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SPECTROSCOPIC AND ANTIMICROBIAL STUDIES OF SOME NOVEL COMPLEXES OFMN (II) AND CU (II)

Hardik kumar D. Chaudhary[1], Jwalant J. Vora[1], Jabali J. Vora[2], Manish H. Chaudhari[2]

1 Department of Chemistry, M.G. Science Institute, Navrangpura, Ahmedabad-380009, Gujarat, India.

2 Department of Chemistry, Hemchandracharya North Gujarat University, Patan - 384 265.Gujarat, India.

2 Department of Chemistry, Mehsana Urban Institute of Sciences, Ganpat University, India.

ABSTRACT

In this study, complexes were synthesized in marginal yields via the coordination of metal perchlorates with the ligand. Kynurenic acid (KYNA) ligand reacts with solution of Mn(II)and Cu(II) perchlorates and solid kynurenic acid – metal complexes are synthesized. The ligand and its complexes have been investigated with IR, UV-VIS, mass spectrometry, elemental analysis, TGA – DSC technique etc. These compounds were subjected to their biocidal efficacy against Escherichia coli , Bacillus, Staphylococcus aureus and Salmonellatyphii A and also results have been compared with standard drugs streptomycin and ampicilin.

Key words: Kynurenic acid, metal complexes, Antibacterial activity.

INTRODUCTION

KYNA is regarded as “privileged ligand” due to its capability to form complexes with a wide range of transition metal ions yielding stable and colored metal complexes with interesting physical and chemical properties and potential biological activities. KYNAacts as a better ligand because

1. It has better co-ordination tendency.

2. It forms more stable complexes.

3. It has the ability to produce some new and unique complexes with highly altered biological andanalytical properties. KYNA usually act as chelating ligand with transition metal ion, bonding through the nitrogen and oxygen atoms. KYNA and its complexes have received considerable attention because oftheir pharmacological activities[1].

KYNA presence was first demonstrated in urine by Liebig. Nevertheless, the compound was not thoroughly analyzed until the 1980's and 1990's when researchers indicated that KYNA is an antagonist of ionotropic glutamate receptor. Subsequently, researchers presumed that KYNA is present in the human brain. Numerous studies were conducted to investigate the role of KYNA in the physiology and pathology of the central nervous system (CNS). Since both the concentration of KYNA in the human brain and penetration of KYNA through a blood-brain barrier are low, studies of peripheral KYNA gained popularity[2].

EXPERIMENTAL

Analytical grade chemicals were used throughout the course of experimental work. Spetroscopic grade solvents were employed for recording the spectra. The compound kynurenic acid (Sigma) was used as the ligand. All metal carbonates used were also A.R. grade. A definite volume of 70% $HClO_4$ was diluted with water to obtain 0.2M perchloric acid solution. The exact strength was determined by pH metric titration against standard 0.2M NaOH solution. 75 ml 0.2 M perchloric acid was taken and solid metal carbonate was added in it till effervescences observed (slight excess addition was done). The solution was stirred for 30 minutes, filtered and thus the metal perchlorate in aqueous solution was obtained. The formation of complexes was carried out by mixing 75 mL (0.133 M) metal perchlorate solution and 50 mL(0.2M) ligand in DMSO solution. The mole ratio of ligand and metal was (1:1). The reaction mixture was refluxed for around 3.0 h at 95 0C temperature. After 3.0 h the reaction mixture was cooled. There was no immediate precipitation, then into this solution, ice water was added and immediately precipitates were obtained. The complexes thus obtained were washed well with double distilled water and alcohol for removal of unreacted metal and ligand. All the complexes were dried in an oven at 40° C to 50 ° C[3]. This way, the complexes of Mn(II) and Cu(II) were prepared and isolated as solid. An antibacterial study was carried using Agar Diffusion Method.

RESULTS AND DISCUSSION

Results of Infrared Spectra

KYNA and metal KYNA complexes were characterized by infrared spectroscopy. IR Spectra of the KYNA and the complexes were recorded on an FTIR instrument in the range 500-4000cm^{-1}. KYNA contains the functional groups, carboxyl, hydroxyl and amine,which are detectable by infrared spectroscopy[4].

IR spectral band (cm^{-1}) of KYNA ligand and its complexes are shown below.

Table 1: Results of Infrared Spectra (figures expressed in cm^{-1})

KYNA	**O-H Phenolic (3434), Acidic –OH (3105), Ar-CH-stretching(2967),C=N(1593), C=O Aromatic stretching(1758), bending, vibrations (748-OH out of plane1245, 1264 CH, CH_2 ,OH in plane1380-wagging and twisting).**		
	Changed	**New peaks**	**Eliminated**
Mn-KYNA	O-H Phenolic(3198), Ar-CH-stretching(3085),C=N(1472), C=O Aromatic stretching(1654),bending vibrations(1472)	M-N, M-O (517,634,664)	Acidic –OH
Cu-KYNA	O-H Phenolic(3126), Ar-CH-stretching(3085),C=N(1447), C=O Aromatic stretching(1654),bending vibrations(1447)	M-N, M-O (501,559,670)	Acidic –OH

Table 2: Results of Physical Measurements

TLC (solvent toluene: methanol 7:3)and M.P. was taken by melting point apparatus. Metal Complex formation was confirmed from TLC single spot observation.The UV – visible spectra were measured on a UV-1800 Shimadzu (Double beam) spectrophotometer.

Complex	**Colour**	**M.W. (gm/mol)**	**M.P. ° C**	**R.F. value ***	**Molar Conductance mho cm^{-1}**	**% yield**
Ligand (KYNA)	Light cream	189.17	269	0.8503	2.55×10^{-3}	_____

Mn-KYNA	cream	640.44	268.4	0.8333	2.00×10^{-3}	27.39
Cu-KYNA	Light blue	477.88	>200	0.9180	1.65×10^{-3}	42.34

* Solvent system : (Toluene: methanol 7:3).

Table 3: Magnetic and Electronic spectra.

Metal Complexes	**Uv-vis spectral λmax (nm)**	**Magn. Sus. (BM)**	**Number of unpaired electrons**	**Oxidation No.**	**Coordination No.**	**Probable shape**
KYNA	346.50 291.50 258.00	---------	_____	_____	_____	_____
Mn-KYNA	361.00 346.00 291.50 241.50 213.50	6.24	5 (hs)	2	7	Pentagonal bipyramid ----or----- Trigonal prism
Cu-KYNA	330.00 306.00 234.50	5.34	1	2	6	Octahedral

Uv-vis =ultra violet- visible, Magn. Sus. = magnetic susceptibility, hs = high spin.

Table 4: CHN and Metal Analysis

Elemental analyses were performed with a Vario-MICRO CUBE C, H, N analyzer.

Metal Complexes	**C (%)**		**H (%)**		**N (%)**		**Metal (%) by TGA**	
	Found	calculated	found	calculated	Found	calculated	found	calculated
Mn-KYNA	61.11	56.21	4.01	3.27	7.03	6.55	8.09	8.57
Cu-KYNA	51.51	50.22	3.48	2.92	5.50	5.85	12.68	13.29

TGA- DSC Analysis

Fig 1:Mn-KYNA

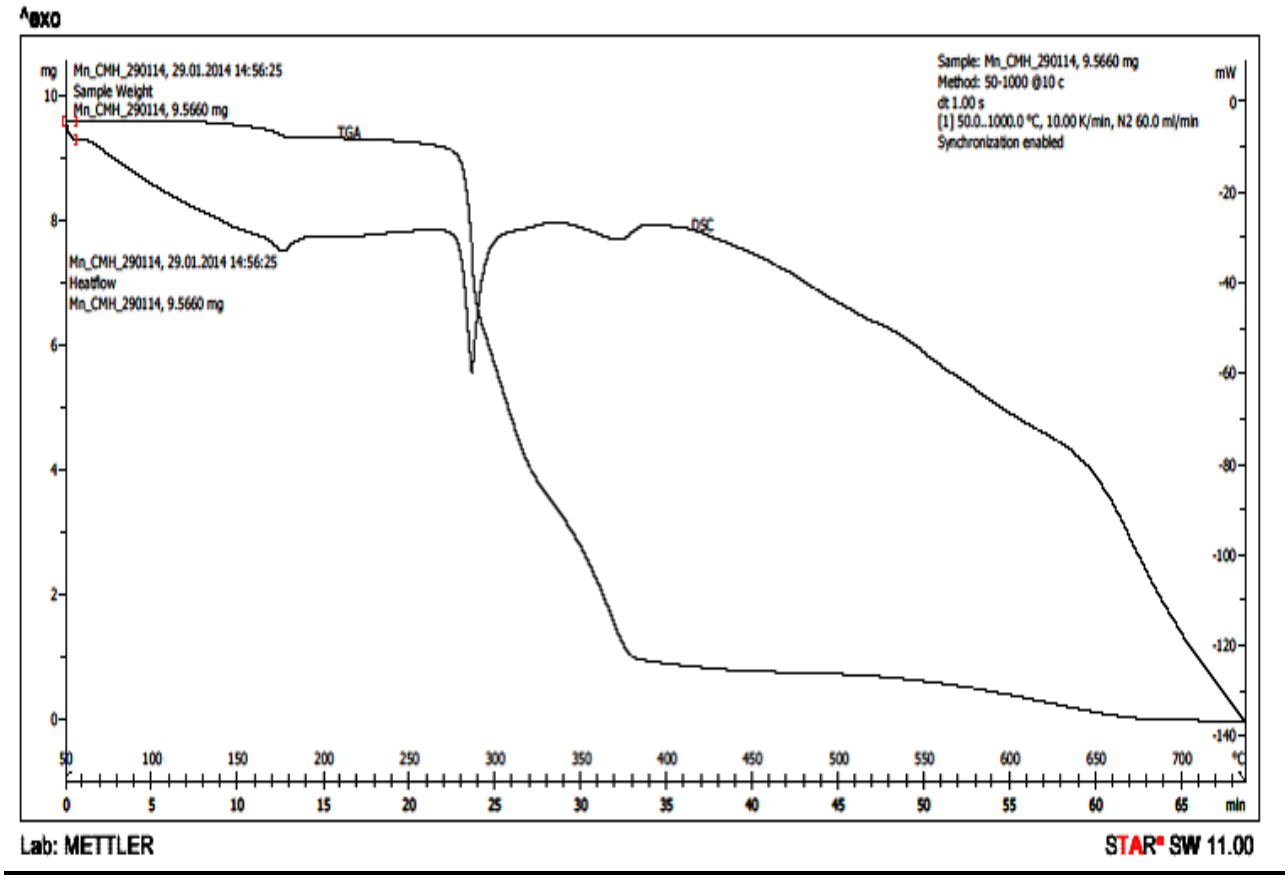
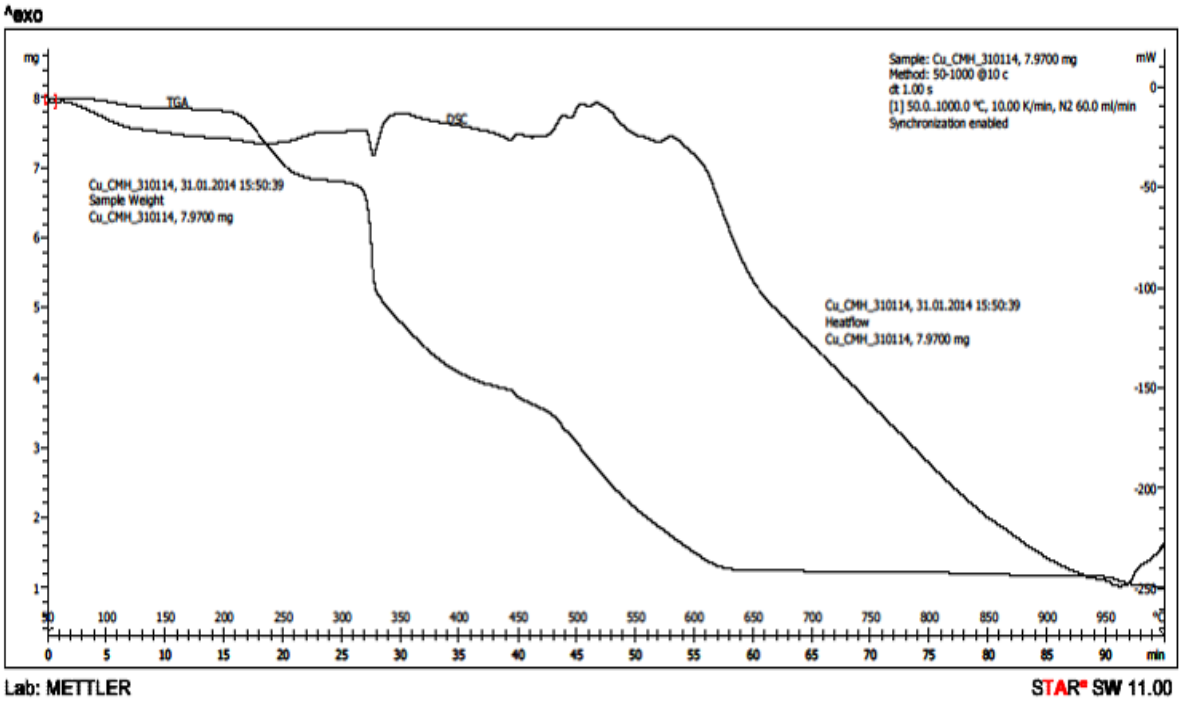


Fig 2: Cu-KYNA



Thermo gravimetric analysis for one mole of Mn-KYNA 3.23 gm weight loss occurred at 150^0Ctemperature, which indicated that no water molecules of crystallization is present in complex. 12.49 gm weight loss occurred by one mole complex at 250^0Ctemperature, which indicates that one coordinated water molecule is present in Mn-KYNA.

For Cu-KYNA7.36 gm weight loss occurred at150^0C, which indicated that practically no water molecule is present as water of crystallization in complex and 44.75 gm weight loss occurred for one mole complex at 250^0C temperature, which indicates thattwo water moleculescoordinate with Cu^{2+}metal ion.

Table 5: Results of TGA

Compound	**RT-150 ^{0}C (Water of crystallization)**			**150 ^{0}C – 250 ^{0}C (water of coordination)**		
	% Loss	**Loss of weight(gm) for 1 mole complex**	**water molecules**	**% Loss**	**Loss of weight(gm) for 1 mole complex**	**water molecules**
KYNA	_____	_____	____	____	_____	_____
Mn-KYNA	0.54	3.23	0	1.77	12.49	1
Cu-KYNA	3.87	7.36	0	2.01	44.75	2

RT= Room Temperature

RESULTS OF MASS SPECTROSCOPY

Fig 3: [KYNA mass spectra]

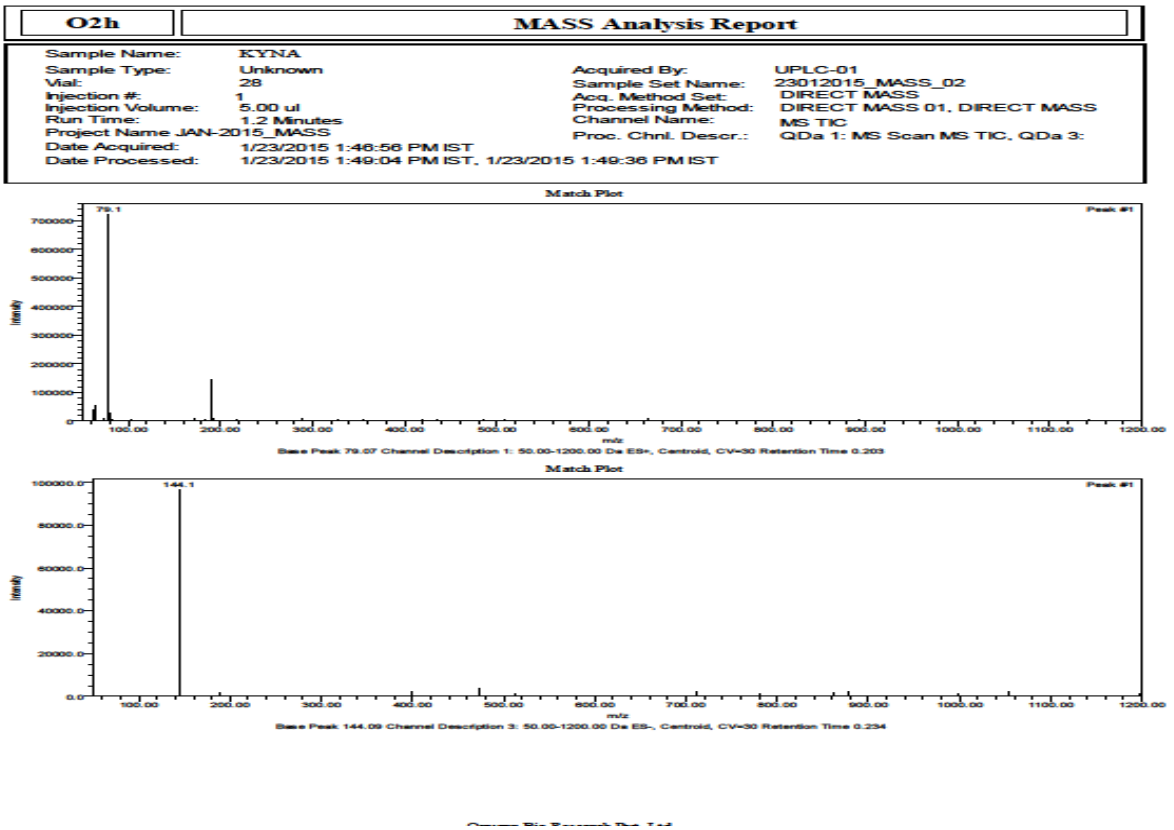


Fig 4: [Mn-KYNA mass spectra]

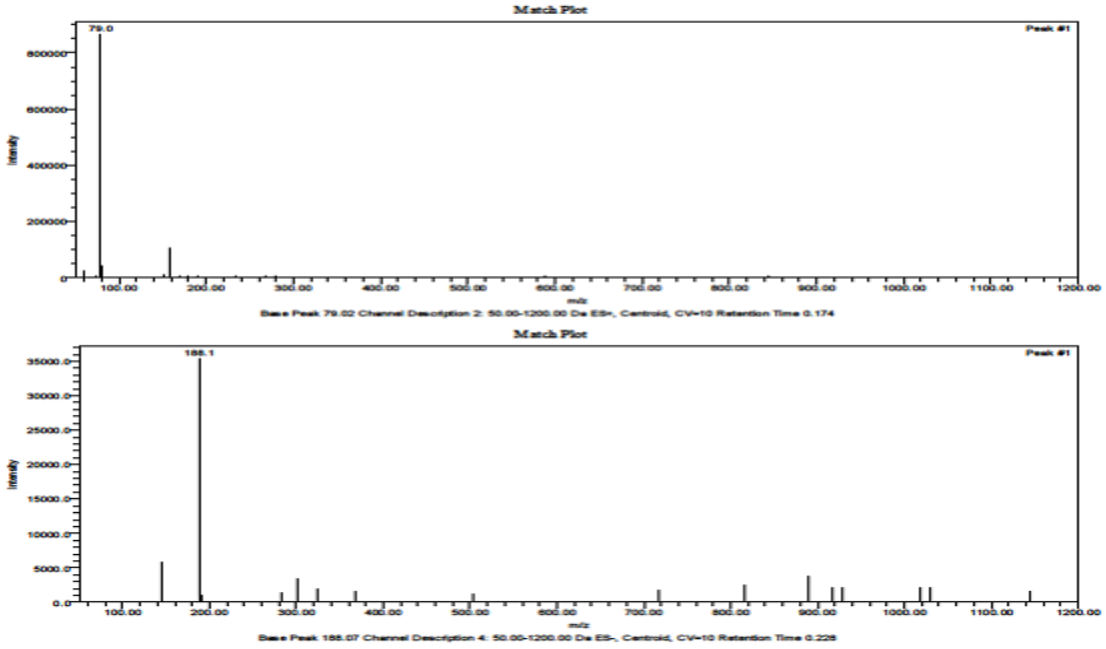
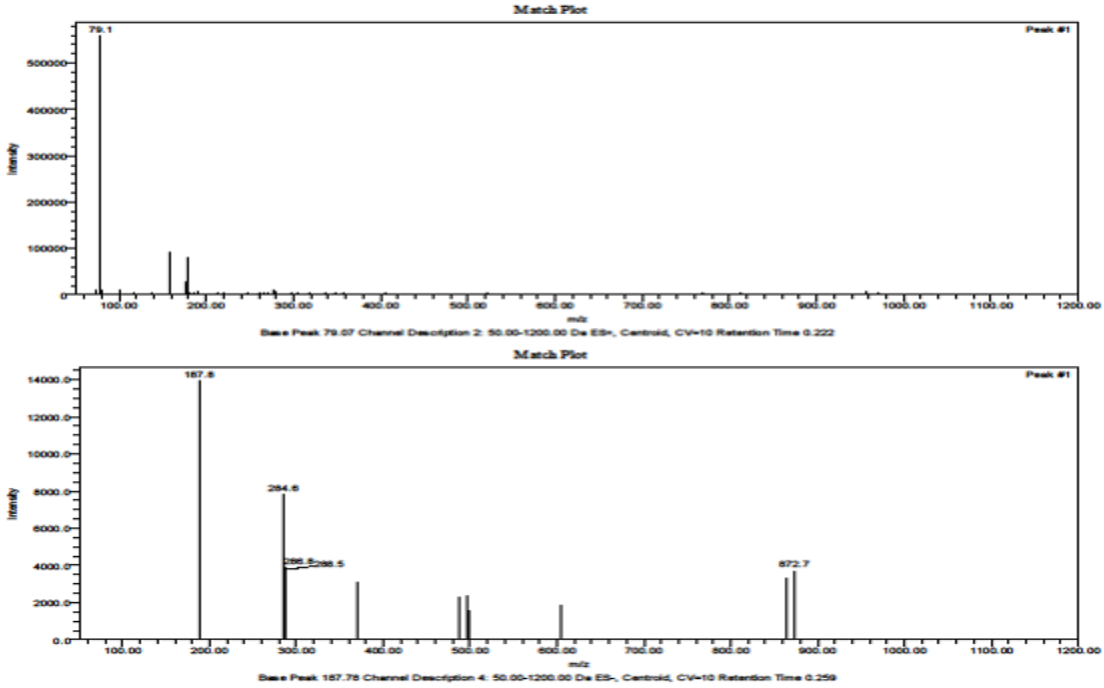


Fig 5: [Cu-KYNAmass spectra]



Mass spectra

Results for KYNA ligand

ES^+: 189 amu is a molecular peak for$C_{10}H_8NO_3$ and 79amu is a base peak due to C_6H_6 and it is present because of removal of $C_4HNO_3$from the hetero cyclic part.

ES^- : 144 amu is the base peak because of removal of –COOH group.

Results for Mn-KYNA

ES^+: 158 amu peak because of removal of O_2

79 amu is the base peak due to C_6H_6

ES^- : 188.1 amu is the base peak for KYNA

144 amu peak because of removal of –COOH group

Results for Cu-KYNA

ES^+: 189amu is a peak due to KYNA

158 amu peak because of removal of O_2

79 amu is the base peak due to C_6H_6

ES^{-} : 187.8 amu is the base peak due to KYNA

284.6 amu and 286.8 amu peaks due to loss of two and four H from –OH groups.

288.5 amu removal of one KYNA without H_2O removal

Fluorescence spectra

Fig 6: Combined Fluorescence spectra

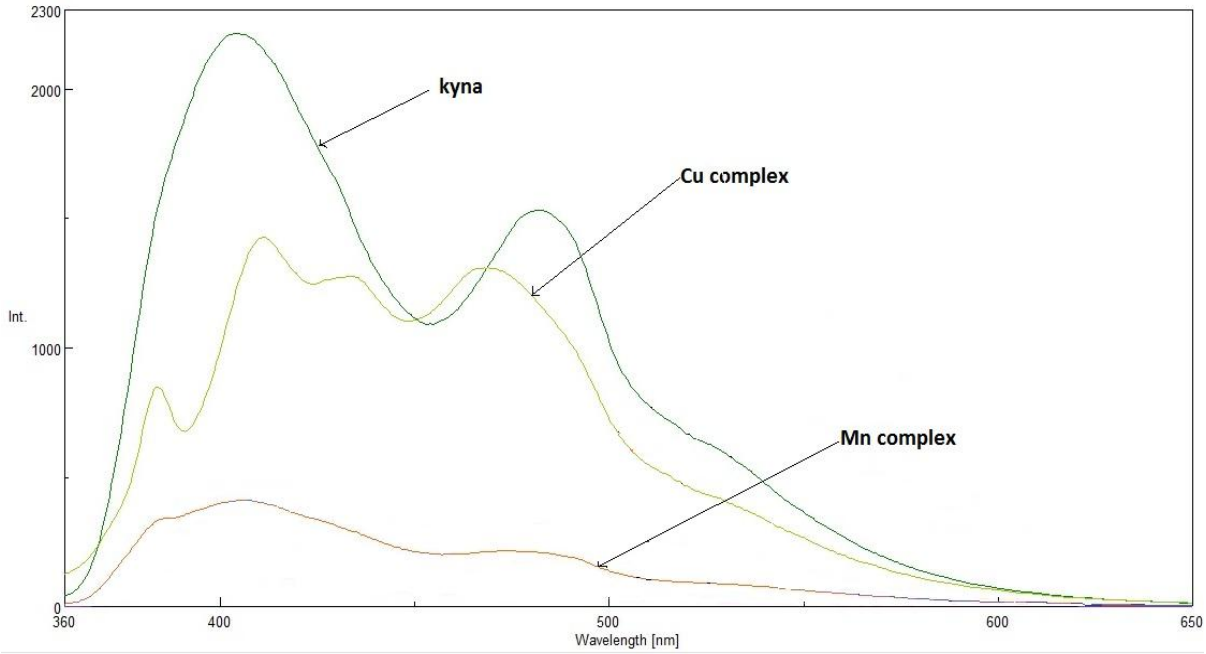


Fig.6. shows the fluorescence spectra of the ligand and the complexes. The spectra is emission type spectra taken in the range of 360 nm to 650 nm. The metal ions Mn^{+2} and Cu^{+2} generally do not exhibit fluorescence activity under normal conditions. However the ligand KYNA indeed exhibits fluorescence activity, therefore it was considered to study the fluorescence behavior of the complexes. The ligand KYNA exhibits UV-visible absorption with λ_{max} below 400 nm but the fluorescence peaks around 405 nm and 480 nm. On co-ordination with the d^{10} metal ions, the fluorescence diminishes to a great extent. The order of reduction in fluorescence intensity is $Mn^{+2} > Cu^{+2}$. The probable reason seems to be due to change in the π(pi) bonding and lone pair electron sharing for the metal coordination.

STRUCTURES

Based upon the physico chemical analyses, the structures of the two complexes can be shown as below.

Fig 7: Mn-KYNA structure

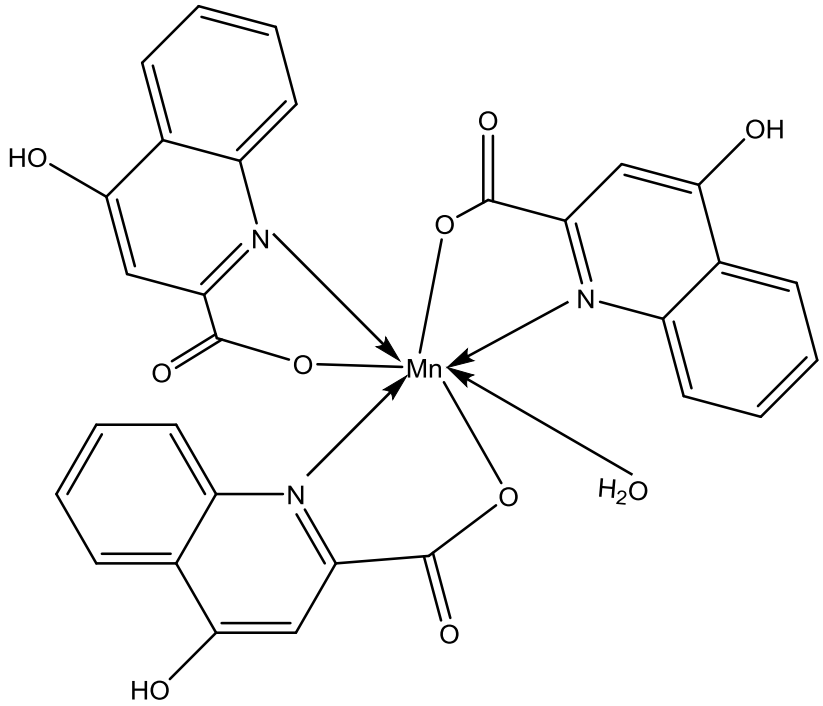
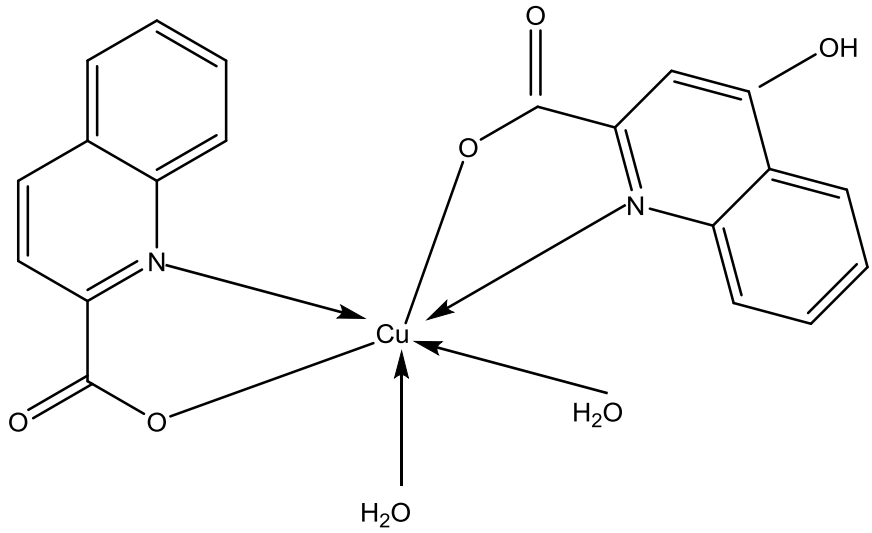


Fig 8: Cu-KYNA structure



Antimicrobial activity

The complexes, which are under observation, were examined against the bacteria: Bacillus subtilis, Staphylococcus aureus, Escherichia coli and Salmonella typhii[5].In this antimicrobial study medium used is agar nutrient and the name of the method is agar diffusion method. Generally compounds are loaded into well made in agar plates and their activities were tested against different organisms streaked on the surface of agar medium [6].

The compounds were dissolved in DMSO to prepare the stock solution of compounds (10^{-2} M).Agar plates were marked for those four cultures, and cork borers wereused to prepare well. Micropipette was used to fill test solution in well and the plate was incubated 24 h for bacteria at 35°C. The growth of the inoculated microorganisms was affected because of interference of the test solution. The test solution partly hampered the growth of microorganisms. The inhibition zone was developed, for which the concentration was noted [7].

Standard Antibacterial

Zone size	Antimicrobial disc used in practical
+++ 2.6 to 3.0 cm	Streptomycin (25μg/disc) for E-coli, S.typhy and S. aureus
++ 2.0 to 2.5 cm	Ampicilin (25μg/disc) for Bacillus sp.
- No zone 0.8 cm	

All antibiotics in standard condition gave +++ results.

Table 6: Results of Antibacterial Studies

Culture	Well no.	Compound		
		Mn-KYNA	Cu-KYNA	KYNA
Bacillus subtilis (Gram-possitive)	1. 25 mcg/ml	+	+	+
	2. 50 mcg/ml	++	+	+
	3. 75 mcg/ml	+++	++	++
	4. 100 mcg/ml	++++	++++	+``++
Staphylococcus aureus (Gram-possitive)	1. 25 mcg/ml	_	_	_
	2. 50 mcg/ml	_	_	_

	3. 75 mcg/ml	_	_	+
	4. 100 mcg/ml	_	++	++
Escherichiacoli (Gram negative)	1. 25 mcg/ml	_	_	_
	2. 50 mcg/ml	+	_	+
	3. 75 mcg/ml	++	_	_
	4. 100 mcg/ml	++	_	_
Salmonellatyphii A (Gram negative)	1. 25 mcg/ml	_	_	_
	2. 50 mcg/ml	_	_	_
	3. 75 mcg/ml	_	_	_
	4. 100 mcg/ml	_	_	_

Results of Antibacterial Activity

Against, Bacillus subtilis, KYNA and both its complexes are active.The activity was observed to increase with increase in concentration of these three entities. It was further observed that when coordination occured by Cu^{+2} and Mn^{+2}, the antibacterial activity increased. The Mn-KYNA showed higher activity compared to Cu-KYNA. The order of antibacterial activity against Bacillus subtilis can be shown as, Mn-KYNA > Cu-KYNA >KYNA. At 100mcg/ml concentration, both the complexes were more active than all the standard antibiotics. Against Staphylococcus aureus, the over all activities of the ligand and complexes was quite less compared to standard antibiotics.

Against the gram –ve E. Coli bacteria, only the Mn-KYNA complex exhibited some antibacterial activity in comparison with Cu-KYNA and ligand. Against the Salmonellatyphii organism, none of the three was found to prossess any effective antibacterial activity.

CONCLUSION

Realizing the significance of kynurenic acid as an important biomolecule as well as versatility of KYNA in forming coordination chelates,two metal ions from 3d series,Mn(II)

and Cu(II) were considered for the current study. These ions gave stable complexes which were characterized by important instrumental methods. On coordination, in the case of B.Subtilis organism, the antibacterial activity of the complex was found to be more than the ligand. This may also be useful in further investigation of the ligand and its coordination compounds.

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