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Synthetic and Structural Studies of Fe (II) and Zn (II) Complexes of 2'-Hydroxy Chalcones Derived from Pyridine-2-carboxaldehyde, Pyrrole-2-carboxaldehyde

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ABSTRACT

Complexes of Fe (II) and Zn (II) with 1-(2′-hydroxy-3′-iodo-5′-chlorophenyl)-3-pyridine-2-propen-1-one (L_3) and 1-(2′-hydroxy-3′-bromo-5′-chlorophenyl)-3-pyrrole-2-propen-1-one (L_5), have been prepared and characterized with the help of elemental analysis, molar conductivity, magnetic measurement, electronic spectra and thermal analysis. Elemental analysis confirmed 1:2 (metal: ligand) stoichiometry. The conductivity data show that all these complexes are non-electrolytic in nature. The infra-red spectral data indicate that the L_3 and L_5 act as mononegative bidentateligands with the Fe (II) complexes have octahedral geometry whereas the Zn (II) complexes have square planar geometry. Presence of coordinated water molecule in the Fe (II) complexes is confirmed by Thermogravimetric Analysis (TGA) studies. In vitro antimicrobial activities of all synthesized compounds have been evaluated against four bacterial strains and four fungal strains. The compounds show net enhancement in activity on coordination of metals with ligand.

Keywords: Chalcones, Transition metal complexes, Structural study, Antimicrobial study

INTRODUCTION

2′-Hydroxychalcone and its derivatives represent wide spectrum of biological activities such as antibacterial [1], antifungal [2], antiviral [3], anticancer [4], anti-HIV [5], antidiabetic agents [6]. 2′-hydroxychalcones known to be pharmacologically active possess coordinating sites and are expected to form different metal ions. The chelating tendency of these compounds generally increases biological activity of these compounds. We report here the synthesis of a series of Fe (II) and Zn (II) complexes obtained by the reaction of metal salts of Fe (II) and Zn (II) with 1-(2′-hydroxy-3′-iodo-5′-chlorophenyl)-3-pyridine-2-propen-1-one and 1-(2′-hydroxy-3′-bromo-5′-chlorophenyl)-3-pyrrole-2-propen-1-one.

EXPERIMENTAL

All the reagents used were chemically pure and are of AR grade. Solvents were dried and distilled before use according to standard procedure [7]. All the melting points were determined in an open capillary tube and are uncorrected. Completion of the reaction was monitored by thin layer chromatography on pre-coated sheets of silica gel-G.

Synthesis of metal complexes

The ligand (0.002 mol) and the metal salt (0.01 mol) in 50 ml methanol was reflux for 2 h. In all the cases the ligand concentration was in slight excess of the 1:2 metal ligand molar ratios. The solid mass separated was filtered through a sintered glass crucible (G4) and the residue was washed several times with hot methanol until the washings were free of excess of ligand. These complexes were finally dried under vacuum desiccator over fused $CaCl_2$. Analytical and physical data is given in Table 1. Molar conductance measurements were carried out in 10^{-4} M in Dimethyl Sulfoxide (DMSO) solution using an Elico Digital Conductometer Model-180. The magnetic susceptibility measurements of the complexes in the solid state were made on Guoy balance at room temperature using Hg $[Co(NCS)_4]$ as standard. Diamagnetic corrections were applied using Pascals constant. The IR spectra of the metal in KBr pallets in the range of 4000-350 cm^{-1} were recorded making use FTIR-SHIMADZU-8400S spectrometer.

UV-Visible spectra in Dimethylformamide (DMF) were recorded on a SHIMADZU multipurpose recording spectrophotometer model 1601 and TGA and Differential Thermal Analysis (DTA) of metal complexes were carried out in nitrogen atmosphere in the range 25-1000°C on Mettler system with a heating rate 10°C min^{-1} using α- Al_2O_3 as a reference (Table 2).

RESULTS AND DISCUSSION

All the complexes are stable at room temperature insoluble in water and most of the common organic solvents but soluble in DMF and DMSO.

The analytical data of the complexes (Table 1) indicates that their stoichiometry may be represented as 1:2 metals to ligand ratio. The molar conductance values of the complexes in DMSO solvents are in the range of 5.67-5.69 S $cm^2.mol^{-1}$ for Fe(II) complex, which are usually observed for the octahedral geometry of the Fe(II) complex suggesting their non-electrolytic nature [8], and due to completely filled 'd' shell of Zn(II) ion it exhibits diamagnetic nature.

IR spectra

The ligand showed a weak broad band around 3047-3029 cm^{-1}, in the IR spectra of Fe (II) complexes there is an intense broad band near 3443-3336 cm^{-1} due to *v*(OH) of coordinated water molecule, but the corresponding IR spectra of Zn(II) complexes do not show any absorbance in this region. In the IR spectra of all the ligands an intense band appearing around 1656 cm^{-1} is attributed to v(C=O) [9]. This band is shifted to lower wave number in the spectra of complexes indicating coordination through oxygen of (C=O) group. The medium intensity band appearing around 1530 cm^{-1} in the ligands and the complexes are assigned to *v*(C=C) (aromatic). The *v* (M-O) band for Fe (II) was observed in the complexes at around 432 cm^{-1}. The literature [10] supports such interpretation.

Proton Nuclear Magnetic Resonance (^{1}H-NMR spectra)

The ^{1}H-NMR spectrum of Fe (II) and Zn (II) complex is recorded in DMSO solvent. The ^{1}H-NMR spectra are of Fe (II) and Zn (II) complexes and ligands show well resolved signals, due to presence of metal ion there observed broad peaks indicating the formation of the complex. In the ^{1}H-NMR spectrum of Fe (II) and Zn (II) complex, the signal due to –OH proton (phenolic) is absent, suggesting the deprotonation of phenolic group attached to benzene ring in the 2'-hydroxychalcone. The ^{1}H-NMR spectra of complex confirms the coordination of the ligand to the metal ion through phenolic oxygen atom. In the Fe (II) complex the broad signal at $\delta=3.50$ is due to proton of coordinated water which is absent in the Zn (II) complex indicating the absence of coordinated water molecule in the Zn (II) complex.

Thermal analysis

Existence of coordinated water molecules in Fe (II) complex is confirmed by TGA studies. Representative $[Fe\ (L_3)_2(H_2O)_2]$ is stable up to 136°C where it loses surface water and consequently at 242°C it loses coordinated water molecule presence of which is indicated by IR spectra. The dry complex than remains unchanged and it loses a large part of ligand at 348°C. There after the complex loses coordinated ligand in small fragments to give metal oxide around 878°C. The percentage weight loss of the organic part contents from the Fe (II) complex are found matching with the theoretical values. After this the weight of the complex remains constant and the horizontal nature of the curve indicates the presence of thermally stable metal oxide. Hence from TGA, it is clear that the complex under study contains two water molecules which are coordinated to central metal ion [10]. Whereas TGA studies of Zn (II) complex shows absence of coordinated water molecule.

X-ray crystallographic study

The X-ray diffractogram of Fe (II) complex shows good intense and sharp peaks, indicating high crystallinity of Fe (II) complex. The Fe (II) complex is successfully indexed to monoclinic crystal system. The standard deviation in lattice parameter for Fe (II) complex is found to be as expected, which is very well supported by value of Z (Z=2). The observed density of Fe (II) complex is 2.037 g/cm^3, while theoretical density from the X-ray data is 1.1921 g/cm^3. The closeness in the value of observed density and calculated density suggest that each reflux of X-ray diffraction pattern is indexed with perfectness. The X-ray data for Fe (II) complex having metal: ligand stoichiometry as 1:2 have formula factor Z=2. Monoclinic crystal system with Z=2 can be assigned space group $P_{2/m}$ without condition on h, k; l values (Figure 1).

The X-ray diffractogram of $[Zn\ (L_3)_2]$ shows good intense and sharp peaks, indicating high crystallinity of Zn (II) complex. The standard deviation in lattice parameters for Zn (II) complex is 0.024% The lattice parameter for Zn (II) complex directed to Tetragonal is found to be as expected value of Z(Z=6). The observed density of Zn (II) complex is 1.2073 g/cm^3, while theoretical density from the X-ray data is 1.0114 g/cm^3.

These values suggest that each reflex of X-ray diffraction pattern is indexed with perfectness.

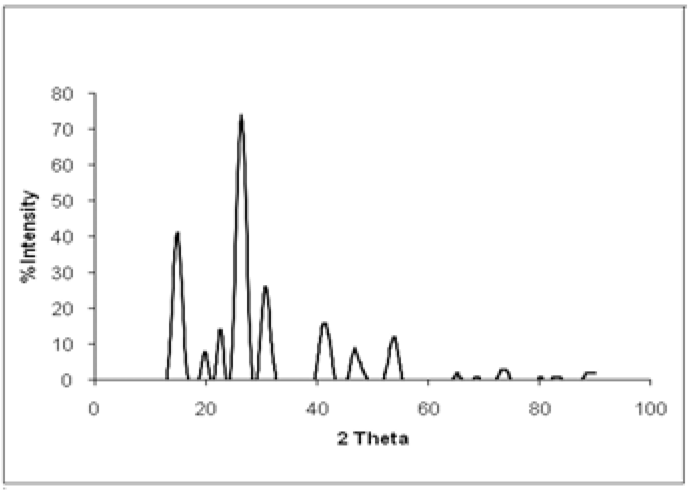
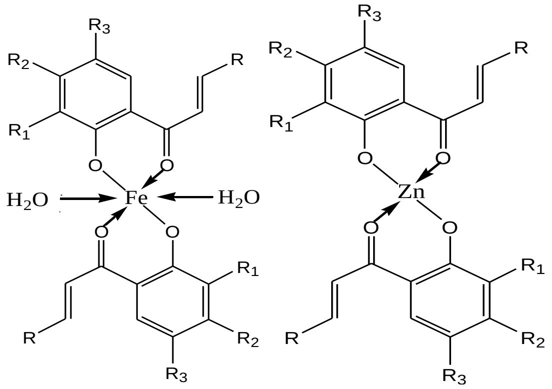


Figure 1: X-ray diffractometer of $[Zn(L_3)_2]$

On the basis of above discussion the Fe (II) and Zn (II) complexes of L_3 and L_5 may be assigned following structures (Scheme 1):



Scheme 1: Fe (II) complex, Zn (II) complex

Table 1: Synthesis of metal complexes

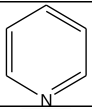
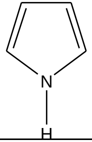
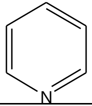
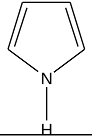
S. No.	Complex	Substituents			
		R_1	R_2	R_3	R
1.	$(L_3)_2(H_2O)_2]$	I	H	Cl	 N
2.	$(L_5)_2(H_2O)_2]$	Br	H	Cl	 N H
3.	$(L_3)_2]$	I	H	Cl	 N
4.	$(L_5)_2]$	Br	H	Cl	 N H

Table 2: Magnetic moment, molar conductivity and analytical data of Fe (II) and Zn (II) complexes

S. No.	Molecular formula	Molecular weight	Colour	M. P./ D.P. (°C)	Elemental analysis		Molar conductivity S cm^2 $mol^{-1} \times 10^{-4}$	$\mu_{eff.}$ B. M.
					Halogen found (Calcd)	Metal found (Calcd)		
1.	$C_{28}H_{20}O_6Cl_2N_2I_2Fe$	861	Dark brown	178	37.05 (37.71)	6.76 (6.48)	15.03	5.67
2.	$C_{26}H_{18}O_6Cl_2N_2Br_2Fe$	741	Brown	208	30.96 (31.13)	7.12 (7.53)	24.04	5.69
3.	$C_{28}H_{16}O_4Cl_2N_2I_2Zn$	834	Brown	180	38.12 (38.93)	7.23 (7.83)	12.02	Diamagnetic
4.	$C_{26}H_{14}O_4Cl_2N_2Br_2Zn$	614	Yellow	188	37.21 (37.57)	10.04 (10.64)	26.17	Diamagnetic

Antimicrobial activity

The antimicrobial activity was assayed by cup plate agar diffusion method [11] by measuring inhibition zones in mm. *In vitro* antimicrobial activity of all synthesized compounds and standard have been evaluated against four strains of bacteria which include *Escherichia coli, Salmonella typhi, Staphylococcal aureus and Bacillus subtilis* and against four fungal strains like *Aspergillus niger, Aspergillus flavus, Fusarium moniliforme* and *Penicillium chrysogenum.* The standard used was penicillin and griseofulvin.

From the results of antimicrobial activity of ligand and complex it is clear that the complexes shows enhance activity than the ligands. The increase in antimicrobial activity is due faster diffusion of metal complexes as a whole through the cell membrane or due to the combined activity of the metal and ligand [12].

CONCLUSION

The Fe (II) and Zn (II) complexes are coloured, insoluble in most of the organic solvent but soluble in most of the organic solvent but soluble in DMF, DMSO and CHCL3. The stoichiometry of the metal complexes obtained has been found to be 1:2. The infrared spectral data indicate that all ligands act as mononegative bidentate species towards Fe (II) and Zn (II) complexes. All the Fe (II) metal complexes are paramagnetic in nature and Zn (II) complexes are diamagnetic in nature. The electronic spectral data suggested that Fe (II) complexes have octahedral, while Zn (II) complexes have square planar geometry.

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