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Synthesis and Antimicrobial Studies of Some Mn(II) Macrocyclic Complexes

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Two new Mn(II) macrocyclic complexes the formulae M[DPODH]$(BF_4)_2$ and M[DCODH]$(BF_4)_2$ where M = Mn(II), [DPODH] = 2,6-diacetyl pyridine-2,2′-oxydiacetoyl dihydrazone, [DCODH] = 2,6-pyridine dicarbonyl dichloride-2,2′-oxydiacetoyl dihydrazone, BF_4 = tetrafluoro borate have been synthesized. These complexes have been analyzed for elemental analysis, spectral investigation and magnetic measurements. These complexes have also been screened *in vitro* antimicrobially against specific bacteria *Escherichia coli*, *Staphylococcus aureus* and fungal strain *Aspergillus niger* and *Candida albicans*. The results of the biological studies have shown that the complexes are at least five to six times more active than the ligand fragments.

Key Words: Antimicrobial Studies, Mn(II) Complexes.

INTRODUCTION

Recently, the chemistry of transition metal complexes containing macrocyclic ligands has become increasingly important[1-5]. There are several reasons for this interest in the complexes, *e.g.*, the azamacrocyclic ligands have been used successfully for diverse processes such as separation of ions by transport through artificial and natural membranes, liquid-liquid or solid-solid phase-transfer reactions, dissolution in a polar solvent of metal and organic salts, preparation of ion-selective electrodes, isotope separations and in the understanding of some natural process through mimicry of metallo enzymes[6-10].

Some Co(II), Ni(II) and Cu(II) complexes of macrocyclic ligands have been synthesized and contained intense biological activity[11-14]. In this paper, synthesis and antimicrobial properties of some Mn(II) complexes are reported.

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EXPERIMENTAL

All reagents and chemicals were of AR grade and purchased from (BDH/E. Merck).

Synthesis of the ligand: The ligand, oxydiacetic acid dihydrazide, was synthesized by mixing 1:2 stoichiometric quantities of oxydiacetic acid ester (1.62 g - 0.01 M) in hydrazine hydrate (0.413 mL, 0.01 M) in 20 mL ethanol was continuous stirring. The solution obtained was refluxed over a water bath for *ca.* 8 h. There after, it was concentrated to one-third of its original volume. The solution was cooled until bright-white crystals appeared. The crystals were filtered, washed with alcohol and either and then dried in vaccum over anhydrous $CaCl_2$ in a desiccator.

Preparation of the metal complexes: Equimolar quantities of oxydiacetic acid dihydrazide (1.62 g, 0.01 M) manganese acetate (2.55 g, 0.01 M) and 2,6-diacetyl pyridine (1.65 g, 0.01 M) were mixed in 15 mL ethanol with continuous stirring. The solution thus obtained was refluxed over a water bath for around 3 h. Subsequently, it was concentrated to one-third of its original voilume. A little of sodium tetrafluoro borate was then added and the solution was cooled was cooled until yellowish green crystals separated out. The crystals were filtered, washed with alcohol and then dried in vaccum over anhydrous $CaCl_2$ in a dessicator.

The other complex was also synthesized by similar procedure, the dusk green crystals were obtained.

RESULTS AND DISCUSSION

Both the coloured solid complexes are stable at room temperature and soluble in DMSO, DMF and propylene glycol but insoluble in common organic solvents. These complexes have molar conductance values in the range 112.80-113.40 ohm^{-1} cm^2 mol^{-1} which indicate their electrolytic nature and suggested 1:1:1 stoichiometry for the complexes (Table-1). The ligand fragment, *i.e.*, oxydiacetic acid dihydrazide exhibits 1:2 stoichiometry.

TABLE-1
ANALYTICAL DATA OF LIGAND AND ITS Mn(II) COMPLEXES

Compound (colour)	m.w. Found (calcd.)	m.p. (°C)	Elemental analysis (%): Found (Calcd.)			Conductivity (ohm^{-1} cm^2 mol^{-1})
			C	H	N	
ODADH	161.5	163	29.35	3.62	34.29	–
(Bright white)	(162.0)		(29.62)	(3.70)	(34.50)	
$Mn[C_{13}H_{15}O_3N_5](BF_4)_2$	576.2	304	26.82	2.54	11.98	112.80
(Yellowish green)	(577.0)		(27.00)	(2.60)	(12.10)	
$Mn[C_{11}H_9O_3N_5Cl_2](BF_4)_2$	546.2	292	23.95	1.58	12.17	113.40
(Dusk green)	(547.0)		(24.10)	(1.64)	(12.80)	

IR spectrum of the ligand fragment revelaed sharp and prominent bands at 3280, 1690, 1740 and 3350 cm^{-1} due to the presence of OH, NH bending, C=O and NH_2 stretching. A sharp band was observed at 2960 cm^{-1} due to CH_2 stretching in the spectrum of oxydiacetic acid dihydrazide.

The phenyl ring deformation bands were also observed around 820 cm^{-1}. The peak due to ν(NH) at 335 cm^{-1} did not undergo any shift in the complexes thus ruling out the coordination of nitrogen of ligand with the central metal ion. An interese band appeared at 1610 cm^{-1} in the spectra of complexes, thus confirming the formation of ν(C=N) in the complexes, a new band relevant only for the complexes. New bands were observed like ν(M-N) and (M-O) at 550 and 460 cm^{-1} for the two complexes supporting the formation of M-N and M-O bands in these complexes (Table-2).

TABLE-2
INFRARED ABSORPTION FREQUENCIES (cm^{-1}) OF ODADH AND ITS MACROCYCLIC COMPLEXES

Functional group	ODADH	$Mn[C_{13}H_{15}O_3N_5](BF_4)_2$	$Mn[C_{11}H_9O_3N_5Cl_2](BF_4)_2$
-OH	3280	3220	3210
-NH bending	1690	1600	1640
$-CH_2$ *str.*	2960	2910	2920
$-NH_2$ *str.*	3350	3350	3350
C=O	1740	1700	1690
C=N	–	1610	1600
M-N	–	550	540
M-O	–	460	450

Electronic spectra of Mn(II) complexes exhibit broad bands at 22500 and 11100 cm^{-1}, 22150 and 11300 cm^{-1} for the formed complexes. The former band may be assigned to $^2E_g \rightarrow {}^2T_{2g}$ transitions suggesting an octahedral geometry of the complexes. The latter bands can be attributed to L-M charge transfer spectrum (Table-3).

TABLE-3
ELECTRONIC SPECTRAL TRANSITIONS OF Mn(II) MACROCYCLIC COMPLEXES (cm^{-1})

Compound	Transitions (cm^{-1})	
	$^2E_g \rightarrow {}^2T_{2g}$	L → M
$Mn[C_{13}H_{15}O_3N_5](BF_4)_2$	11100	22500
$Mn[C_{11}H_9O_3N_5Cl_2](BF_4)_2$	11300	22150

Antimicrobial activity: The complexes were assayed for their antimicrobial activities against four test organisms, namely *S. aureus, E. coli, A. niger* and *C. albicans*.

The MIC values against these organisms were determined by 'Serial dilution method' using DMF as a solvent. The results are given in Table-4.

TABLE-4
MIC VALUES IN MOLAR CONCENTRATION (× 10^{-4}) OF SYNTHESIZED DIHYDRAZIDE AND THEIR MACROCYCLIC COMPLEXES (cm^{-1})

Compound	Bacteria		Fungi		
	E. coli	*S. aureus*	*A. niger*	*C. albicans*	*A. flavus*
ODADH	0.610	0.615	0.620	0.615	0.610
Mn(II)[DOPDH]$(BF_4)_2$	0.225	0.215	0.210	0.214	0.204
Mn(II)[DCODH]$(BF_4)_2$	0.210	0.205	0.200	0.206	0.196

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