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X-Ray Diffraction Studies on Some Complexes of Schiff Base Derived from 3-Chloro-*N*'-[(1*E*)-1-(Pyridin-3-YL) Ethylidene]-1-Benzothiophene-2-Carbohydrazide

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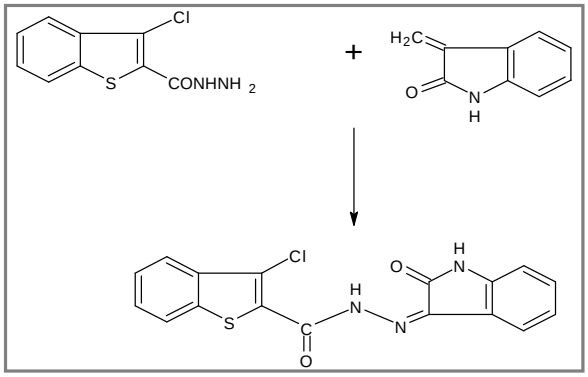
ABSTRACT

Complexes of Co (II), and Fe (III) with the Schiff base derived from 3-chloro-n'-[(1e)-1-(pyridin-3-yl) ethylidene]-1-benzothiophene-2-carbohydrazide has been synthesized and characterized on the basis a detailed study of X-Ray diffraction has been undertaken. The synthesized ligand and complexes are coloured, amorphous, solid and highly insoluble in aqueous and common organic solvents. On the basis of X-Ray diffraction data, a hexagonal or tetragonal crystal system has been proposed for the complexes. The diffraction data were also used to index the compounds and for determination of various parameters.

Graphical Abstract



Synthesis of ligand.

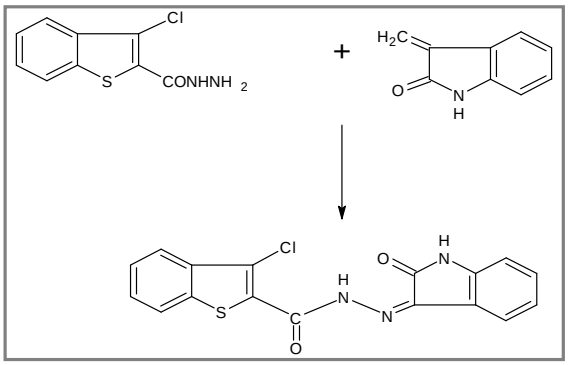
Keywords: Carbohydrazide, Schiff base, X-Ray diffraction.

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 Co (II), and Fe (III) complexes of 3-chloro-*n*'-[(1*e*)-1-(pyridin-3-yl) ethylidene]-1-benzothiophene-2-carbohydrazide. It is also interesting to note that the above ligand and complexes 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 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**].

MATERIALS AND METHODS

Syntheses of Ligand and Its Co (II) And Fe (III) Complexes: A mixture of 3-chlorobenzo(b) thiophene-2-carbohydrazide [**12**] (0.001mol) and 3-acetylpyridine (0.001 mol) in ethanolic media containing few drops of glacial acetic acid was refluxed for about 5 h on water bath. The reaction mixture was cooled to room temperature; the separated compounds (Ligand) were collected by filtration and recrystallized from absolute ethanol (Scheme 1). m.p. of ligand 199-202°C. To a hot solution of ligand (0.001 mol) in ethanol (30 mL) was added a solution of the appropriate metal (II) chlorides (0.001 mol) in ethanol (10 mL) and the mixture was refluxed for 6-8 h. The resulting solid complexes were collected by filtration and washed with hot ethanol and dried in a vacuum over anhydrous calcium chloride in desiccators (Yield 68-73%). These newly synthesized complexes were found to be insoluble in almost all organic solvents. The purity of these complexes was ascertained by repeated washings as recrystallzation was not possible. The final product appeared as amorphous powder. These newly synthesized complexes were stable at room temperature.



Scheme 1. Syntheses of Ligand.

RESULTS AND DISCUSSION

A good quality X-Ray diffraction of complexes 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 ($n\lambda = 2d \sin\theta$). All the complexes 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 to 3.

Powder X-ray diffraction pattern of the ligand has been depicted in figure 1. From the figure it is clear that the ligand consists of eight reflections in the range 3-90° (2θ) arising from the diffraction of X-rays by the planes of the compound. The calculated spacing together with relative intensities with respect to most intense peaks is recorded in the table 1. The 2θ values with maximum intensity of the peak for this ligand were found to be 5.324^0 (2θ), which correspond to d=16.58558 Å. 2θ values for all the prominent peaks have been listed in the table 1.

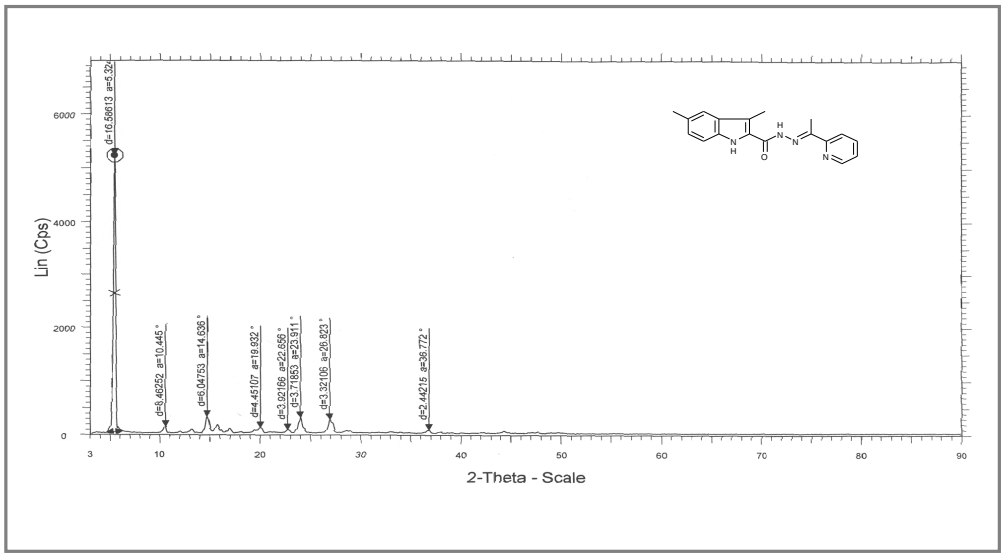


Figure 1. Powder XRD pattern of the ligand

Table 1. Powder X-ray diffraction data of the ligand

Peak No.	2θ	θ	Sinθ	$Sin^2θ$	$h^2+k^2+l^2$	h k l	d		a in A°
							Calc.	Obser.	
1	5.324	2.662	0.04644	0.00216	1	1 0 0	16.58558	16.58558	16.59
2	10.445	5.2225	0.09102	0.00829	4	2 0 0	8.46264	8.46264	16.59
3	14.636	7.318	0.12738	0.01622	8	2 2 0	6.04744	6.04744	16.59
4	19.932	9.966	0.17306	0.02995	14	3 2 1	4.45096	4.45096	16.59
5	22.656	11.328	0.19643	0.03858	18	3 3 0	3.92159	3.92159	16.59
6	23.911	11.9555	0.20715	0.04291	20	4 2 0	3.71853	3.71853	16.59
7	26.832	13.416	0.23202	0.05383	25	5 0 0	3.31998	3.31998	16.59
8	36.772	18.386	0.31542	0.09949	46	6 3 1	2.44216	2.44216	16.59

The experimental values of $sin^2θ$/common factor are recorded for each peak in the table 1. The $(h^2+k^2+l^2)$ values are 1, 4, 8, 14, 18, 20, 25 and 46. The absence of forbidden number 7, 15 and 23 confirms the cubic symmetry. The experimental values are in good agreement with $(h^2+k^2+l^2)$ values of primitive type cubic cell with lattice parameter a=b=c=16.59 Å.

Powder XRD patterns for Co (II), and Fe (III) Complexes of ligand have been depicted in figure 2 and 3 respectively. The diffraction pattern for the Co (II) complex showed 10 reflections in the range $5\text{-}80^o$ (2θ) arising from the diffraction of X-rays by planes of Co (II) complex, whereas Fe (III) complex showed 12 reflections in the range $3\text{-}80^o$ (2θ) to the diffraction of X-rays by planes of the complexes. The inter-planar spacing 'd' has been calculated from the positions of intense peaks using the Bragg's relation nλ=2dsinθ. The calculated inter planar spacing together with relative intensities with respect to most intense peaks are recorded in table 2 and 3. The 2θ values with maximum intensities of the peak for the complexes were found to be 5.4548 and 7.534^o (2θ), that correspond to

d=16.18817, 11.72465 Å for Co(II) and Fe(III) complexes respectively. All the important peaks have been indexed and the observed values of inter planar distances have been compared with the calculated ones. It was observed that there is good agreement between the calculated and observed values [**14**].

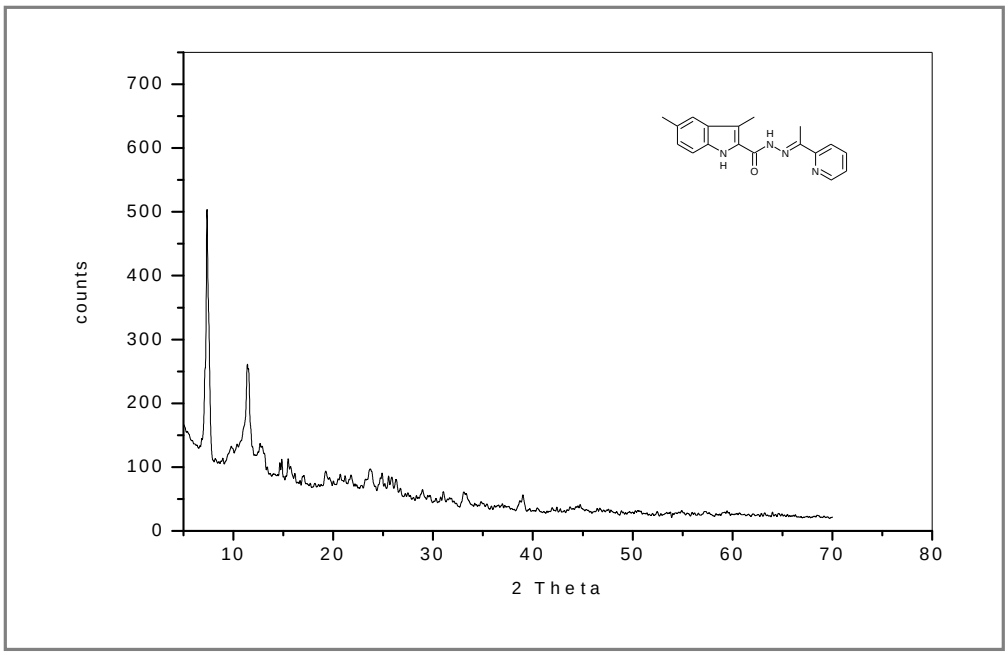


Figure 2. Powder XRD pattern of the Co(II) complex of the ligand.

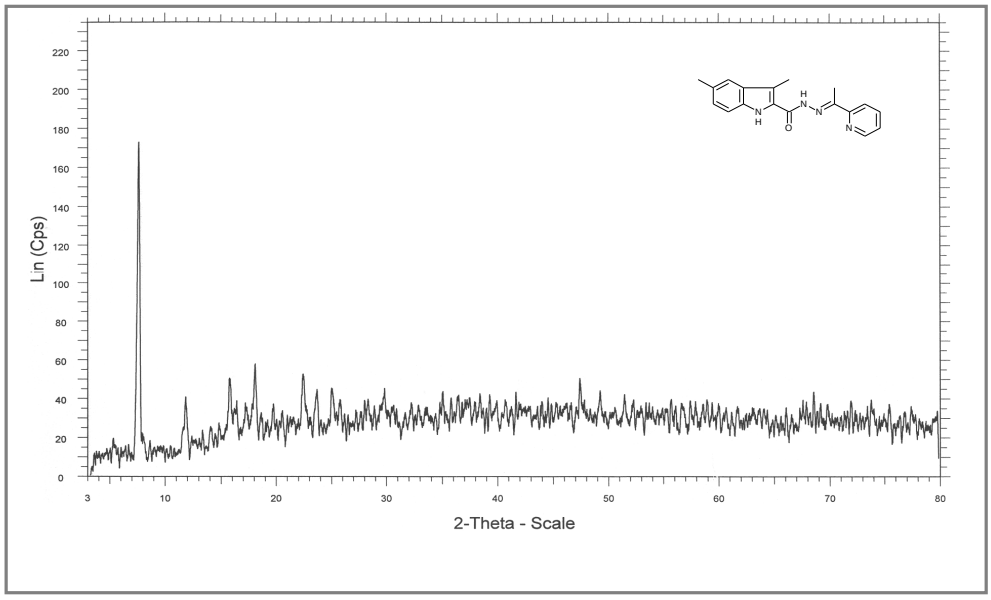


Figure 3. Powder XRD pattern of the Fe(III) complex of the ligand.

The experimental values of $\sin^2\theta$/common factor are recorded for each peak in the table 2. The $(h^2+k^2+l^2)$ values obtained for Co (II) complex were 1, 5, 6, 8, 9, 13 16, 19, 21 and 37. The absence of forbidden number 7, 15 and 23 confirms the cubic symmetry [**14**]. The experimental values are in good agreement with $(h^2+k^2+l^2)$ values of primitive type cubic cell with lattice parameter a=b=c=16.19Å.

Table 2. Powder X-ray diffraction data of Co(II) complex of the Ligand

Peak No.	2θ	θ	Sinθ	Sin2θ	$h^2+k^2+l^2$	h k l	d		a in A°
							Calc.	Obser.	
1	5.4548	2.7274	0.04758	0.00226	1	1 0 0	16.18817	16.18817	16.19
2	11.82	5.91	0.10297	0.0106	5	2 1 0	7.4811	7.4811	16.19
3	12.843	6.4215	0.11184	0.01251	6	2 1 1	6.88741	6.88741	16.19
4	15.214	7.607	0.13238	0.01752	8	2 2 0	5.81897	5.81897	16.19
5	16.84	8.42	0.14643	0.02144	9	3 0 0	5.26059	5.26059	16.19
6	19.554	9.777	0.16981	0.02884	13	3 2 0	4.53614	4.53614	16.19
7	21.782	10.891	0.18894	0.0357	16	4 0 0	4.07693	4.07693	16.19
8	23.887	11.9435	0.20695	0.04283	19	3 3 1	3.72221	3.72221	16.19
9	25.051	12.5255	0.21687	0.04703	21	4 2 1	3.55183	3.55183	16.19
10	33.428	16.714	0.28759	0.08271	37	6 1 0	2.67842	2.67842	16.19

The experimental values of $\sin^2\theta$/common factor are recorded for each peak in the table 3. The $(h^2+k^2+l^2)$ values obtained for Fe (II) complex were 1, 2, 4, 6, 9, 11, 29, 37, 69, 74, 80 and 87. The presence of forbidden number 87 indicates the complex may belong to hexagonal or tetragonal system.

Table 3. Powder X-ray diffraction data of Fe(III) complex of the Ligand

Peak No.	2θ	θ	Sinθ	Sin2θ	h2+k2+l2	h k l	d		a in A°
							Calc.	Obser.	
1	7.534	3.767	0.0657	0.00432	1	1 0 0	11.72465	11.72465	11.72
2	11.753	5.8765	0.10238	0.01048	2	1 1 0	7.5236	7.5236	11.72
3	15.709	7.8545	0.13666	0.01868	4	2 0 0	5.6367	5.6367	11.72
4	18.068	9.034	0.15702	0.02466	6	2 1 1	4.90573	4.90573	11.72
5	22.378	11.189	0.19405	0.03765	9	3 0 0	3.96968	3.96968	11.72
6	24.897	12.4485	0.21556	0.04647	11	3 1 1	3.57345	3.57345	11.72
7	41.674	20.837	0.35571	0.12653	29	5 2 0	2.16552	2.16552	11.72
8	47.443	23.7215	0.40229	0.16184	37	6 1 0	1.91478	1.91478	11.72
9	66.152	33.076	0.54575	0.29784	69	8 2 1	1.41145	1.41145	11.72
10	68.652	34.326	0.5639	0.31798	74	8 3 1	1.36602	1.36602	11.72
11	72.054	36.027	0.58817	0.34594	80	8 4 0	1.30966	1.30966	11.72
12	75.555	37.7775	0.6126	0.37527	87	--	1.25743	1.25743	11.72

APPLICATION

This study is useful to determine the geometrical structure of complexes.

CONCLUSION

On the basis of X-Ray diffraction studies, it has been found that all the newly synthesized complexes of 3-chloro-*n*'-[(1*e*)-1-(pyridin-3-yl) ethylidene]-1-benzothiophene-2-carbohydrazide are semi crystalline (cobalt and iron are amorphous in nature) and others have to hexagonal or tetragonal system.

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