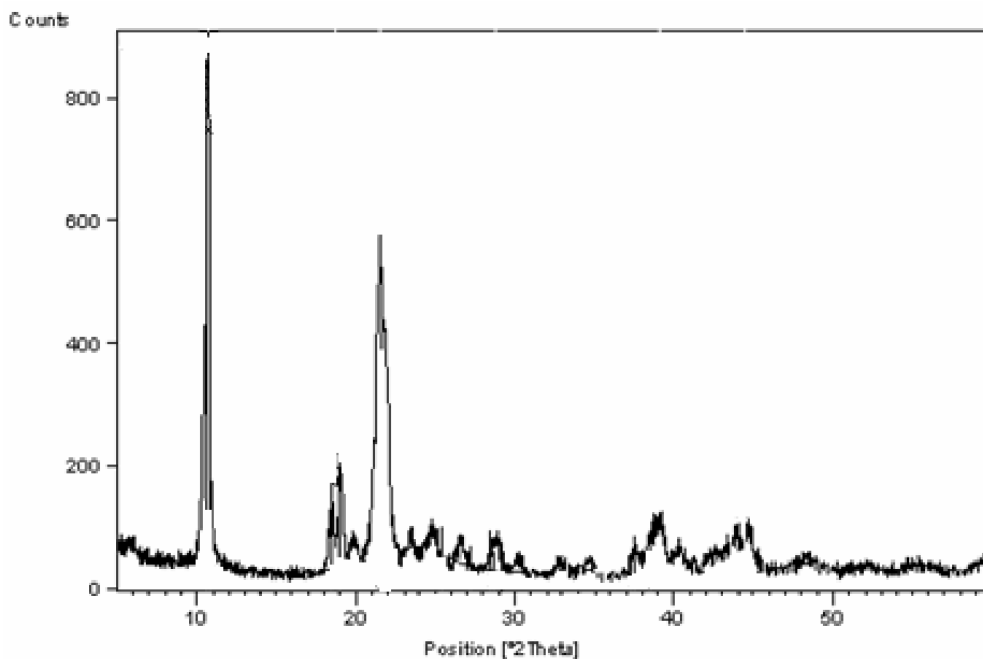
Fig. 3 : X-Ray diffraction data of [Zn(II)(ABABT)]ₙ chelate polymer

Table 3

d observed	d calculated	I/Io (%)	h	k	l
8.2739	8.2739	100	0	0	2
4.7328	4.7333	10.3	0	5	0
4.1456	4.1439	5.2	5	0	9
3.0956	3.0956	5.6	8	0	10
2.3053	2.3053	9.6	5	0	0
2.0375	2.0363	5.6	31	0	13

Type of crystal system-Orthorhombic; Lattice parameters; a = 11.5265 Å; b = 23.6665 Å; c = 16.5478 Å; Volume of unit cell = 4514.106(Å)^3.
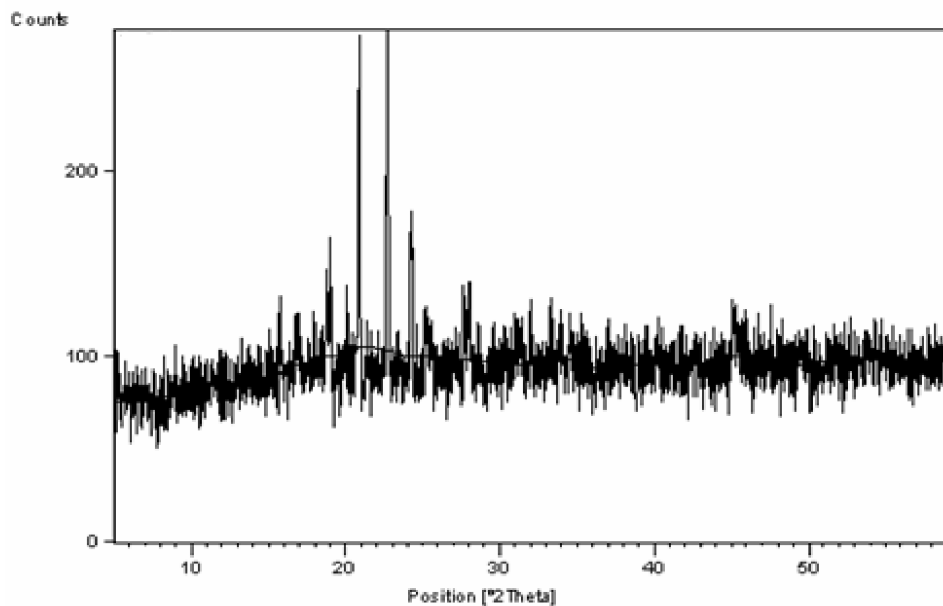
Fig. 4: [Co (II) (ABABT)] $_n$ chelate polymer is amorphous in nature
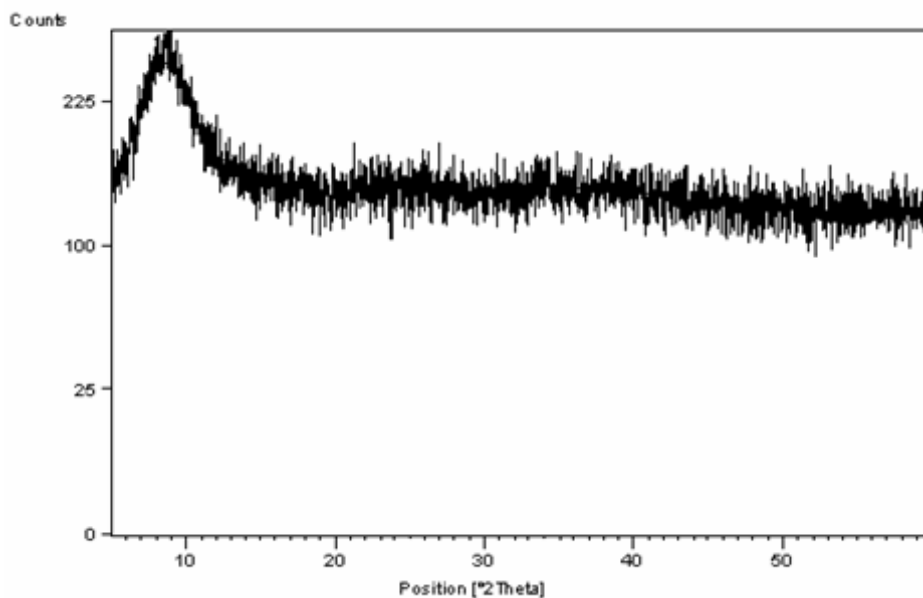

Fig. 5: [Ni (II) (ABABT)]$_n$ chelate polymer is amorphous in nature

CONCLUSION

On the basis of X-Ray diffraction studies, it has been found that all the newly synthesized chelate polymers of adipyl bis-2-aminobenzothiazole are semicrystalline (Nickel and cobalt are amorphous in nature) and others have orthorhombic crystal systems.

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