INTERNATIONAL JOURNAL OF RESEARCH IN PHARMACY AND CHEMISTRY

Available online at www.ijrpc.com

Research Article

SYNTHESIS, PHYSICO-CHEMICAL CHARACTERIZATION OF COPPER METAL COMPLEXES WITH ISOXAZOLE DERIVATIVES

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Abstract: In this work the Cu (II) metal complexes of with isoxazole synthesized and characterization of complexes was done by, UV-Vis, IR, TGA as well as the electrical conductance, magnetic susceptibility. The thermal behaviour provided confirmation of the complex composition as well as the number and the nature of water molecules and the intervals of thermal stability. Theantimicrobial activity assay of all the complexes was carried out.

Keywords: Isoxazoles, Metal complexes, Thermal studies, studies, Antibacterial activity.

INTRODUCTION

Among the five-member nitrogen and oxygen heterocycles, synthesis of oxazole derivatives is of considerable interest as they are known to be associated with a very much ImportantBiological activities[1-5]. The derivatives show anti-inflammatory[6], antifungal[7], cardiovascular[8], antimicrobial[9], herbicidal[10], hypoglycaemic[11], hypotension[12], antiviral[13] and anti-tumour activities[14], electronic (LEDs) [15], anticonulsant[16] oxidative cyclizations[17], pharmacologically active compounds[18-21], showing a wide range of biological activities[22-26]. Thus, the biological importance of these organic ligands[27, 28] we report the synthesis and characterization of complexes of these ligands with transition metal such as Copper.

EXPERIMENTAL

All reagents were of commercial analytical quality and have been used without further purification.

Synthesis of Isoxazole Ligands

The ligands were prepared by reacting 2-Hydroxy acetophenone(1 mM) &diacetylformamide(1 mM) were mixed in methanol gives intermediate, The intermediate with hydroxyl amine gives isoxazolederivative. The reaction was carried out in Microwave oven. After completion of reaction, reaction mixture was poured into crushed ice. Obtained Precipitate was filtered & dried. In all the cases, the product obtained after the usual work up gave satisfactory spectral data.

Synthesis of Metal complexes

All the complexes of Copper were prepared following the same procedure. Hot methanolic solution of ligand (0.5 mol) and hot methanolic solution of corresponding Copper chloride (0.55 mol)were mixed together with constant stirring. The mixture wasrefluxed for 2–3 h at 70–80 ◦C on water bath. On cooling, colored solid metal complex was precipitated out. The product was filtered, washed with cold methanol and dried. Purity of the complex was checked by TLC andmelting points.

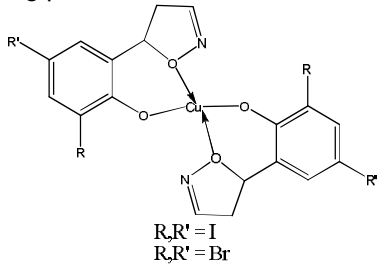

Fig. 1: Proposed structure of Cu complex

INSTRUMENTAL

Molar conductivity is measured by the conductivity instrument. All complexes molar conductance measured in solvent DMSO at room temperature. The magnetic susceptibility measurements were done by Gouy method at room temperature, using Hg[Co(NCS)4] as standard. The electronic spectra of the ligands and metal complexes in DMSO were recorded on Shimadzu-61.UV-Visible spectrometer in the region 200-700 nm. IR spectra were recorded in KBr pellets with a Perkin Elmer spectrometer in the range 400–4000 cm-1 and the Thermo gravimetric analysis (TGA) were carried out using Perkin Elmer TA/SDT-2960 in the temperature range of 25-1000 ^{o}C at Chemistry Department of Pune University.

RESULTS AND DISCUSSION

Examination of elemental analyses data shows that complexes are monomeric, given in Table 1 and also indicates the stoichiometry of metal to ligands 1:2. All the complexes are colored solids, stable to air and moisture. The complexes do not have sharp melting point, but decomposed on heating beyond 269 °C. The molar conductivity determined in DMSO solvent at 10^{-3}concentration suggests that all the complexes are non-electrolyte in nature.

Magnetic properties and Electronic spectra

Transition metal ions with d^9 configuration are generally paramagnetic in nature due to presence of one or more no. of unpaired electrons. Theeffective magnetic moment values of the complexes are presented in Table 1. The Cu(II) complex exhibits a value of 1.75- 1.84μB, expected for S=1/2 system having square planar geometry[18].

The electronic spectra of the ligands and all the complexes were recorded in DMSO. The electronic transition in the ligands and metal complexes are due to the azomethine group and aromatic ring.

Infrared spectra

The absence of the band in the region 3350–3420 cm^{-1} assigned to the -OH stretching vibrations due to presence of water molecule. Ligands shows 3000-2900 cm^{-1}The phenolic –OH groups in the ligand and the shift to lower wave number of v(C-O) by ~25cm^{-1}confirmed the participation of phenolic oxygen in co-ordination[24]. The phenolic –OH group on deprotonation forms covalent bond with central metal atom through oxygen atom.

The band at ~1600 cm-1 for free ligands is attributed to *v*(C=N) stretching vibrations of the ligands nucleus is moved towards lower wave numbers by 25-45 cm^{-1} in the spectra of the complexes, which confirms the coordination of the nitrogen atom to the metallic ion[25].The bonding of the metal(II) ion is further supported by the broad absorption bands in the region 550-580 and 450-477 cmwhich can be assigned to M-O and M-N stretching vibrations, respectively. Therefore, from these IR Spectra it concluded that metal complexes are formed.

Thermal studies

The simultaneous use of TG and DTA is mode in the present study of metal complexes with a view to understand stoichiometry, thermal stability, the presence and nature of water molecules. The water in inorganic compounds may be classified as lattice water and coordinated water. There is however, no definite border line between the two. The former term denotes water molecules trapped in the crystalline lattice, either by weak bonds to the anion or by weak ionic bonds to the metal or by both, whereas the latter denotes water molecules bonded to the metal through partial covalent bonds or coordinate bonds. The water eliminated below 150 °C can be considered as lattice water and above 150 °C as water coordinated to metal ion. Noncoordinated water molecules Cu(II) complex has been reported on the basis of 5.9% weight loss at 126 °C.The TGA-DTA curve (Figure 2) of Cu(II) complex with shows two step decomposition. The first weight loss 6%, at 126–245 ^{o}C could be correlated with the loss ofwater (Cal. 5.9%) [32'33].

Table 1: Physicochemical data and elemental analysis

Sr. No	Molecular formula	Colour	Yield	Elemental Analysis		Molar conductivity	Magnetic susceptibility
				Halogen Cal.(Found)	Metal Cal.(Fond)		
1	$C_{18}H_{12}CuI_4N_2O_4$	Black	72	56.94(56.60)	7.13 (7.02)	20.5	1.76
2	$C_{18}H_{12}CuBr_4N_2O_4$	Brown	79	45.43(45.19)	9.03(8.70)	21.3	1.80

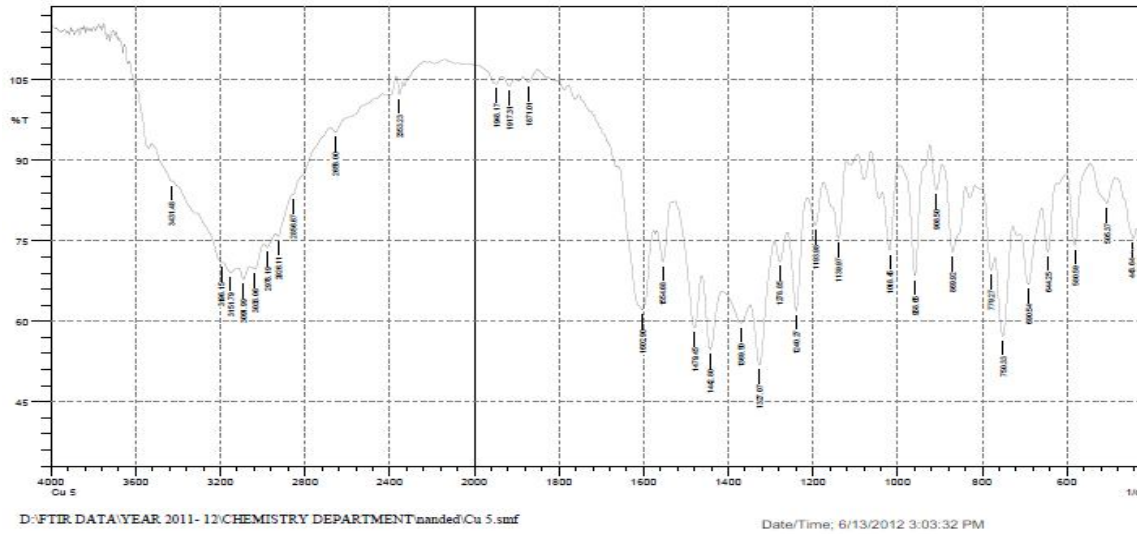

Fig. 2: IR of Complexes

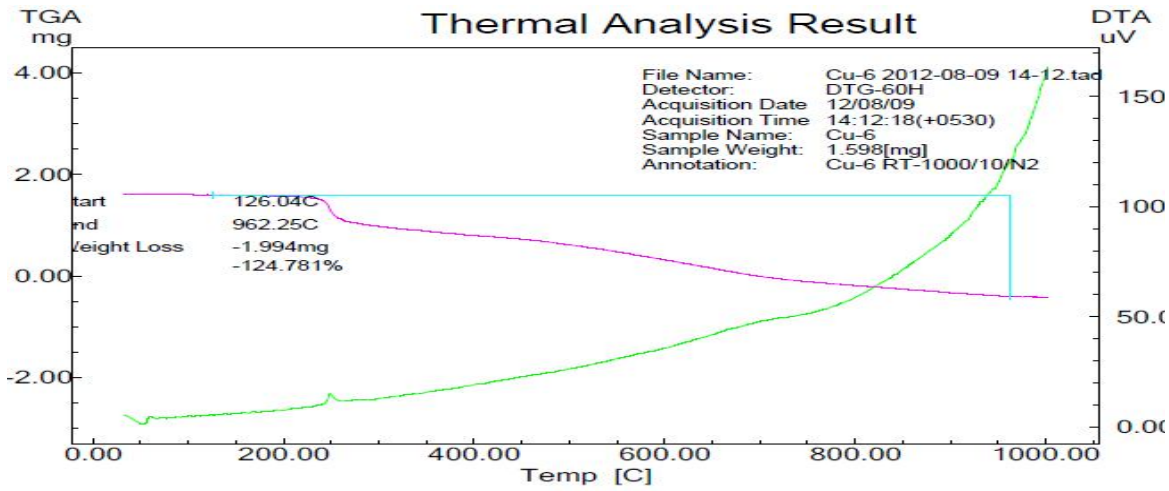

Fig. 3: TGA-DTA curve of Complex

Antimicrobial activity

The complexes are screened antimicrobial activity.The test compounds were evaluated for antifungal and antibacterial activity (Table 2). From the data it was observed that all compounds exhibited broad spectrum antimicrobial activity. The growth of *Aspergillusflavus* and *A. niger* was effectively inhibited by Complex1 and Complex2 as compared to fluconazole (≥ 25mm). This indicates that dibromo-, derivatives may enhance the antifungal activity of Isoxazolephenoxy compounds. The growth of *Escherichia coli*was not significantly inhibited by any of the test compounds when compared with streptomycin (<32 mm). These findings further substantiate that thedibromo, derivativeshas shown significant antifungal activity while diido-derivatives has potent antibacterial activity.

Table 2: Antimicrobial activity

Compound Code	Name	Zone of inhibition (mm)			
		Fungal species		Bacterial species	
		Aspergillusflavus	*Aspergillusniger*	*Escherichia coli*	*Bacillus subtilis*
Complex1	bis(2-4,5-dihydroisoxazole-5-yl)-4,6-diidophenoxy)copper	35	40	20	26
Complex2	bis(2,4-dibromo-6 (4,5dihyd-roxazoleyl)phenoxy)copper	30	36	22	28
Control	Dimethyl sulphoxide	06	06	06	06
Positive control	Streptomycin and fluconazole for bacteria and fungi respectively and fungi respectively	26	25	32	30

On the basis of elemental analysis, UV-Vis, IR, molar conductivities, magnetic susceptibilities and thermal studies, the structures in Figure 1 are proposed for the reported complexes.

ACKNOWLEDGEMENT

Author is thankful to the departmentof chemistry, N.E.S. Science college College, Nanded, Maharashtra, is also duly acknowledged for providing and necessary facilities to carry out this work.

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