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A NEW CLASS OF 16 TO 22-MEMBERED TETRAAZA TETRAOXO MACROCYCLIC COMPLEXES OF TIN(II): SYNTHESIS, STRUCTURAL ELUCIDATION AND FUNGICIDAL PROPERTIES

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ABSTRACT

Tin(II) complexes of tetraaza macrocycles have been prepared by template process using malonic, succinic and adipic acids with 1,3-diaminobenzene and 1,4-diaminobenzene. The reaction proceeds smoothly to completion. The complexes were characterized by elemental analyses, molecular weight determinations, infrared and ^{1}H NMR spectral studies. The elemental analyses are consistant with the formulation of complexes as [Sn(MacroC_n)Cl_2]. All the complexes are stable and monomeric as indicate by molecular weight determinations. The spectral studies confirm the proposed framework of the new macrocyclic complexes and indicate an octahedral environment around the central tin atom. The potential binding sites being the nitrogen atoms of the ligand. The biocidal activities of starting materials and their metal complexes have been studied by screening the compounds against *Fusarium oxysporum* and *Aspergillus niger*.

Key Words: Macrocyclic, Tin(II), Spectroscopic, Fungicidal.

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INTRODUCTION

Template reactions lie at the heart of macrocyclic chemistry. The use of metals as templated in such reactions has led to the synthesis of a large number of metal complexes of macrocyclic ligands[1]. They are of considerable interest as they provide an environment of control geometry and ligand field strength to the metal ions[2,3]. The noval approach to macrocyclic synthesis therefore overcomes the unusual limitations of the more traditional template routes where the metal tends to be "locked" into the macrocycle with demetallation often resulting in decomposition[4]. The influence on metal complexation of the variation of the structural feature, namely the length of the alkyl bridge linking the benzyl nitrogen atoms, was investigated[5]. The macrocyclic complexes have attracted both inorganic and bioinorganic chemists in recent years[6]. Reorganizing the importance of the complexes containing macrocyclic ligands considerable efforts are being invested in developing reliable inexpensive synthetic route of the complexes.

The complexes of metal ions with macrocyclic ligands are significant because of their resemblance with many natural systems such as porphyrin[7] and cobalamines. The applications[8,9] of macrocyclic complexes in bioinorganic chemistry, catalysis, extraction of metal ions from solution and the activation of small molecule gave impetus to their endeavour. Macrocyclic complexes found applications in analytical and industrial chemistry, stablization of high oxidation states, selective ion recognition, catalytic and extraction properties. In coordination chemistry, macrocyclic complexes have been widely used as they selectively form strong polynuclear complexes with a variety of metal ions[10]. Much of the current interest in macrocyclic coordination chemistry arise from the hope that the unusual geometrical relationship imposed on the metal ions by the macrocyclic donor set, may be transformed into unusual bonding situations. The six coordinated complexes of porphyrins and related aromatic macrocycles with Tin(IV) have been of interest in recent years, mainly for their potential medical applications. Most studies have concentrated on the ability of tin(IV) complexes of protoporphyrin (and other similar ligands) to inhibit the enzyme hemeoxygenase, which is responsible for hyperbilirubinemia in neonate[11], while these results were initially

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encouraging, concern has been expressed about the deleterious side effects of such agents, since they are also potent photosensitizers[12]. Indeed the use of Tin(IV) complexes of porphyrins and purpurins for photodynamic cancer therapy has also been reported[13]. Some of these complexes have also been shown to be immunostimularory[14].

In this paper we describe the synthesis, characterization and biological properties of some tin(II) macrocycles, resulting from the condensation reaction of dicarboxylic acids and diamines.

MATERIALS AND METHODS

All the glass apparatus with standard quick fit joints was used thoroughout. Adequate precautions were taken to exclude moisture from the system. The chemicals and solvents used were dried and purified by standard methods.

Preparation of the Complexes

For the preparation of metal complexes, an ice cold solution of $SnCl_2.2H_2O$ (4.49 mmol) in methanol (50ml) was reacted with 1,3-phenylenediamine / 1,4-phenylenediamine (8.98 m mol) at 0° C and put in magnetically stirred 100ml round-bottom flask. This is followed by the addition of methanolic solution of malonic, succinic, glutaric or adipic acid (8.98 mmol). The reaction mixture was stirred continuously at room temperature for 10h. The resulting solid product was recovered by filtration, washed with methanol and dried in vacuo. These were recrystallized from a 1:1 solution of methanol and chloroform.

The purity of the compounds was checked by TLC on Silica Gel-G using anhydrous tetrahedrofuran as a solvent. Each of the compound moves as a single spot indicating the presence of only one component and hence their purity. The physical properties and analytical data of the complexes are given in Table-1.

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Table 1: Physical properties and analytical data of the complexes

Compound	M.P.^{0}C and Colour	Analysis, Found (Calcd.) %					Mol. Wt. Found (Calcd.)
		C	H	N	Cl	Sn	
$[Sn(MaC_1)Cl_2]$	107 Off white	39.69 (39.89)	2.87 (2.98)	9.46 (10.34)	12.80 (13.1)	21.45 (21.90)	514 (541.97)
$[Sn(MaC_2)Cl_2]$	142 Off white	42.01 (42.14)	3.34 (3.54)	8.97 (9.83)	12.12 (12.44)	20.53 (20.83)	547 (570.02)
$[Sn(MaC_3)Cl_2]$	169 Off white	44.06 (44.18)	3.86 (4.04)	8.45 (9.37)	11.51 (11.86)	19.45 (19.85)	573 (598.08)
$Sn(MaC_4)Cl_2]$	134 Off white	46.00 (46.04)	4.41 (4.51)	8.15 (9.0)	11.01 (11.32)	18.61 (18.96)	602 (626.03)
$[Sn(MaC_5)Cl_2]$	129 white	39.69 (39.89)	2.88 (2.98)	9.45 (10.34)	13.01 (13.10)	21.55 (21.90)	510 (541.97)
$[Sn(MaC_6)Cl_2]$	147 white	42.01 (42.14)	3.31 (3.54)	8.99 (9.83)	12.12 (12.44)	20.43 (20.83)	545 (570.02)
$[Sn(MaC_7)Cl_2]$	159 white	14.05 (44.18)	4.00 (4.04)	8.55 (9.37)	11.63 (11.86)	19.43 (19.85)	570 (598.08)
$[Sn(MaC_8)Cl_2]$	120 white	46.01 (46.04)	4.32 (4.51)	8.14 (9.0)	11.00 (11.32)	18.58 (18.96)	604 (626.03)

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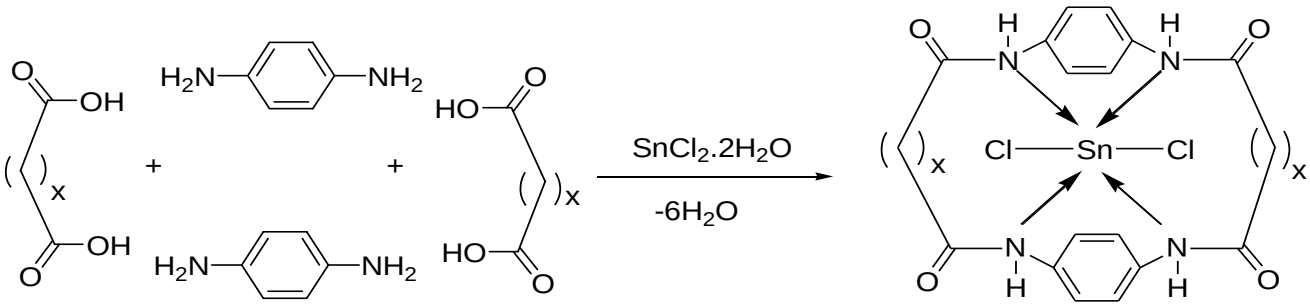
RESULTS AND DISCUSSION

All the complexes are coloured solids. These are slightly soluble in cold methanol and benzene but freely soluble in DMF, DMSO and THF. The complexes have sharp melting points. The metal derivatives are stable at room temperature and are non-hygroscopic. Conductance values 12-23 ohm^{-1} cm^{2} mol^{-1} in anhydrous DMF at 10^{-3} M concentration show them to be non-electrolytes.



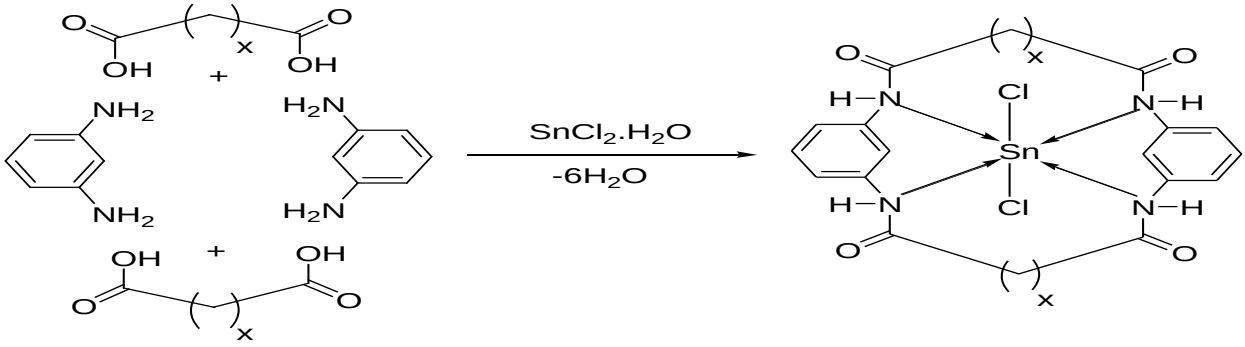


Fig.1

Infrared Spectra

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The infrared spectra of starting materials and their metal complexes were studied and some important features may be summarized as follows:

The IR spectra of diamines and dicarboxylic acids show the bands due to hydroxyl and primary amino groups, which disappear in the corresponding metal complexes, indicating the condensation of diamines with the dicarboxylic acids and formation of the proposed macrocyclic framework. In the spectra of all the complexes a single peak is observed in the region 3216-3286 cm^{-1} due to ν(NH) of amide group. In addition the appearance of four bands mainly in the regions, 1648-1707, 1544-1587, 1252-1275, and 628-684 cm^{-1} may be assigned to amide I, amide II, amide III, and amide IV in plane deformation vibrations, respectively[1,] further suggest the formation of macrocyclic complexes. The bands in the region 436-480 cm^{-1} in the spectra of the complexes may be assigned to Sn-N streching vibrations[16]. The IR bands appearing in the region 485-496 cm^{-1} are due to (Sn-Cl). The infrared spectral data of the complexes are given in Table-2.

Table 2: IR Spectral data (in cm^{-1}) of Tin(II) macrocyclic complexes

Compound	ν(NH)	Amide				ν (Sn-N)	ν (Sn-Cl)
		I	II	III	IV		
$[Sn(MaC_1)Cl_2]$	3245	1648	1558	1252	661	441	489
$[Sn(MaC_2)Cl_2]$	3269	1669	1544	1265	665	436	485
$[Sn(MaC_3)Cl_2]$	3286	1683	1567	1271	628	450	493
$[Sn(MaC_4)Cl_2]$	3216	1675	1571	1267	659	462	490
$[Sn(MaC_5)Cl_2]$	3227	1707	1580	1275	678	471	496
$[Sn(MaC_6)Cl_2]$	3238	1692	1587	1254	684	480	492
$[Sn(MaC_7)Cl_2]$	3220	1670	1581	1273	681	478	490
$[Sn(MaC_8)Cl_2]$	3270	1705	1586	1269	639	477	494

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^{1}H NMR Spectra

A comparative study of the ^{1}H NMR spectra of starting materials and complexes showed that the proton resonance signals due to $–NH_2$ and –OH groups were found to be absent in the respective metal complexes suggesting that the proposed macrocyclic skelton has been formed through a condensation reaction. In the spectra of all the complexes a broad signal observed in the regions δ7.86 – 8.13 ppm due to the amide (CO-NH) proton[17]. A singlet appearing in the region δ2.80-2.91 and δ3.17-3.19 ppm may be ascribed to methylene protons of malonic acid and succinic acid, and a multiplet appearing in the region δ3.24-3.25and 3.27-3.29 ppm may be assigned to methylene protons of adipic acid moiety which are adjacent to the nitrogen atom. The ^{1}H NMR spectral data of the complexes are given in Table-3.

Table 3: ^{1}H NMR Spectral data (δ ppm) of Tin(II) macrocyclic complexes

Compound	(CO-NH)	$H_{4,6}$/ $H_{3,6}$	H_2	H_5	CO-CH_2-CO	$CO(CH_2)_2$ CO	$CO(CH_2)_3$ CO	$CO(CH_2)_4$ CO
$[Sn(MaC_1)Cl_2]$	8.09	8.42	7.38	7.61	2.80	-	-	
$[Sn(MaC_2)Cl_2]$	7.86	8.33	7.34	7.86	-	3.19	-	
$[Sn(MaC_3)Cl_2]$	7.97	8.58	7.62	7.59	-	-	3.24	
$[Sn(MaC_4)Cl_2]$	8.01	8.49	7.54	7.54	-	-	-	3.27
$[Sn(MaC_5)Cl_2]$	8.04	7.62	7.60	7.61	2.91	-		
$[Sn(MaC_6)Cl_2]$	8.13	7.61	7.61	7.62		3.17		
$[Sn(MaC_7)Cl_2]$	8.11	7.61	7.62	7.62			3.25	
$[Sn(MaC_8)Cl_2]$	8.24	7.62	7.61	7.62				3.29

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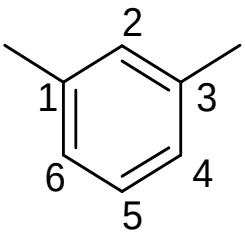
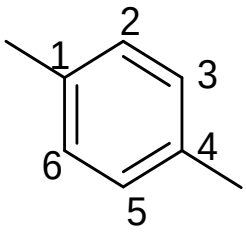
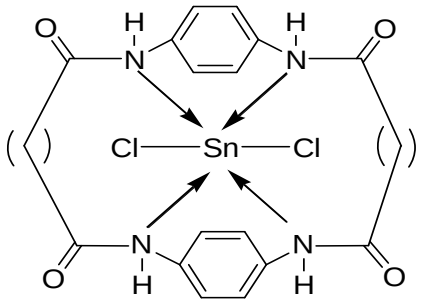




Thus on the basis of above discussion it seems that the macrocycles act as tetradentate chelating agents having four coordination sites, and hence a hexa-coordinated environment around the tin atom. According to the spectral studies the following structure for the tin macrocyclic complexes may be tentatively proposed (Fig.2).



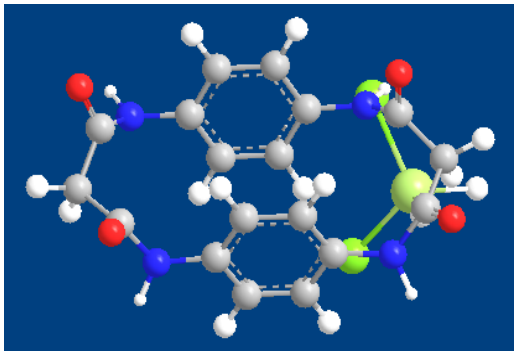


Fig.2

ANTIFUNGAL ACTITITY

The antifungal activity of the starting materials and their corresponding complexes has been evaluated against *Fusarium osysporum* and *Aspergillus niger* by the radial growth method[19] using Czapek's agar medium. The compounds were directly mixed with the medium in 50, 100 and 200 ppm concentrations. Controls were also run and three replicates were used in each case. The linear growth of the fungus was obtained by measuring the diameter of the fungal colony after four days. The amount of growth inhibition in all the replicates was calculated by the equation, Percent inhibition = (C-T) x 100/C, where C is the diameter of the fungal colony in the control plate and T, the diameter of the fungal colony in the test plate.

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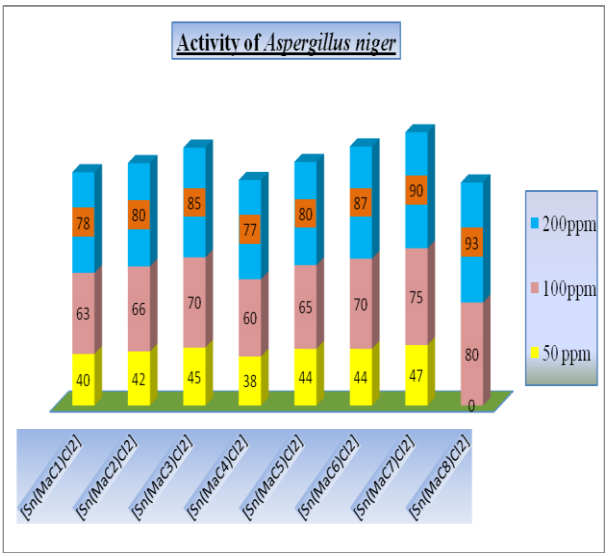
The experimental data of antifungal screening reveals that the metal complexes are more fungi toxic than the starting materials. The fungi toxicity of precursor and their complexes decreases on lowering the concentration. The results recorded from the biological activity were also compared with the standard fungicide Bavistin. The increased fungi toxicity of the complexes may be due to the chelation as the polarity of the metal ion in the complexes which reduces considerably due to the partial sharing of its positive charge with the donor groups and possible π electon delocalization over the whole chelate ring system. This in turn increases its permeation through the lipoid layers of the fungal membrane[20].

The enhanced activities of the metal complexes comparatively to free macrocycles can be ascribed to the increased lipophilic nature of these complexes arising due to chelation[21]. It is reasonable to hypothesize that more lipophilic compounds are more active simply because they enter the lipoid layers of cell membranes more rapidly.



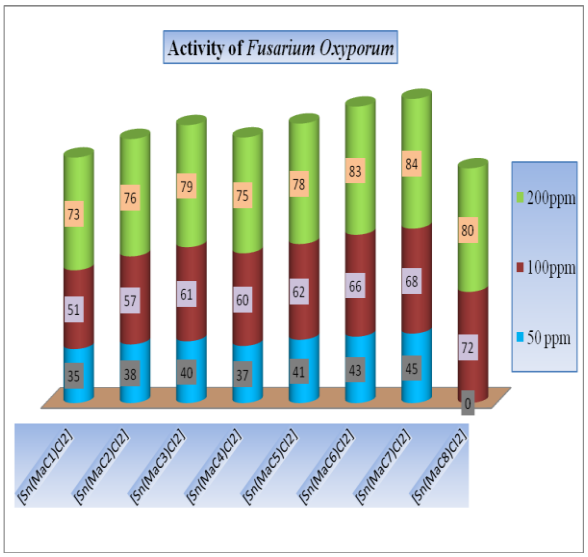


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Table 4: Fungicidal screening data of precursors and their tin(II) macrocyclic complexes (Percent growth inhibition after 4 days at 25± 2°C, Conc in ppm)

Compound	*Fusarium Oxysporum*			*Aspergillus niger*		
	50	100	200	50	100	200
Standard (Bavistin)	85	100	100	86	100	100
$SnCl_2.2H_2O$	25	34	60	29	38	57
1,3-phenylene-diamine	20	29	54	26	35	62
1,4-phenylene-diamine	22	30	55	30	40	66
$C_3H_4O_4$	21	33	58	28	40	65
$C_4H_6O_4$	21	34	60	27	42	67
$C_6H_{14}O_4$	24	35	61	32	48	69
$[Sn(MaC_1)Cl_2]$	35	51	73	40	63	78
$[Sn(MaC_2)Cl_2]$	38	57	76	42	66	80
$[Sn(MaC_3)Cl_2]$	40	61	79	45	70	85
$[Sn(MaC_4)Cl_2]$	37	60	75	38	60	77
$[Sn(MaC_5)Cl_2]$	41	62	78	44	65	80
$[Sn(MaC_6)Cl_2]$	43	66	83	44	70	87
$[Sn(MaC_7)Cl_2]$	45	68	84	47	75	90
$[Sn(MaC_8)Cl_2]$	-	72	80	-	80	93

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