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X-ray diffraction, spectral and biological studies of Cu (II), Co (II) and Zn (II) complexes of substituted thiosemicarbazones

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ABSTRACT

Comparative study of X-ray diffraction patterns of transition metal complexes like Cu (II), Co (II) and Zn (II) of thiosemicarbazone is carried out. These metal complexes have different physicochemical properties as well as different crystal system. The X-ray diffraction studies were also being used for the determination of various parameters such as unit cell volume and miller indices values h, k, l. These complexes also tested for their antibacterial and antifungal activity in comparison with standard drug ciprofloxacin.

Keywords- N-4-diethyl thiosemicarbazone, biological screening

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INTRODUCTION

A large number of metal complexes of thiosemicarbazones, because of their versatile properties and wide variation in the modes of bonding and stereochemistry are reported [1-2]. The chelating behavior of Fe (II), Co (II) ions with the heterocyclic system containing nitrogen and sulphur atoms has been extensive studies because of the antitumor activity associated with these complexes [3-5]. The X-ray diffractogram of complexes were recorded in the range of 5-80° 2θ value. The wavelengths are important part of crystal system of complexes to determine the peak position, miller (h, k, l) value, unit cell parameters and 2θ value with d radiation source of CuKα by used as X-ray diffractometer range [6-7]. Thiosemicarbazones obtained by condensation of thiosemicarbazides with salicyaldehyde form versatile NS / NSO chelating ligands and having diverse biological activities. These ligands behave as monoanionic tridentate ligand coordinating to the metal centre through deprotonated phenolic oxygen, thione sulphur and the azomethine nitrogen [8]. However, they also coordinate as bidentate NS donor [9] in spite of having phenolic oxygen as a potential third donor site. Thiosemicarbazones and their transition metal complexes are important because they exhibit interesting chemical properties and potential biological activities [10-15].

In present paper we report the synthesis of Cu (II), Co (II) and Zn (II) metal complexes of with thiosemicarbazone (LA) derived from salicyaldehyde and N-4-diethyl-3-thiosemicarbazide.

MATERIALS AND METHODS

All the chemicals used were as AR grade obtained from the commercial source. Salicyaldehyde were of reagent grade purchased from sigma-Aldrich.

Synthesis of Schiff base ligand
The Schiff base (E)-1-(2-hydroxybenzylidene)-4-diethylthiosemicarbazide prepared by modifying reported method of Scovil [16].

Synthesis of metal complexes
Hot methanolic solution of (0.01mmol) of metal salt is mixed with (0.2mmol) solution of (E)-1-(2-hydroxybenzylidene)-4-diethylthiosemicarbazide (L1). The reaction mixture was refluxed for 2-3 hours and allows keeping for 5-6 hours at room temperature and decomposes above 300°C.

RESULT AND DISCUSSION

FTIR spectra
The experimental assignments of the IR spectral bands to confirm the structural identity of the ligand and its metal complexes are given in table no.1

According to study the binding mode of ligand to metal in complexes. IR spectrum of ligand was compared with IR spectrum of metal complexes. In the solid state the ligand (L1) remain in the thione form. A sharp ν (N-H) band expected to be at 2976 cm^{-1} for O-N-S donor ligand. A sharp ν (C=S) band and low intensity δ (C=S) band are observed in ligand at 1276 cm^{-1}. While in metal complexes it is in the range of 1240-1270 cm^{-1} and 700-753 cm^{-1}. Ligand (L1) show ν (OH) band at 3220 cm^{-1} due to intramolecular hydrogen bonding and free δ (OH) at 1418 cm^{-1}. Bands in the range of 420-440 cm^{-1} due to M-O, M-N, M-S bond.

Table- 1-FTIR spectral data of ligand and its metal complexes (in cm^{-1})

Ligand/complex	ν (OH)	ν (NH)	ν(C=N)	ν(C=S)	ν(C=O)	M-S	M-N	M-O
Ligand	3220	2976	1538	1276,753	1186	-	-	-
Cu(II)	-	2970	1520	1255,750	1154	497	613	437
Co(II)	-	2960	1530	1250,751	1160	490	620	430
Zn(II)	-	2959	1525	1244,743	1170	488	621	421

X-ray diffraction study
X-ray diffraction of all metal complexes was performed to obtain further probability related to the structure of the complexes. The x-ray diffractogram of complexes were recorded in the range of 0-80° 2θ value and wavelength of 1.5405 Å. Major refluxes were calculated and related 'd' values were determined by using Bragg's equation. The independent indexing of major refluxes was carried out by using least square method. All reflections have been indexed for h, k, l values using reported procedures in the literature [17]. Zn (II) complex having triclinic crystal system, while Cu (II) and Co (II) has monoclinic crystal system. Unit cell volume for each system is determined by respective equation.

Table-2-Lattice constant, Unit cell volume, Crystal system, Interplanar spacing of metal

Unit cell of complexes	Lattice constant			Unit cell volume V ($Å^3$)	Interaxial angle	Crystal system	2θ	d value (Å)
	a (Å)	b (Å)	c (Å)					
Cu (II)	10.23	15.23	22.36	3036.30	α=β=90≠γ	Monoclinic	12.79	6.91
Co (II)	16.23	10.02	10.02	1440.33	α=β=90≠γ	Monoclinic	20.76	8.21
Zn (II)	5.23	13.02	9.02	604.113	α≠β≠γ≠90	Triclinic	9.79	9.02

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

2θ(Obs)	2θ(Cal.)	d(Obs)	d(Cal.)	h	k	l	Intensity (%)
9.05	9.07	9.76	9.73	0	0	2	100
11.30	11.21	7.82	7.88	-1	1	2	9.84
12.72	12.79	6.95	6.91	1	0	1	12.78
20.54	20.50	4.37	4.32	1	0	3	15.42
20.97	20.90	4.23	4.24	-2	2	2	9.20

Fig.1 X-ray diffraction data of [Cu $(L1)_2$] Complex

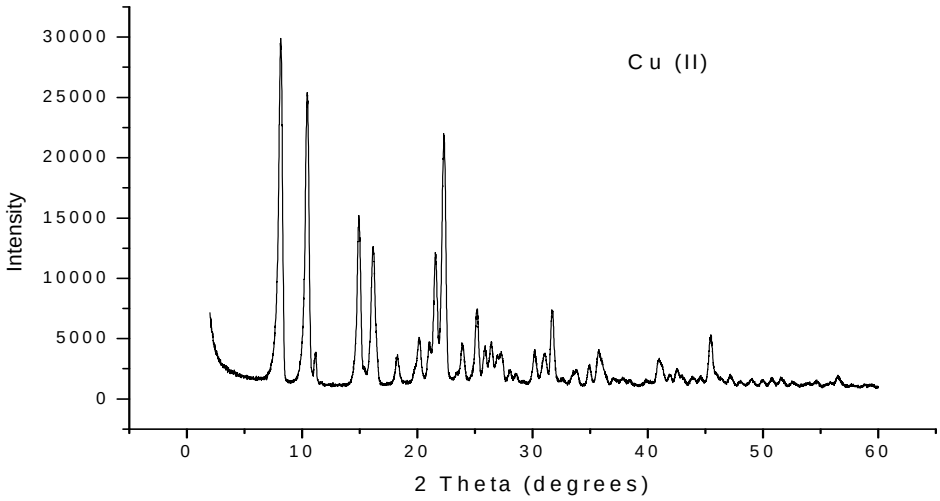


Fig-2 X-ray diffraction data of [Co $(L1)_2$] complex

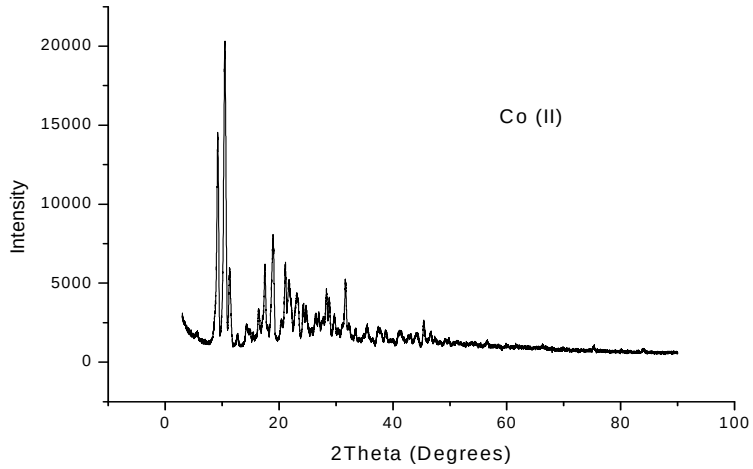


Table-4 Miller Indices and interplanar distances of Co (II) complex

2θ(Obs)	2θ(Cal.)	d(Obs)	d(Cal.)	h	k	l	Intensity (%)
6.15	6.16	14.34	14.33	-1	0	0	100
7.08	6.16	12.45	14.33	-1	0	0	45.93
8.81	8.81	10.02	10.02	0	1	0	82.92
10.58	10.76	8.35	8.21	-1	1	0	70.46
19.16	19.23	4.62	4.61	2	0	1	46.13

Fig-3 X-ray diffraction data of [Zn (L1)$_2$] complex

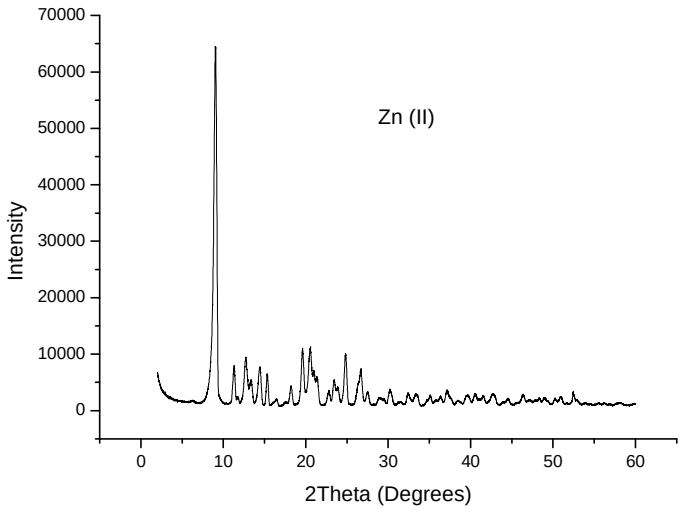


Table-5- Miller indices and interplanar distances of Zn (II) complex

2θ(Obs)	2θ(Cal.)	d(Obs)	d(Cal.)	h	k	l	Intensity (%)
10.49	9.79	8.41	9.02	0	0	1	100
9.27	9.79	9.52	9.02	0	0	1	70.80
11.35	11.98	7.78	7.37	0	1	1	24.44
17.52	17.30	5.05	5.11	1	-1	0	24.44
21.76	21.98	4.08	4.03	1	1	1	18.77

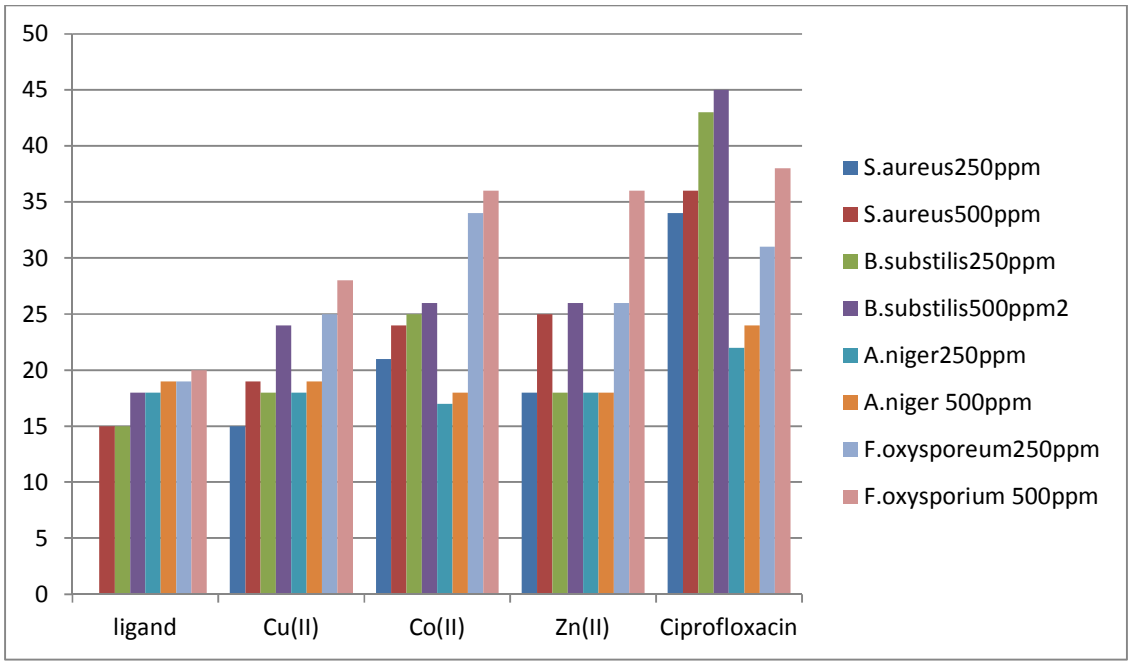
Biological Screening

Thiosemicarbazone ligand and their transition metal complexes having a wide range of biological activity [18, 19]. Complexes of thiosemicarbazone ligand are essential because of their antibacterial, antifungal antimalarial, antiviral and antitumor activities [20, 21]. The antibacterial and antifungal activity ofligand and its Transition metal complexes were given in Table.5. The ligand as well as metal complexes are more active against bacteria and fungi shows good activity compared with standard ciprofloxacin.

Table-6-Antibacterial and Antifungal activity of ligand and their transition metal complexes. [Diameter of inhibition zone in (mm)]

Ligand / Metal Complex	Antibacterial activity				Antifungal activity			
	Staphylococcus aureus		*Bacillus substilis*		*Aspergillus Niger*		*Fusarium Oxysporium*	
	250 ppm	500 ppm	250 ppm	500 ppm	250 ppm	500 Ppm	250 Ppm	500 Ppm
Ligand (L1)	00	15	15	18	18	19	19	20
[Cu(L1)$_2$]	15	19	18	24	18	19	25	28
[Co(L1)$_2$]	27	24	25	26	17	18	34	36
[Zn(L1)$_2$]	18	25	18	26	18	18	26	36
Ciprofloxacin	34	36	43	45	22	24	31	38

Fig-4-Comparative study of antimicrobial and antifungal activity of ligand and its metal complexes



CONCLUSION

The transition metal complexes Cu (II), Co (II) and Zn (II) of thiosemicarbazone ligand were studied by X-ray diffraction. X-ray diffraction study shows that Cu (II) and Co (II) having monoclinic crystal system while Zn (II) complex having triclinic crystal system are crystalline in nature and may have octahedral geometry. All the metal complexes of thiosemicarbazones are biologically active.

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