Int. J. Chem. Sci. : 3 (2), 2005, 229–236

X–RAY DIFFRACTION STUDIES OF SOME CHELATE POLYMERS OF HYDROXAMIC ACID

VAISHALI V. UKEY, K. G. REWATKAR, S. D. BORKAR, A. D. BONDE, S. NAZ and H. D. JUNEJA*

*Department of Chemistry, PGTD, Nagpur University, NAGPUR–440033 (M. S.) INDIA
Email:–chemdeptnu@yahoo.co & Vaishali296@rediffmail.com

ABSTRACT

Chelate polymers of Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) have been prepared with the ligand derived from suberoyl bis–N–phenyl hydroxamic acid having equimolar stoichiometry of the cations and ligand. A detailed X–ray diffraction studies have been undertaken in the present communication. These 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 same. The X–ray diffraction data was also used to index the compounds and for determination of various parameters.

Key words : X–ray diffraction studies, Chelate polymer, Hydroxamic acid

INTRODUCTION

Many transition metal complexes have been synthesized for their analytical commercial applications[1–3]. Literature survey also reveals that transition metal complexes generally crystallize with octahedral, tetrahedral or square planar geometry[4]. But the systematic studies 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 suberoyl bis–N–phenyl hydroxamic acid. An attempt has been made to evaluate lattice parameters. It is also interesting to note that the above chelate polymers exhibit good thermal stability. X–ray diffractometry is an important technique for structural determination because, it is non–destructive, non contrast fast and sensitive one.

EXPERIMENTAL

All the chemicals used were AR grade (Merck). The solvents used were double distilled before used.

The X–ray diffraction pattern have been recorded at RSIC, Nagpur University, Nagpur on Philips (Holland) automated X–ray Powder Diffractometer. The experimental conditions employed in reading the pattern were as under. The operating target voltage was 35 KV, and the

tube current was 20 mA. The scanning speed was 0.5 20/min. Radiation used was (Cu – K , Wavelength 1.54056 Å using monochromator for filtering radiations and reducing noise due to white radiations and also to increase resolution.

Synthesis of chelate polymers

Chelate polymers of SBPHA with Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) have been prepared by dissolving metal acetate (0.01 M) separately in minimum amount of DMF and was added to a solution of suberoyl bis hydroxamic acid (0.01 M) in (25 mL) DMF[5]. The reaction mixtures were heated on an oil bath with constant stirring at 120°C temperature. The chelate polymers generally appeared after 24 hrs heating on an oil bath. These chelate polymers obtained were filtered, washed thoroughly first with hot DMF and then with absolute alcohol and 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, dioxane, dimethyl sulphoxide etc. The purity of these chelate polymers was ascertained by repeated washing, as recrystallization was not possible. The final products appeared as amorphous powder. These newly synthesized chelate polymers were stable at room temperature.

RESULTS AND DISCUSSION

A good quality of X–ray diffractograms of chelate polymers indicates high crystallinity complexes. All the reflection has been indexed for hkl values using methods reported in literature[6]. The 'd' values of reflection were obtained using Bragg's equation. ($n\lambda = 2d \sin\theta$). All these chelate polymers have been found to be orthorhombic crystal a : 1 : c. These values of $\sin^2\theta$ for each peak have been calculated with the help of the 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 1–5. The diffractograms of chelate polymers have shown in Figs. 1–5.

Table 1. X–ray diffraction data of $[Mn(II)(SBPHA)]_n$ chelate polymer

Peak No.	d Observed	d Calculated	I/I_o (%)	h	k	l
1	13.181	13.181	100	1	0	0
2	6.609	6.609	4.1	0	0	4
3	5.315	5.323	7.9	1	3	0
4	4.364	4.364	6.4	0	4	0
5	2.663	2.663	4.3	0	6	4

Type of crystal system – Orthorhombic
Lattice parameters: a = 13.182 Å b = 26.436 Å c = 19.827 Å
Volume of unit cell = 6909.30 $(Å)^3$

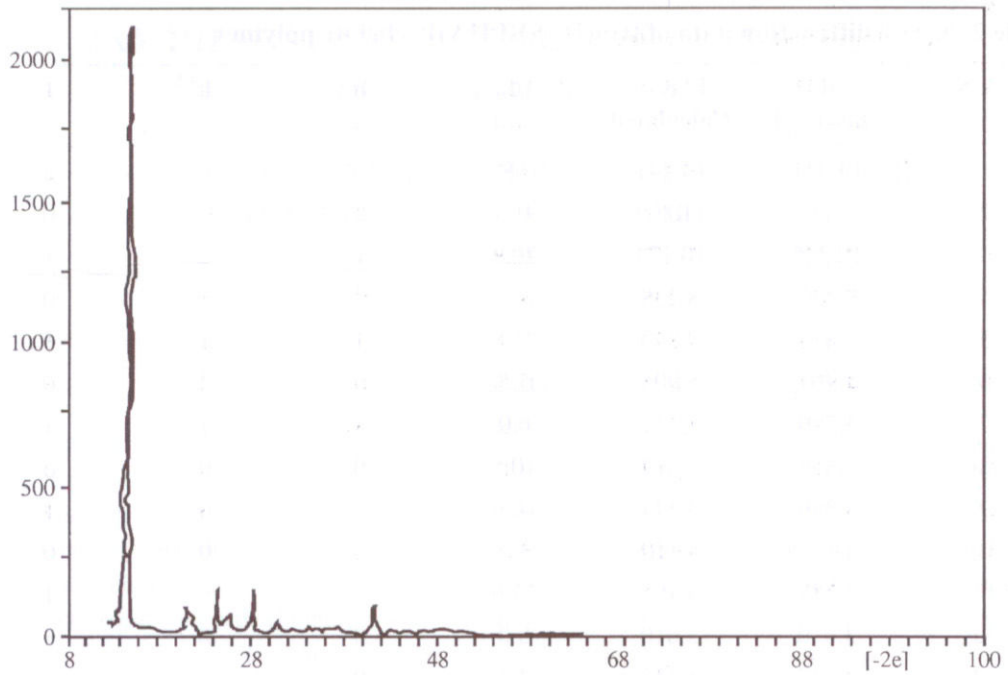

Figure 1. Diffractogram of Mn (II) SBPHA chelate polymer

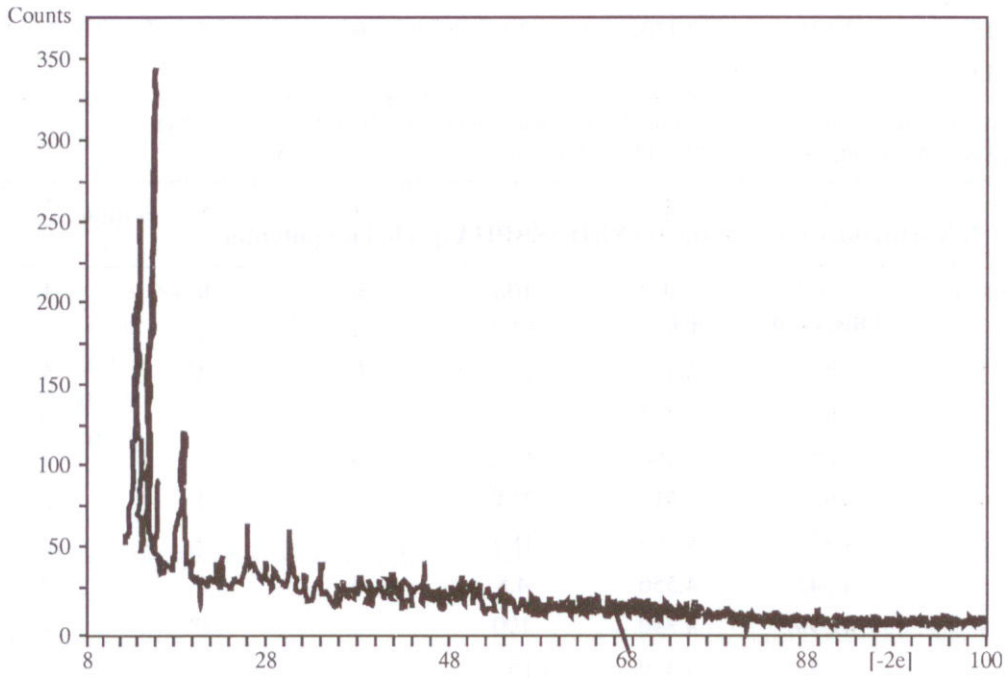

Figure 2. Diffractogram of Co (II) SBPHA chelate polymer

Table 2. X–ray diffraction data of $[Co(II)(SBPHA)]_n$ chelate polymer

Peak No.	d Observed	d Calculated	I/I_o (%)	h	k	l
1	14.441	14.441	68	0	0	2
2	11.809	11.809	100	0	2	0
3	10.345	10.174	20.9	1	2	1
4	8.230	8.238	18.1	2	0	0
5	7.817	7.840	31.8	1	1	3
6	5.907	5.905	5.5	0	4	0
7	5.710	5.757	6.0	3	1	1
8	4.828	4.814	10.5	0	0	6
9	4.386	4.371	4.5	3	0	4
10	4.118	4.119	4.1	4	0	0
11	3.789	3.795	11.6	1	6	1
12	3.610	3.610	5.0	0	0	8
13	3.347	3.351	4.3	0	7	1
14	2.905	20905	2.2	1	8	0
15	2.131	2.130	3.1	6	7	0
16	2.054	2.059	2.2	0	0	8

Type of crystal system – Orthorhombic; Lattice parameters: a = 16.476 Å; b = 23.618 Å; c = 28.882 Å; Volume of unit cell = 11238.85 $(Å)^3$

Table 3. X–ray diffraction data of $[Ni(II)(SBPHA)]_n$ chelate polymer

Peak No.	d Observed	d Calculated	I/I_o (%)	h	k	l
1	5.860	5.860	19.0	0	0	5
2	5.461	5.461	19.5	0	4	0
3	5.094	5.084	17.2	3	4	7
4	4.928	4.912	23.2	3	5	6
5	4.811	4.808	18.1	1	2	5
6	4.542	4.556	4.8	3	2	2
7	4.390	4.390	100	3	0	0
8	4.344	4.349	15.2	2	3	7
9	4.117	4.117	16.3	6	10	7

Continued.,...

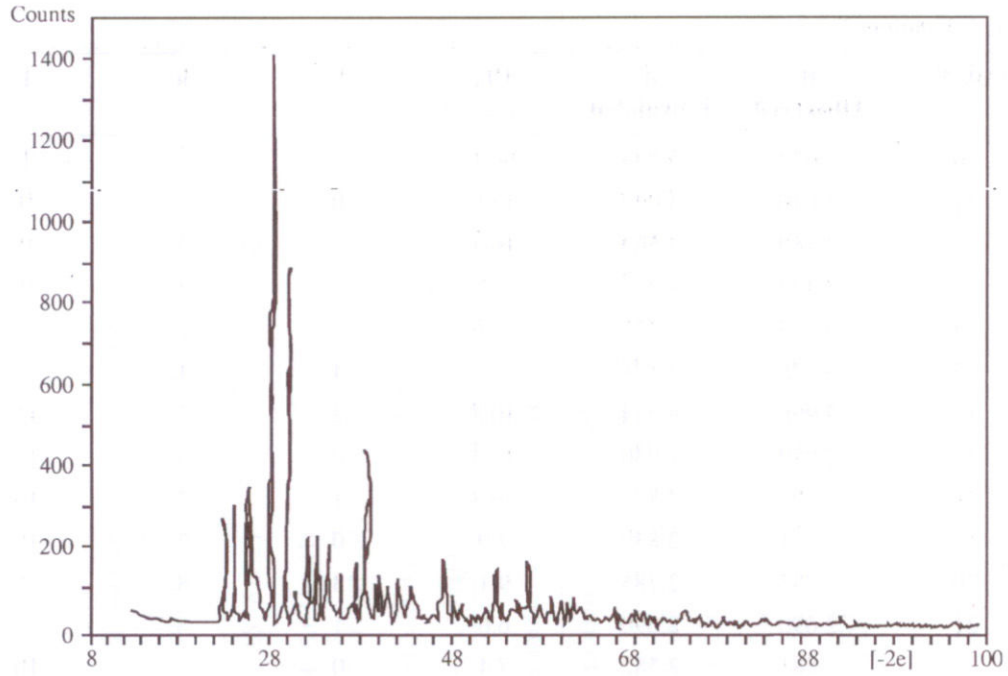

Figure 3. Diffractogram of Ni (II) SBPHA chelate polymer

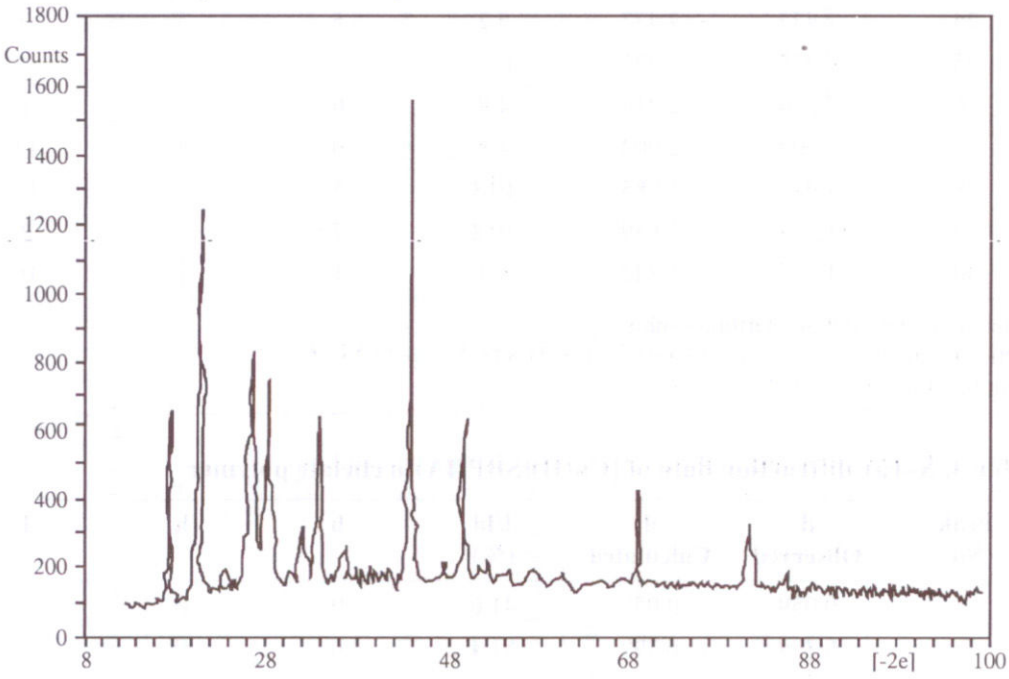

Figure 4. Diffractogram of Cu (II) SBPHA chelate polymer

Table 3. Continued.,...

Peak No.	d Observed	d Calculated	I/I_o (%)	h	k	l
10	4.022	4.034	66.1	3	2	1
11	3.640	3.640	14.8	0	6	0
12	3.559	3.563	16.3	2	3	0
13	3.452	3.452	7.3	4	7	9
14	3.355	3.358	13.6	1	2	8
15	3.178	3.178	9.8	4	1	2
16	2.996	2.994	10.8	2	5	11
17	2.929	2.930	18.3	0	0	10
18	2.898	2.898	30.3	1	2	10
19	2.831	2.830	7.0	0	2	10
20	2.785	2.785	9.1	3	8	7
21	2.690	2.690	6.6	1	8	1
22	2.581	2.582	7.4	0	4	10
23	2.508	2.508	5.7	5	4	4
24	2.477	2.477	5.2	5	3	0
25	2.275	2.275	12.3	1	1	12
26	2.214	2.214	4.9	6	2	2
27	2.003	2.003	4.8	0	5	13
28	1.987	1.985	10.8	5	9	13
29	1.859	1.859	10.8	7	1	2
30	1.842	1.842	4.3	1	1	16

Type of crystal system – Orthorhombic
Lattice parameters: a = 13.170 Å; b = 21.848 Å; c = 29.305 Å
Volume of unit cell = 8432.166 $(Å)^3$

Table 4. X–ray diffraction data of [Cu(II)(SBPHA)]n chelate polymer

Peak No.	d Observed	d Calculated	I/Io (%)	h	k	l
1	9.059	9.059	41.6	0	0	3
2	6.799	6.799	81.4	0	0	4
3	5.529	5.565	4.4	0	4	1

Continued.,...

Table 4. Continued.,...

Peak No.	d Observed	d Calculated	I/Io (%)	h	k	l
4	4.740	4.724	49.3	3	0	1
5	4.517	4.529	23.3	0	0	6
6	4.362	4.362	40.6	0	5	0
7	3.598	3.598	11.7	4	0	0
8	3.394	3.394	34.3	0	0	8
9	3.024	3.020	8.3	0	0	9
10	2.469	2.470	100	0	0	11
11	2.136	2.136	33.6	0	9	6
12	1.721	1.722	5.3	4	11	2
13	1.510	1.510	20.2	0	0	18
14	1.287	1.286	12.0	0	16	7

Type of crystal system – Orthorhombic
Lattice parameters : a = 14392 Å; b = 21.810 Å; c = 27.177 Å
Volume of unit cell = 8530.575 $(Å)^3$

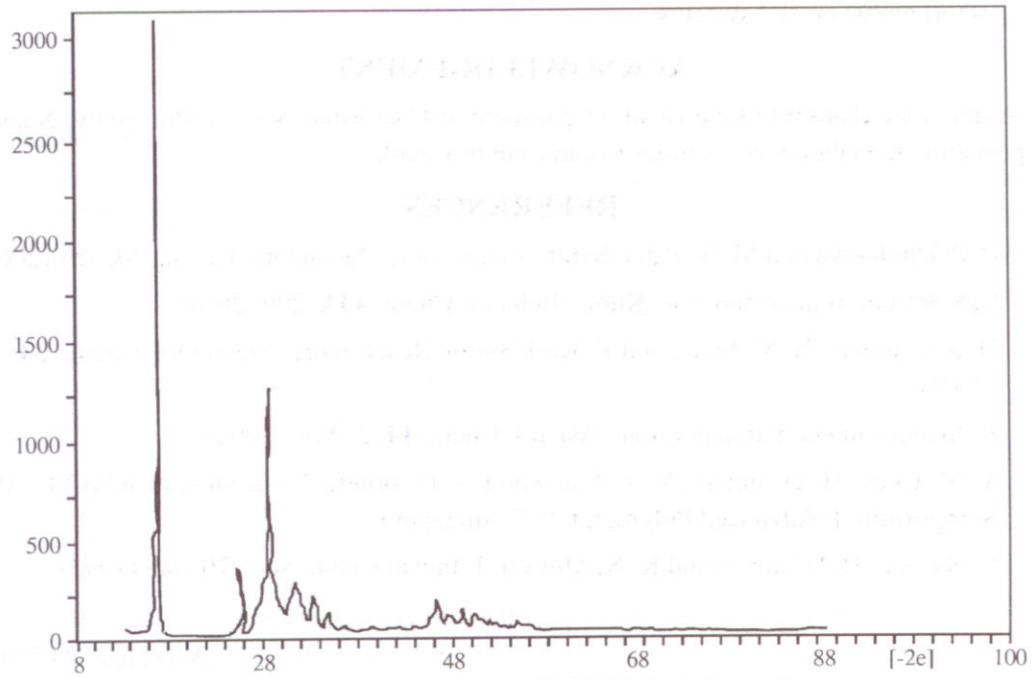

Figure 5. Diffractogram of Zn (II) SBPHA chelate polymer

Table 5. X–ray diffraction data of $[Zn(II)(SBPHA)]_n$ chelate polymer

Peak No.	d Observed	d Calculated	I/I_0 (%)	h	k	l
1	10.363	10.363	100	1	0	0
2	5.190	5.182	9.2	2	0	0
3	4.668	4.668	5.5	0	5	0
4	4.547	4.547	7.2	1	0	6
5	4.337	4.337	42.4	0	0	7
6	3.849	3.858	8.8	0	6	1
7	3.524	3.523	6.0	1	1	8
8	3.282	3.283	3.1	1	6	4
9	2.323	2.323	3.9	0	1	13

Type of crystal system – Orthorhombic; Lattice parameters : a = 10.363 Å; b = 23.340 Å; c = 30.359 Å; Volume of unit cell = 7343.004 $(Å)^3$

CONCLUSION

On the basis of X–ray diffraction studies, it has been found that all the newly synthesized chelate polymers of suberoyl bis–phenyl hydroxamic acid are semi crystalline in nature and have orthorhombic crystal systems.

ACKNOWLEDGEMENT

Authors are thankful to the Head, Department of Chemistry, Nagpur University, Nagpur, for providing the laboratory facilities to carry out this work.

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Accepted : 24.2.2005