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Synthesis, Structural Characterization and Biological Screening of Manganese(II) Complexes Derived from Schiff Bases Containing Semicarbazone

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The synthesis and structural characterization of the complexes of Mn(II) is reported with general composition of $[MnL_1(H_2O)_2]Cl_2$ (L_1 = Schiff bases ligands containing semicarbazone moiety). Complexes of manganese(II) with *bis*(furfuryl-2-aldehyde)semicarbazone (FALSCZ), *bis*(indole-3-aldehyde)semicarbazone (IALSCZ), *bis*(3-methylsalicylaldehyde)semicarbazone (MSALSCZ), *bis*(5-methylsalicylaldehyde)-semicarbazone (M′SALSCZ), *bis*(5-bromosalicylaldehyde) semicarbazone (BSALSCZ), *bis*(cinnamaldehyde)semicarbazone (CALSCZ), *bis*(4-chlorobenzaldehyde)semicarbazone (CHBALSCZ), *bis*(3,4,5,trimethoxybenzaldehyde)semicarbazone (TMBALSCZ), *bis*(pyridine-2-aldehyde) semicarbazone (PALSCZ) and *bis*(thiophene-2-aldehyde)semicarbazone (TPHALSCZ) have been synthesized and characterized by elemental analysis, molar conductivity, magnetic moments, thermal studies, EPR, IR and electronic spectra. The spectral data reveals that all the complexes show octahedral geometry around the metal ion. These complexes were also screened for their antibacterial and antifungal activities. The results reveal that the metal chelates are more potent than the parent ligands.

Key Words: Manganese(II), Schiff bases, Complexes, Antibacterial and Antifungal activities.

INTRODUCTION

The synthesis and characterization of the complexes of manganese(II) of different ligands are of growing interest in coordination chemistry. The pronounced biological activities[1-3] of the Schiff bases form the class of important compounds in medicine and pharmaceutical field. The coordination chemistry of manganese complexes with nitrogen donor moieties is of interest as these complexes give information about the functional role of manganese(II) in biological system[4,5]. Several manganese(II) complexes are known to exhibit the antifungal activity[6,7]. We have successfully prepared the complexes of manganese(II) of the $[MnL_1(H_2O)_2]Cl_2$. (L_1 = Schiff bases ligand containing semicarbazone moiety). New manganese(II) complexes of Schiff bases ligand containing semicarbazone moiety have been synthesized and characterized by elemental analysis, molar conductivity, magnetic moment,

thermal studies, EPR, IR spectra and electronic spectra. These studies indicate octahedral geometry around the metal ion[8,9]. These complexes were also screened for antibacterial and antifungal activity.

EXPERIMENTAL

All the chemicals used in the investigation were of A.R. grade. The purity of these compounds was checked by melting point determination. All the solvents were purified by standard methods, before the preparation of Schiff bases.

Synthesis: The Schiff bases were prepared by the condensation of respective aldehyde with semicarbazide in molar ratio of 2:1. The reaction mixture was refluxed, in ethanol for 0.5 h and the requisite amount of respective aldehyde was added into the reaction vessel and refluxed for 6 h. It was allowed to stand over-night to yield the crystals of the Schiff bases. Purification was effected by recrystallization.

Preparation of manganese(II) complexes: All the complexes were prepared by following the general procedure. The solution of manganese(II) chloride (0.1mol) in ethanol to the solution of ligand in ethanol (*ca.* 20 mL) in required molar ratio were added dropwise with stirring. The mixture was refluxed for 6-10 h and then the volume was reduced to *ca.* 15 mL by rota-vapour. Coloured precipitate (yellow, brown, orange) formed on addition of a small amount of ether, was filtered off, washed with ethanol and dried in oven at 90 ºC.

RESULTS AND DISCUSSION

All the complexes were found to be coloured, stable in air and non-hygroscopic. The compounds were soluble in ethanol, DMF but sparingly soluble in water. The molar conductance value of manganese(II) in MeOH, DMF and DMSO reveals their 1:2 electrolytic nature[10] (Table-1).

The reported complexes are paramagnetic in nature and magnetic moment values were in the range of 5.85 to 5.92 BM that were in the good agreement with the presence of d^5 system[11].

The thermogram run on the complexes of manganese(II) reveals interesting facts and corroborates some of the assumption made on the basis on spectral studies. The complex loses the two molecules of water at *ca.* 230 ºC, which indicates that these occupy the coordinate position of the complex[12].

The IR spectra of reported ligands show important peak between 1630-1535 cm^{-1} which was shifted to 1640-1606 cm^{-1} in the spectra of all the complexes indicating that the coordination occurred through N atom of ν(C=N) group[13,14] and S atom. In all the complexes of manganese(II) a peak between 880-730 cm^{-1} show the presence of coordinated water molecules.

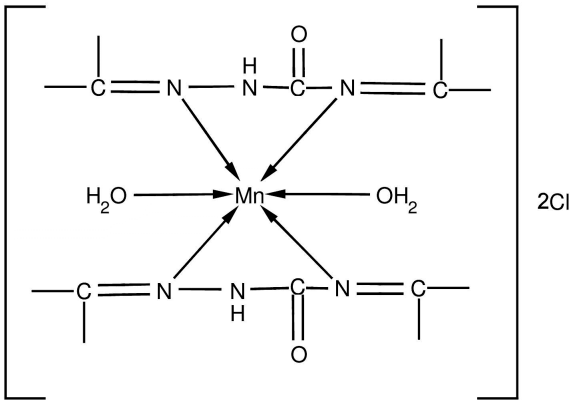
The electronic spectra of the complexes exhibit weak bands in the region 17000-18500, 20700-22200, 24900-26000, 27000-29000 cm^{-1}. The three low energy bands arising from the sextet quartet t_2g^3 eg^2 configuration have been assigned[15] to $^6A_{1g} \rightarrow {}^4T_{1g}$ (G) (17000-18500 cm^{-1}), $^6A_{1g} \rightarrow {}^4T_{2g}$ (G) (20700-22200 cm^{-1}) and $^6A_{1g} \rightarrow {}^4E_g$

TABLE-1
PHYSICAL & ANALYTICAL DATA OF COMPLEXES

S. No.	Compd. (colour)	m.p., ºC (μ_{eff}, BM)	Molar conductance			Metal (%)	ν(C=N)	Coordinated H_2O molecule
			CH_3OH	DMF	DMSO			
1	$[(FALSCZ)\cdot 2H_2OMn]Cl_2$ (Yellowish brown)	260 (5.85)	180	154	53	(8.81) 7.71	1630	800
2	$[(IALSCZ)\cdot 2H_2OMn]Cl_2$ (Brown)	290 (5.91)	205	140	58	(6.70) 5.12	1625	730
3	$[(MSALSCZ)\cdot 2H_2OMn]Cl_2$ (Pale yellow)	310 (5.89)	210	125	54	(7.01) 6.21	1618	740
4	$[(MSALSCZ)\cdot 2H_2OMn]Cl_2$ (Orange)	295 (5.92)	205	130	55	(7.01) 6.17	1606	848
5	$[(BSALSCZ)\cdot 2H_2OMn]Cl_2$ (Yellow)	315 (5.84)	175	135	49	(6.22) 5.13	1615	880
6	$[(CALSCZ)\cdot 2H_2OMn]Cl_2$ (Brown)	165 (5.85)	205	145	53	(7.15) 6.86	1629	800
7	$[(CHBALSCZ)\cdot 2H_2OMn]Cl_2$ (Yellowish brown)	290 (5.90)	210	135	70	(6.84) 5.31	1615	730
8	$[(TMBALSCZ)\cdot 2H_2OMn]Cl_2$ (Pale Yellow)	320 (5.87)	210	115	59	(6.60) 5.45	1616	740
9	$[(PALSCZ)\cdot 2H_2OMn]Cl_2$ (Golden yellow)	245 (5.85)	220	160	75	(8.23) 7.83	1606	848
10	$[(TPHALSCZ)\cdot 2H_2OMn]Cl_2$ (Yellow)	198 (5.92)	195	140	65	(7.98) 6.97	1610	870

(G) (24900-26100 cm^{-1}). The other bands around 27500 and 29000 cm^{-1} are assigned to the transition $^6A_{1g}\rightarrow{}^4T_{2g}$ (D) and $^6A_{1g}\rightarrow{}^4E_g$ (D), respectively in an octahedral. The lower energy bands assigned to transitions $^6A_{1g}\rightarrow{}^4T_{1g}$ (G), $^4T_{2g}\rightarrow{}^4E_g$ (G), were used to calculate[16] the higher energy bands and the values thus obtained are quite close to those observed.

On the basis of available evidences octahedral geometry has been proposed for all manganese(II) complexes as follows:



Antibacterial and antifungal activities of manganese(II) complexes: Schiff bases and their metal complexes have been reported as anticancer[17], antifungal[18], antitumor[19] and antituberculosis[20] compounds. The results reveals that the metal chelates are more potent than the parent ligands. The increased potency of metal complexes may be attributed to their increased lipophillic nature arising due to chelation[21,22]. Mode of action of antimicrobials may involve various targets in microorganisms, *e.g.*, interface with cell wall synthesis damage to the cytoplasmic membrane as a result of which cell permeability may be altered or they may disorganize the lipoproteins leading to cell death[23]. All the manganese(II) complexes were screened for antibacterial and antifungal activity and minimum inhibitory concentration (MIC) values in molar concentrations ($\times 10^{-4}$) of metal chelates are presented in Table-2.

TABLE-2
MINIMUM INHIBITORY CONCENTRATION (MIC) VALUES IN MOLAR CONCENTRATIONS ($\times 10^{-4}$)

Complex	Bacteria		Fungi	
	E. coli	*S. aureus*	*A. niger*	*C. albicans*
1	0.174	0.212	0.205	0.286
2	0.172	0.211	0.212	0.284
3	0.171	0.208	0.208	0.281
4	0.169	0.211	0.209	0.283
5	0.174	0.209	0.206	0.285
6	0.171	0.216	0.206	0.284
7	0.176	0.211	0.208	0.278
8	0.169	0.207	0.206	0.281
9	0.176	0.216	0.201	0.278
10	0.174	0.224	0.203	0.285

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