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Physico–Chemical and Bio-Chemical Studies on Some Mn (II) ion chelates with Physiological active Mixed Ligands

R.N. Sharma[1*], Ashok Kumar Mishra[2], B. Laxmi Kanth[3] and Soni Kumari[4]

[1]Principal, SHS Govt. PG College, Dhanapur ,Chandauli, UP (India)
[2]Deptt of Chemistry , K N Govt PG College, Gyanpur (India)
[3]Prof andHead in Biochemistry , SSIMS , Bhilai, C.G. (India)
[4]Deptt of Botany, P.P.K College,Bundu, Jharkhand (India)
Corresponding Author Email: drramnareshsharma@gmail.com

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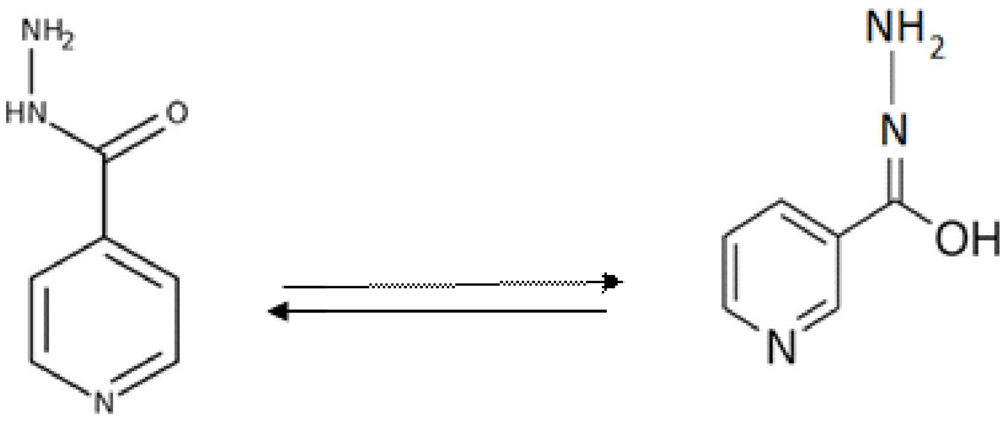
Abstract

Some air stable electrolytic and non-electrolytic mixed ligand complexes of Mn(ll) ion with isonicotinic acid hydrazide have been synthesized and characterized by various physico chemical data based on micro analytical analysis, magnetic measurement, conductivity measurement, near and far infrared and electronic spectrophotometric studies. Various vibrational and spectral bands of ligand and complexes were studied and compared. The mode of shifting were used to diagnose the coordinating behaviour of donor element of ligand with Mn (ll) ions. All complexes were screened against Aspergillus flavus and classified as a mixed fungicide. Tentative octahedral geometry has been assigned for all Mn (ll)complexes.

Key words : Ligand, Complexes, Biochemical, Fungicide

Introduction

Complexes of certain metals specially transition metal complexes have powerful antimicrobial activities such as silver bandages for treatment of burns, zinc antiseptic creams and metal clusters as anti HIV drugs.[13-16] Metal complexes are also used as anti microbial and anti fungal agent. Metal coordination compound based on isonicotinic acid hydrazide continually attract many researchers because of their wide pharmacological applications[1-3]. isonicotinic acid hydrazide shows kenotic and enolic tautomeric isomerism as show in fig 1 :



(A) Kenotic from (B) Enolic from

Fig1 : isonicotinic acid hydrazide (INTAH)

The present paper studies the synthesis, characterization and anti-fungal activities of some Mn(ll) ion complexes with some mixed ligands. isonicotinic acid hydrazide is used as primary and thio urea and diphenyl thio urea are used as secondary ligand.

Experimental

Isonicotinic acid hydrazide (INTAH), thio urea (TU) and diphenyl thio urea (DPTU) were obtained by E Merk company and were used after double crystallization. Its purity were checked by spectroscopically and melting point measurement.

The complexes were prepared generally by refluxing on magnetic stirrer in 1:2(molar ratio) mixture of 50ml alcoholic metal ions and ligand (INTAH) solutions each with few drops of corresponding mineral acids up to 3 hours. The pH of mixture solutions was mentioned at ~ 6 using corresponding mineral acid and conc NaOH solutions.

It was evaporated near about 20ml and cooled on ice. The separated complexes were filtered, washed with absolute alcohol and dried over anhydrous $CaCl_2$ in a vacuum desiccator. The filtrate of above complexes were diluted upto 50 ml with alcohol and divided into two part. 2 molar ratio in 25 ml alcoholic solution of TU and DPTU were mixed with continuous stirring in each above filter at and refluxed near about one and half hours at 80° C. Then it was evaporated near to dryness. Complexes were filtered washed with absolute alcohol and dried on $CaCl_2$ in vacuum desiccator. The magnetic measurements were made by Gouy balance at room temperature and calibration was done with mercury tetra thio cyanato cobaltite (ll). IR spectra of ligand and complexes were recorded in 4000-200 cm^{-1} using KBr pellets. The U V and visible spectra were recorded with help of Backmann DU-6 spectrophotometer in DMF.

Results and Discussion

Isonicotinic acid hydrazide (INTAH) contains several donor site (fig 1). It is from very stable complex with Mn (ll) ion.[4-8] The analytical data of complexes has been shown in table 1. These complexes are insoluble in common organic solvents such as methanol, ethanol, benzene, carbon tetrachloride, nitro benzene, chloroform but fairly soluble in DMF. All choro complex are none electrolytic in nature and there general stoichiometry of complexes (table1) are supported by conductance measurement as well as qualitative analysis.[9-12] Magnetic measurement data shows paramagnetic nature of all Mn(ll) complexes as expected.

Some spectral data of ligand and complexes were given in table 2. All Mn (II) complexes contain water molecule in their stoichiometry and do not lose weight on heating below 120°C, indicating the water molecules are under the coordinating sphere in all complexes. A strong broad band appeared at 3700-3500 cm^{-1} in all Mn(ll) complexes in IR spectroscopy. These are non-ligand band assigned as νH_2O. The broadness of band shows hydrogen bounded lattice layer water molecules present in side the coordination sphere as mono dentade ligand[4-5]. νNH, νasymNH and νsym NH mode of vibration of INTAH were observed at 3400(s), 3310(m) and 3210(s) cm^{-1} respectively and νNH band is almost disappeared after complexation in all Mn(ll) complexes . All other bands are red shifted (~5 to 40 cm^{-1}) with reduced splitting on complexation in all Mn (ll) complexes suggesting the coordination of ligand through NH_2 ground of hydrazine moiety[6-7].This is further supported by red shifting of 5 cm^{-1} of τ NH mode of vibrations present at 785 cm^{-1} of INTAH. None ligand band at 1470(m)cm^{-1} are appeared in IR spectra of $[Mn(INTAH)(DPTU)(H_2O)_2 Cl_2]$ and $[Mn(INTAH)_2 (DPTU)_2(H_2O)_2]SO_4$ suggesting the presence of DPTU as secondary ligand in these complexes[8]. Similarly the non-ligand band at 1515 cm^{-1} of $[Mn(INTAH)(TU) (H_2O)_2Cl_2]$ and $[Mn(INTAH)_2(TU)_2(H_2O)_2] SO_4$ showed the presence of thio urea[9] as secondary ligand in these complexes. The bands at 1105(m) and 615 (s) cm^{-1} in all sulphato complexes are assigned as ionic sulphate[10] on comparison with various modes of vibration regarding sulpheto group. The new band at 415 and 405cm^{-1} in $[Mn(INTAH)_2(H_2O)_2Cl_2]$, $[Mn(INTAH)(DPTU)(H_2O)_2Cl_2]$ and $[Mn(INTAH)(TU)(H_2O)_2Cl_2]$ are assigned as νMn-Cl mode of vibrations. Since appearance of only two vibrational band for νMn Cl suggests the trans position[11] of Cl_2 atoms in complexes. The bonding of Mn-NH_2 hydrazine moiety is further supported by appearance of new band as νMn-N-N at 445 cm^{-1} in all Mn(II) complexes.

UV and visible spectroscopy of ligand (INTAH) shows broad absorption band at 350nm may be assigned due to n—>π*/CT bands. This band is

Table 1. Analytical and Physical data of complexes

Complex compound	Colour	µeff in BM	Moral Cond $ohm^{-1}cm^{-2}$ $mole^{-1}$	M.P. (°C)	Microanalytical Data in % found/calculated			
					Mn	C	H	N
$[Mn(INTAH)_2(H_2O)_2Cl_2]$	Black	5.84	9.63	223	12.33 12.61	32.79 33.03	4.01 4.13	19.13 19.27
$[Mn(INTAH)(DPTU)(H_2O)_2Cl_2]$	Yellow	5.91	7.01	198	10.21 10.44	43.06 43.26	4.21 4.36	13.13 13.28
$[Mn(INTAH)(TU)(H_2O)_2Cl_2]$	Yellowish green	7.01	10.12	211	14..1 14.14	25.07 25.19	3.56 3.86	17.71 17.99
$[Mn(INTAH)_2(H_2O)_4]SO_4$	Black Brown	5.89	32.01	186	10.85 11.07	28.61 28.97	4.32 4.43	16.71 16.90
$[Mn(INTAH)_2(H_2O)_2(DPTU)_2]SO_4$	Black	5.97	29.79	172	7.51 7.89	42.71 43.04	5.67 6.03	19.81 20.09
$[Mn(INTAH)_2(TU)_2(H_2O)_2]SO_4$	Black	5.92	31.76	196	9.79 10.01	30.46 30.60	4.39 4.74	25.25 25.80

Table 2. Spectral and antimicrobial data of Mn(II) complexes

Complex compound	υ H_2O	υ NH	υ_{asym} NH	υ_{asym} NH	υ DPTU	υ_{TU}	υ SO_4	υ CO-NH	Aspergilles flavropus		
									1000 ppm	500 ppm	100 pm
INTAH		3400	3310	3210				1640 1560			
$[Mn(INTAH)_2(H_2O)_2Cl_2]$	3650		3290	3200				1640 1540	59	49	51
$[Mn(INTAH)(DPTU)(H_2O)_2Cl_2]$	3700		3270	3205	1470			1640 1540	58	52	43
$[Mn(INTAH)(TU)(H_2O)_2Cl_2]$	3500		3280	3205		1515		1640 1540	56	52	45
$[Mn(INTAH)_2(H_2O)_2]SO_4$	3340		3300	3210			1105 615	1640 1540	52	51	48
$[Mn(INTAH)_2(H_2O)_2(DPTU)_2]SO_4$	3540		3300	3190	1470		1105 615	1640 1540	55	53	44
$[Mn(INTAH)_2(TU)_2(H_2O)_2]SO_2$	3500		3300	3195		1515	1105 615	1640 1540	65	61	47
carbendazim									98.6	55.7	81.8

blue shifted in all complexes indicating the tactness of ligand with Mn (II) ion after complexation. Three more new band in region at (410-402), (590-572) and (775-745) nm are appeared in all Mn(ll) complexes. Following the Gray and coworkers[12] and Lever[13] bands at 402-410nm is due to ${}^2B_2$ –>${}^2A_1$ or d_{xy}—>d_{yz},d_{xz}; 572-590nm is due to ${}^2B_2$—>${}^2B_1$ or d_{xy}— >$d_{x2—y2}$ and 745—775 nm is due to ${}^2B_2$—>${}^2B_1$ or d_{xy}—>d_{z2} having octahedral configurations.

It is also supported by normal coordinate analysis of octahedral configuration of $Mx_2y_2z_2$, Mx_2y_4 and $Mwxy_2z_2$ type of complexes.

Antimicrobial tactility of Mn (II) complexes :

The method used for toxic studies was modified paper disc method[14]. Potato dextoge agar medium is prepared and sterilized. A square piece of blotting paper was placed in standard petri-disk. Aspergillus flavus colony were developed. The DMSO solution of all Mn (II) complexes were spread at 1000, 500 and 100 ppm concentrations. The inhibition zone formed around each filter paper after inoculation for 72 hour at room temperature were measured. The standard fungicides used for comparison was carbendazim, a commercial fangicide.

All Mn(II) complexes exhibits significant antifungal activity and activities data are shown in table 2. The bioactivity of complexes increases on increasing the concentration .The antifungal activities on Aspergillus flavus of all Mn (II) complexes are in the range of 52-65% in 1000 ppm.

Conclusion

All Mn(ll) complexes may be placed as

moderate type of fungicides. Since complexes contain more than two donor sides. Therefore all Mn(ll) complexes may be classified as mixed fungicides[15-16]. All Mn (ll) reported complexes have tentative octahedral configurations.

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