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X-Ray Diffraction Study and Biological Analysis of Transition Metal Complexes of N-4-Disubstituted Thiosemicarbazone

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Abstract

Comparative studies on the X-ray diffraction parameters of some transition metal complexes like Fe (III), Cu (II), Zn (II) of ligand (L1) has been prepared by using N-4-Ethyl, phenyl-3-thiosemicarbazide and 2-hydroxybenzaldehyde in equimolar ratio. These complexes show various physicochemical properties. X-ray powder diffraction of Fe (III) complex has triclinic crystal system while Cu (II) and Zn (II) complex of ligand (L1) having monoclinic crystal systems with various unit cell parameters. These complexes also tested for biological analysis and shows considerable activity against bacteria and fungi in comparison with standard drug ciprofloxacin.

Keywords: N-4-Disubstituted thiosemicarbazone, biological analysis.

Introduction

Thiosemicarbazones are known as versatile ligands. Thiosemicarbazones and their transition metal complexes having importance in inorganic chemistry and medicinal chemistry[1-4]. The wavelengths are necessary part of crystal system of metal complexes to determine the peak position, miller indices (h, k, l) values, unit cell parameters and 2Θ value with radiation source of CuKα by used as X-ray diffractometer range[5-6]. The target of X-ray diffraction is to determine the probable structure of the metal complexes. To accomplish this target we must be able to express mathematically the nature of the measured interference pattern in terms of the position of the various atoms within the crystal[7]. To determine the crystalline compounds they are using XRD instrumental technique[8]. Literature survey shows that transition metal complexes generally crystalline as well as amorphous in nature with tetrahedral, octahedral or square planar geometry[9]. In present paper the powder X-ray diffraction of Fe (III), Cu (II) and Zn (II) complexes of N-4-disubstituted thiosemicarbazones scanned in the range of $0\text{-}80^0$ at wavelength 1.540598Å. Biological analysis of complexes was tested on *Staphylococcus aureus, Bacillus substilis, Aspergillus niger* and *Fusarium oxysporium species.*

Material and Methods

All chemicals and solvents used were of A. R. grade and used as received. The transition metal salts (Metal chlorides) obtained from Aldrich. The powder XRD was recorded on Perkin Elmer TA/SDT-2960 and Philips 3701, respectively at the range of $0\text{-}80^0$ at wavelength 1.540598Å.

Synthesis of Schiff base ligand: The Schiff base (E)-1-(2-hydroxybenzylidene)-4-ethyl-4-phenyl thiosemicarbazide (L1) prepared by modifying reported method of scovil[10]. 2-hydroxybenzaldehyde (0.1mol) and N-4-ethyl, phenyl-3-thiosemicarbazide refluxed for 30 minutes. The yellow solid formed was filtered, washed with ether, dried in the desiccators and recrystallized with hot ethanol-DCM (1:2) proportion. Yield: 80%.

Synthesis of Metal complexes: Hot methanolic solution (0.1mmol) of metal salt is mixed with (0.2mmol) solution of (E)-1- (2-hydroxybenzylidene) -4-ethyl-4-phenyl thiosemicarbazide (L1). The resulting solution mixture was refluxed for 2-3 hours and allowed to kept overnight at room temperature. The precipitated complex were filtered off, washed with ether, water and dried in vacuum over anhydrous calcium chloride in desiccators. The complexes obtained are microcrystalline solids which are stable in air and decompose above 300^0C. They are insoluble in organic solvents such as acetone, chloroform but soluble in DMF and DMSO.

Results and Discussion

The X-ray diffractogram of some transition metal complexes of ligand (L1) are crystalline as well as amorphous in nature. To determine the h,k,l values of reflection by using reported methods[11]. The X-ray diffraction was performed to obtain further evidence about the structure of the metal complexes. The diffractogram obtained for the Fe (III), Cu (II) and Zn (II) complexes were given in figures-1, 2, 3. And the XRD patterns indicated crystalline nature of Zn (II) complex while Fe (III) and Cu (II) complexes are amorphous in nature. The values of sin 2 d for each peak have been determined by cell parameters and corresponding h, k, l values. The lattice constants a, b and c for each unit cell have been found out and given tables-1 to 4. The XRD patterns the major peak which showed relative intensity greater than 10% indexed by computer programme[12].

Experimental density values of the complexes were determined by using specific gravity method[13]. In a figure 1-3 show that the relative intensity vs. 2Θ values.

Biological Analysis: Antimicrobial and Antifungal activity: Derivatives of thiosemicarbazones and their transition metal complexes exhibit a wide variety of biological activity[14]. The antimicrobial and antifungal activity of ligand and their transition metal complexes were carried out successfully on *Aspergillus niger, Fusarium oxasporium, Staphylococcus aureus* and *Bacillus substilis species.* The results show that the ligand as well as metal complexes are more active against bacteria and fungi and shows almost equal activity of standard ciprofloxacin shown in table-5.

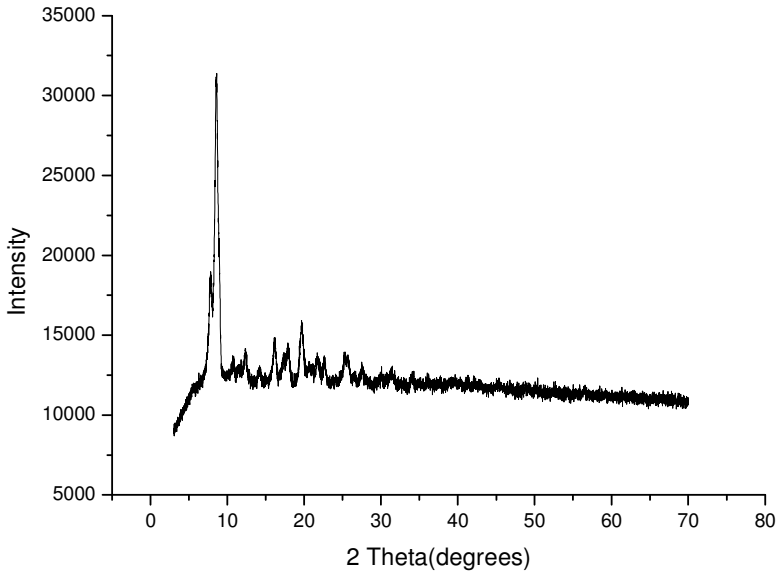

Figure-1
Xray diffractogram of [Fe $(L1)_2$] Complex

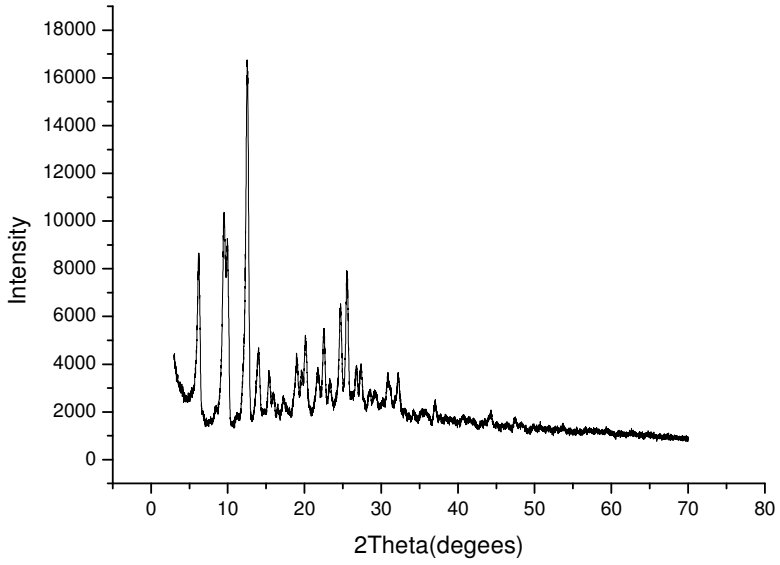

Figure-2
Xray diffractogram of [Cu $(L1)_2$] Complex

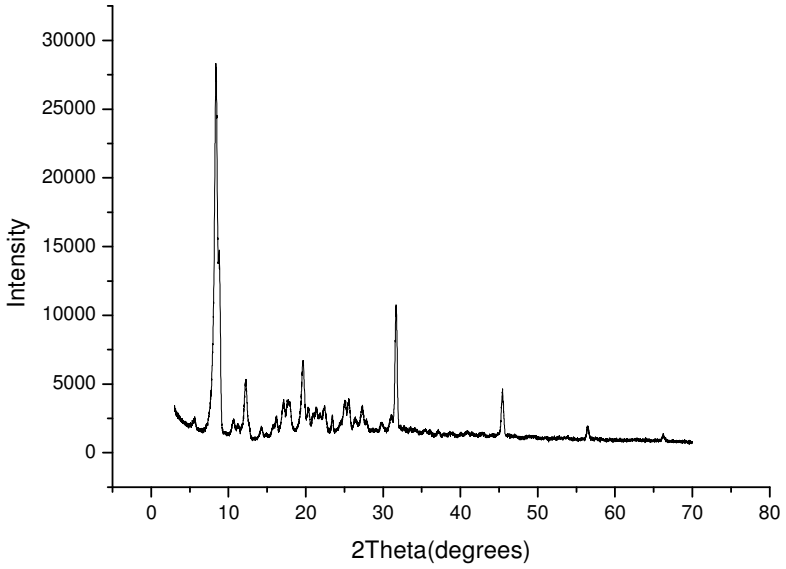

Figure-3
Xray diffractogram of [Zn $(L1)_2(H_2O)_2$] Complex

Table-1
Lattice constant, unit cell volume, Crystal system, Inter-planar spacing of metal

Unit cell of complexes	Lattice constant			Unit cell Volume	Inter axial angle	Crystal system	2Ɵ	d value Å
	a (Å)	b (Å)	c (Å)					
Fe(III)	15.23	10.32	7.89	111.6	α=β=90≠γ	Monoclinic	12.25	7.21
Cu(II)	14.26	10.02	14.23	203.5	α=β=90≠γ	Monoclinic	12.55	7.04
Zn(II)	9.32	10.23	8.23	785.6	α≠β≠γ≠90	Triclinic	8.38	10.53

Table-2
Millar indices and interplanar distances of Fe (III) complex

2Ɵ(Cal)	2Ɵ(Obs)	h	K	L	d (Obs)	d (Cal)	Intensity (%)
12.25	12.46	0	0	1	7.21	7.09	100
20.88	20.56	-1	2	1	4.25	4.31	68.75
17.47	17.16	0	2	0	5.06	5.16	55.86
25.21	25.07	0	0	2	3.52	3.54	40.30
13.96	14.14	-1	1	1	6.33	6.25	16.72

Table-3
Millar indices and interplanar distances of Cu (II) complex

2Θ(Cal)	2Θ(Obs)	h	K	L	d (Obs)	d (Cal)	Intensity (%)
6.22	6.27	-1	0	0	14.19	14.06	42.20
9.95	9.60	1	0	1	8.88	9.19	50.04
9.60	9.60	1	0	1	9.26	9.19	58.18
8.45	8.11	-1	0	1	10.48	10.88	4.10
15.37	15.37	-2	1	0	5.75	5.75	10.90

Table-4
Millar indices and interplanar distances of Zn (II) complex

2Θ(Cal)	2Θ(Obs)	H	K	L	d (Obs)	d (Cal)	Intensity (%)
19.62	19.49	1	-2	0	4.51	4.55	18.67
8.38	8.63	0	-1	0	10.53	10.22	100
17.75	17.32	0	-2	0	4.99	5.11	8.39
11.23	10.73	0	0	1	8.28	8.23	4.05
21.37	21.20	-2	-1	0	4.15	4.18	6.04

Table-5
Antimicrobial and Antifungal activity of ligand (L1) and its transition metal complexes

Ligand/metal complex	Antibacterial activity				Antifungal activity			
	Staphylococcus aureus		*Bacillus substilis*		*Aspergillus niger*		*Fusarium oxysporium*	
	250ppm	500ppm	250ppm	500ppm	250ppm	500ppm	250ppm	500ppm
Ligand (L1)	16	20	20	23	19	22	20	22
Fe(III)	17	20	22	25	19	20	19	22
Cu (II)	22	27	26	30	18	19	25	28
Zn (II)	17	17	20	24	22	24	23	23
Ciprofloxacin	34	36	43	45	22	24	31	38

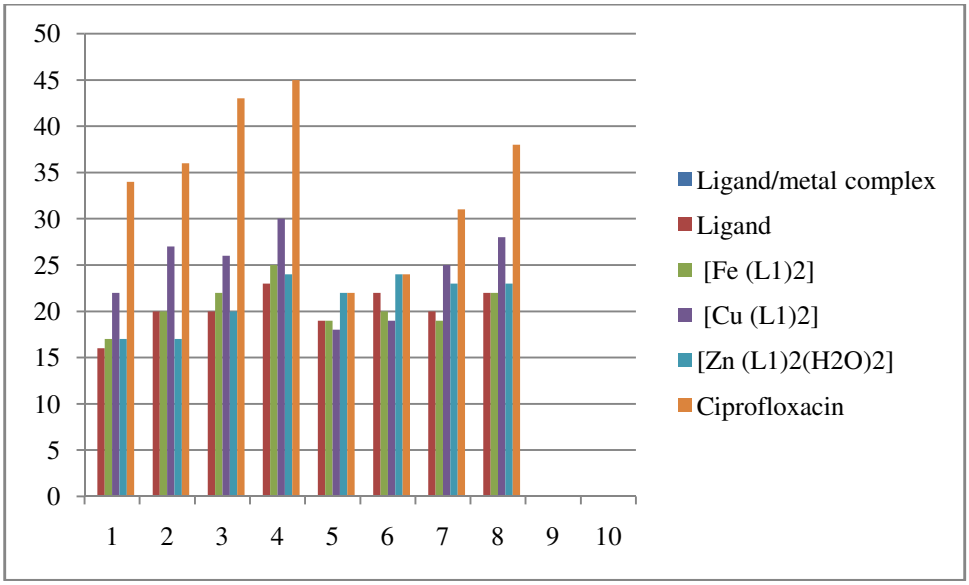

Figure-4
Comparative study of antimicrobial and antifungal activity of ligand (L1) and its metal complexes

Conclusion

The transition metal complexes like Fe (III), Cu (II), and Zn (II) of O, N and S donor thiosemicarbazone ligand (L1) were studied by X-ray diffraction. The X-ray diffraction studies of Fe (III) complex having monoclinic crystal system with Z = 1 while Cu (II) complex also monoclinic with Z = 1 and are amorphous in nature. Zn (II) complex having triclinic crystal system with Z = 1 are crystalline in nature and having octahedral geometry. These metal complexes of thiosemicarbazones are biologically active.

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