Indian J.Sci.Res. 4(2) : 115-118, 2013
ISSN : 0976-2876 (Print)
ISSN : 2250-0138 (Online)

SYNTHESIS AND COMPARATIVE ANTIBACTERAL ACTIVITY OF Zn(II) AND Fe(II) TRANSITION METAL COMPLEXES WITH N-N-S-S DONOR LIGAND

DURGESH KUMAR RAI[1]

Department of Chemistry, Sam Higginbottom Institute of Technology and Sciences, Allahabad, Uttar Pradesh, India

ABSTRACT

A series of metal complexes of Fe(II) and Zn(II) having the general composition $[M(L)X_2]$ with benzil bis (thiosemicarbazone) has been prepared and characterized by element chemical analysis, magnetic susceptibility measurements, and spectral (FTIR) studies.The IR spectral data suggest the involvement of Sulphur and Azomethane nitrogen in coordination to the central metal ion. On the basis of spectral studies, complexes of Zn (II) and Fe (II) show octahedral geometry. The antibacterial properties of the ligand and its metal complexes were also examined and it was observed that the complexes are more potent bactericides than the free ligand ,against the sensitive organisms *Staphylococcus aureus* , *Bacillus macerans* as Gram positive bacteria, *Vibro cholerae*,*Somonella typhi* as Gram negative bacteria. Ciprofloxin as standard drug.

KEYWORDS : Benzil bis (Thiosemicarbazone) , Fe (II) Zn (II), Antibacterial, FTIR

The chemistry of thiosemicarbazones has received considerable attention in view of their variable bonding modes, promising biological implications, structural diversity, and ion-sensing ability. They have been used as drugs and are reported to possess a wide variety of biological activities against bacteria, fungi, and certain type of tumors and they are also a useful model for bioinorganic processes. As regards biological implications, thiosemicarbazone complexes have been intensively investigated for antiviral, anticancer, antitumoral, antimicrobial, antiamoebic, and anti-inflammatory activities. The inhibitory action is attributed due to their chelating properties. The activity of thesecompounds is strongly dependent upon the nature of the heteroatomic ring and the position of attachment to the ring as well as the form of thiosemicarbazone moiety (Chandra and Kumar, 2007). These are studied extensively due to their flexibility, their selectivity and sensitivity towards the central metal atom, structural and similarities with natural biological substances, due to the presence of imine group (−N=CH−) which imparts the biological activity . In view of the above applications, the present work relates to the synthesis, spectroscopic, and antimicrobial studies of Fe(II) and Zn(II) complexes with benzilbis (thiosemicarbazone) (Jeragh and El-Dissouky, 2005; Chandra and Gupta, 2005).

MATERIALS AND METHODS

Material

All the chemicals used of analytical R grade and procured from Qualikem and Loba metal salts were purchased from Ranbaxy and used as received.

Methods

Synthesis of ligand (L)

Hot ethanolic solution of thiosemicarbazide (1.82 g, 0.02 mol) and ethanolic solution of benzil (2.1 g, 0.01mol) were mixed in the presence of few drops of conc.HCl with constant stirring. This mixture was refluxed at 60-70^{0}C for 3 hours. The completion of the reaction was confirmed by the TLC. The reaction mass was degassed on a rotator evaporator, over a water bath. The degassed reaction mass on cooling gives cream-colored crystals. It was filtered, washed with cold EtOH, and dried under vacuum over P_4O_{10}, (yield (65%), mp 164^{0}C). Element chemical analysis data are shown in (Table,1).

Synthesis of Complexes

Hot ethanolic solution (20 mL) of corresponding metal salts (0.01mol) was mixed with hot ethanolic solution of the respective ligand (0.01mol). The mixture was refluxed for 3-4 hours at 50-60^{0}C. On cooling the contents, the colored complex separated out in each case. It was filtered and washed with 50% ethanol and dried under vacuum over P_4O_{10}. Purity of the complexes was checked by TLC.

Characterization

The C, H, and N were analyzed on Perkin elemental analyzer2400II.elemental analyzer.Magnetic susceptibilities were measured at room temperature on a Gouy balance using $Hg[Co(SCN)_4]$ as callibrant.

[1]Corresponding author

Diamagnetic corrections were made by using Pascal's constants. spectrometer. FTIR spectra (KBr) were recorded Perkin - 2989.

RESULTS AND DISCUSSION

Magnetic Susceptibility

The observed magnetic moments of Fe(II) and Zn(II) complexes are given in table 1. The best summary of the results on the magnetic behavior of Fe(II) and Zn(II) compounds was given by (Figgis and Nyholm,1958).The observed values of magnetic moment for complexes are generally diagnostic of the coordination geometry about the metal ion. Fe(II) has the exhibit a magnetic moment (2.8-3.2 BM) and Zn(II) (5.92-5.95 BM) complexes, whereas its octahedral complexes would be diamagnetic. The magnetic moment observed for Fe(II) and Zn(II) complexes lies in the range of 2.89-2.95BM and 5.92-5.95 BM which is consistent with the octahedral stereochemistry of the complexes(Tang et al., 2003).

Infrared Spectra

The assignments of the significant IR spectral bands of ligand and itsmetal complexes are presented in Table 2. In principle, the ligand can exhibit thione-thiol tautomerism since it contains a thioamide−NH−C=S functional group. Theν(S−H) band at 2565 cm^{-1} is absent in the IR spectrum of ligand but ν(N−H) band at 3230 cm^{-1} is present, indicating that in the solid state, the ligand remains as the thione tautomer. The position of ν(C=N) band of the thiosemicarbazone appeared at 1536 cm^{-1} is shifted towards lower wave number in the complexes indicating coordination via the azomethane nitrogen. This is also confirmed by the appearance of bands in the range of 424-425 cm^{-1}, this has been assigned to the ν(M−N). A strong band found at 1178 cm^{-1} is due to the ν(N−N) group of the thiosemicarbazone. The position of this band is shifted towards higher wave number in the spectra of complexes. It is due to the increase in the bond strength, which again confirms the coordination via the azomethane nitrogen. The band appearing at 832 cm^{-1} ν(C=S) in the IR spectrum of ligand is shifted towards lower wave number. It indicates that thione sulphur coordinates to the metal ion . Thus, it may be concluded that the ligand behaves as tetradentate chelating agent coordinating through azomethane nitrogen and thiolate sulphur(Agarwal et al., 2011; Bashir and Halim.,2012).

Antibacterial Activity

The antibacterial activity of the ligand and its metal complexes were tested by using paper disc diffusion method against *Staphylococeus aureus, Bacillus macerans* (gram-positive) and *Vibro cholerae*, *Salmonella typhi* (gram-negative). Nutrient agar medium was prepared by using peptone, beef extract, NaCl, agar-agar, and distilled water. The test compounds in measured quantities were dissolved in DMF to get concentrations of 250, 125, and

Table 1: Physical Measurements and Elemental Analysis Magnetic Susceptibilities

Compounds	Yield (%)	Color	Mp(C)	C %	H %	N %	μeff (BM)
Ligand(L)	65	Cream	164 C	53.92	4.41	23.58	------
$[Fe(L)Cl_2]$	66	Brown	282 C	34.43	3.12	23.43	5.94
$[Zn(L)Cl_2]$	62	Off-white	286 C	34.50	3.29	22.89	2.95

Table 2 : Infrared Spectral Bands (cm^{-1})

Compounds	ν (N - H)	ν (N - N)	N(C=N)	ν (C=S)	ν (M - N)
Ligand (L)	3230	1178	1536	832	—
$[Fe(L)Cl_2]$	3232	1133	1588	829	424
$[Zn(L)Cl_2]$	3231	1132	1599	830	425

Table 3 : Antibacterial Activity of Fe(II)and Zn(II)BBTSCZ by Disc Diffusion

Compound	**Concentration (mg/ml)**	**Zones of inhibtion of bacteria (mm)**			
		V.cholerae	*S.typhi*	*S.aureus*	*B.macerans*
Ligand (L)	100	11.00±2.65	12.00±1.45	11.00±1.34	8.00±1.23
$[Fe(L)Cl_2]$	100	17.00±1.76	18.00±3.98	13.00±1.03	12.00±1.96
$[Zn(L)Cl_2]$	100	14.00±2.32	16.00±1.65	14.00±3.23	14.00±1.21
-ve control	100	7.00±1.45	8.00±1.23	7.00±2.45	8.00±1.73
+ ve control	100	22.00±1.24	22.00±2.76	11.00±3.54	22.33±1.91

Values were expressed as Mean + S.D. (n=4)
SE =0.732, CD =1.593

63.5 ppm of compounds. Twenty five milliliter nutrient agar media (NA) was poured in each Petri plates. After solidification, 0.1mL of test bacteria spread over the medium using a spreader. The discs of Whatmann no. 1 filter paper having the diameter 4.00 mm, were placed at four equidistant places at a distance of 2 cm from the center in the inoculated Petri plates. Filter paper disc treated with DMF served as control and ciprofloxin used as a standard drug. All determination was made in duplicate for each of the compounds. An average of two independent readings for each compound was recorded. These Petri plates were kept in refrigerator for 24 hours for pre diffusion. Finally, Petri plates were incubated for 26-30 hours 28 ± 2^{0}C. The zone of inhibition was calculated in millimeters carefully. (Table, 3) *(*Kumari et al., 2012; Singh and Singh,2001).

CONCLUSION

It may be concluded that the ligand behaves as tetradentate chelating agent coordinating through azomethane nitrogen and thiolate sulphur. The magnetic moment observed for the Fe(II) and Zn(II) complexes lies in the range of 2.89-5.95BM which is consistent with the octahedral stereochemistry of the complexes. The antimicrobial screening data showed that the compounds exhibit antimicrobial properties, and it is important to note that the metal chelates exhibit more inhibitory effects than the parent ligands. It is clear that the metal complexes showed antibacterial activities against the gram-positive bacteria (*Bacillus macerans*) *Staphylocecus aureus* and *Salmonella typhi* ,*Vibro cholerae* (gram-negative) bacteria. The increased activity of the metal chelates can be explained on the basis of chelation theory. It is known that chelation tends to make the ligand act as more powerful. and potent bactericidal agents.It is observed that, in a complex, the positive charge of the metal is partially shared with the donor atoms present in the ligands, and there may be π-electron delocalization over the whole chelating.This increases the lipophilic character of the metal chelate and favours its permeation through the lipoid layer of the bacterial memberanes.There are other factors which also increase the activity, which are solubility, conductivity, and bond length between the metal and the ligand.

REFERENCES

Agarwal R.K., Singh L.,and Sharma D. K., 2011. Synthesis, spectral and biological properties of copper(II) complexes of thiosemicarbazones 2-(pyrrolidin-2-ylidene) hydrazine carbothiamino pyrine and aromatic aldehyde. Bioinorganic Chemistry and Applications, **10**:59-65.

Bashir S., and Halim S.N.A., 2012. Synthesis and characterization of mixed nickel thiosemicarbazone complexes. Malaysian Journal of Fundamental & Applied Sciences, **8**:162-166.

Chandra S., and Kumar A., 2007. Spectral studies on Co(II), Ni(II) and Cu(II) complexes with thiosemicarbazone and semicarbazone derived from 2-acetyl furan. Spectrochimica Acta Part A, **66**:1347-1351.

Chandra S., and Gupta L. K., 2005. EPR, mass, IR, electronic, and magnetic studies on copper(II) complexes of semicarbazones and thiosemicarbazones. Spectrochimica Acta Part A, **61**: 269-275.

Figgis B. N., and Nyholm R. S., 1958. A convenient solid for calibration of the Gouy susceptibilitity apparatus. Journal of Chemical Society, 4190-4191,

Jeragh B. J. A., and El-Dissouky A., 2005. Synthesis, spectroscopic and the biological activity studies of thiosemicarbazones containing ferrocene and their copper(II) complexes. Journal of Coordination Chemistry, **58**:1029-1038.

Kumari S., Sharma N.K., and Kohli S., 2012. Synthesis, characterization and antimicrobial studies of copper (II) complexes of semicarbazone and Thiosemicarbazone of m- hydroxy benzaldehyde and p-hydroxy benzaldehyd. Orient. J. Chem, **28**: 969-974.

Singh N. K., and Singh S. B., 2001. Synthesis, characterization and biological properties of manganese(II), cobalt(II), nickel(II),copper(II), zinc(II), chromium(III) and iron(III) complexes with a new thiosemicarbazide derivative. Indian Journal of Chemistry, **40**: 1070-1075.

Tang H. A., Wang L. F., and Yang R. D., 2003. Synthesis, characterization and antibacterial activities of manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes with soluble vitamin K3 thiosemicarbazone. Transition Metal Chemistry, 2**8**: 395-398.