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Repellent Action of Macrocyclic Complexes of Tin(II) against Adult Khapra Beetle, *Trogoderma Granarium* (Everls) Infesting Wheat Grain

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Abstract

Tin(II) complexes of tetraaza macrocycles have been prepared by template process using malonic, succinic, glutaric 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. Acetone and methanol solution of macrocyclic complexes of tin were screened for their repellent action against khapra beetle. The khapra beetle showed strong repellent behaviour against $[Sn(MacroC_1)Cl_2]$. However, repellent property has been confirmed in all the compounds.

Keywords: Macrocyclic, Tin(II), Repellent action, Trogoderma granarium.

1. Introduction

The complexes of metal ions with macrocyclic ligands are significant because of their resemblance with many natural systems such as porphyrin[1] and cobalamines. The applications[2,3] 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, stabilization 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[4]. 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[5], while these results were initially encouraging, concern has been expressed about the deleterious side effects of such agents, since they are also potent photosensitizers[6]. Indeed the use of Tin(IV) complexes of porphyrins and purpurins for photodynamic cancer therapy has also been reported[7]. Some of these complexes have also been shown to be immunostimularory[8].

In this paper we describe the synthesis, characterization and repellent action of macrocyclic complexes of Tin(II) against adult Khapra beetle, *Trogoderma granarium* (Everls) Infesting wheat grain, resulting from the condensation reaction of dicarboxylic acids and diamines.

2. 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.

2.1 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.

Table 1: Physical properties and analytical data of the complexes.

Compound	M.P.0C and Colour	Analysis, Found (Calcd.) %					Mol. Wt. Found (Calcd.)
		C	H	N	Cl	Sn	
[Sn(MaC1)Cl2]	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(MaC2)Cl2]	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(MaC3)Cl2]	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(MaC4)Cl2]	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(MaC5)Cl2]	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(MaC6)Cl2]	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(MaC7)Cl2]	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(MaC8)Cl2]	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)

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.

3. 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.

3.1 Infrared Spectra

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. The infra-red spectral data of the complexes are given in Table-2.

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

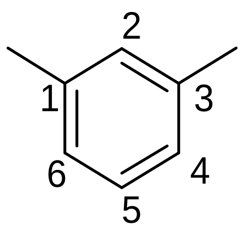
Compound	**ν(NH)**	**Amide**				**ν (Sn-N)**	**ν (Sn-Cl)**
		I	**II**	**III**	**IV**		
[Sn(MaC1)Cl2]	3245	1648	1558	1252	661	441	489
[Sn(MaC2)Cl2]	3269	1669	1544	1265	665	436	485
[Sn(MaC3)Cl2]	3286	1683	1567	1271	628	450	493
[Sn(MaC4)Cl2]	3216	1675	1571	1267	659	462	490
[Sn(MaC5)Cl2]	3227	1707	1580	1275	678	471	496
[Sn(MaC6)Cl2]	3238	1692	1587	1254	684	480	492
[Sn(MaC7)Cl2]	3220	1670	1581	1273	681	478	490
[Sn(MaC8)Cl2]	3270	1705	1586	1269	639	477	494

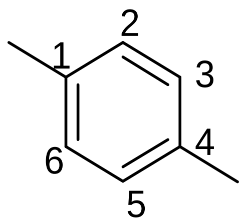
3.2 ^{1}H NMR Spectra

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 skeleton has been formed through a condensation reaction. 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)	H4,6/ H3,6	H2	H5	CO-CH2-CO	CO(CH2)2CO	CO(CH2)3CO	CO(CH2)4CO
[Sn(MaC1)Cl2]	8.09	8.42	7.38	7.61	2.80	-	-	
[Sn(MaC2)Cl2]	7.86	8.33	7.34	7.86	-	3.19	-	
[Sn(MaC3)Cl2]	7.97	8.58	7.62	7.59	-	-	3.24	
[Sn(MaC4)Cl2]	8.01	8.49	7.54	7.54	-	-	-	3.27
[Sn(MaC5)Cl2]	8.04	7.62	7.60	7.61	2.91	-		
[Sn(MaC6)Cl2]	8.13	7.61	7.61	7.62		3.17		
[Sn(MaC7)Cl2]	8.11	7.61	7.62	7.62			3.25	
[Sn(MaC8)Cl2]	8.24	7.62	7.61	7.62				3.29





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.1).

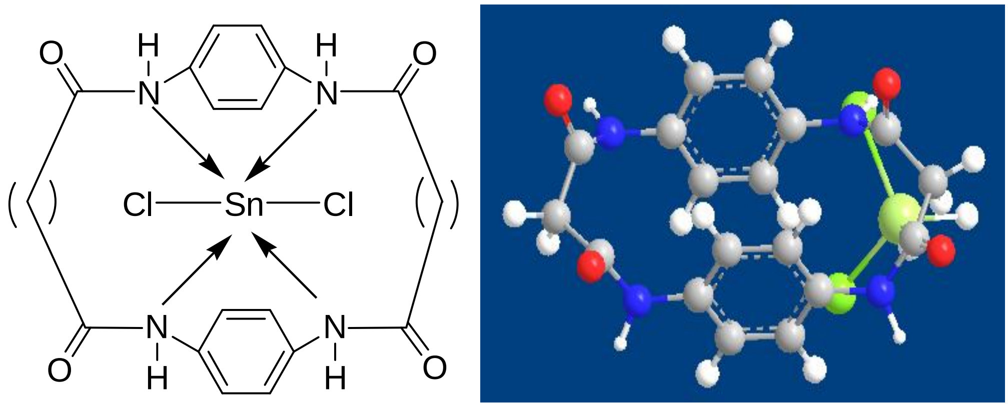
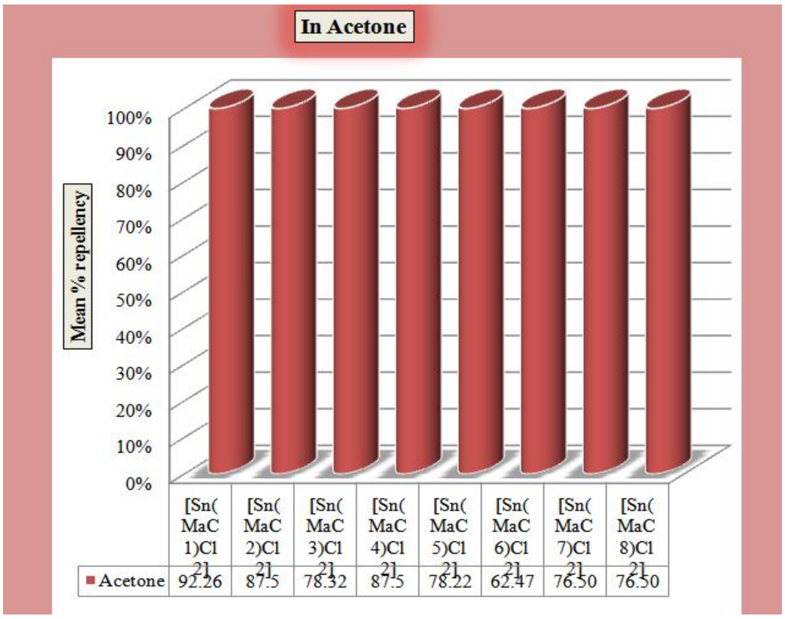


Figure 1: Proposed structure for the tin macrocyclic complexes.

3.3 Repellent Activity against adult Khapra beetle, Trogoderma granarium (Everls) Infesting wheat grain

The repellency was estimated by 'Y' shaped alfactometer following Read et al (1970)[9]. The repellency percentage was calculated using the formula suggested by Granett et al. (1949)[10].

$$\% \text{ Repellency} = \frac{\text{Insects in Cont. arm-insects in expt arm}}{\text{Insect in Cont. arm}} \times 100$$



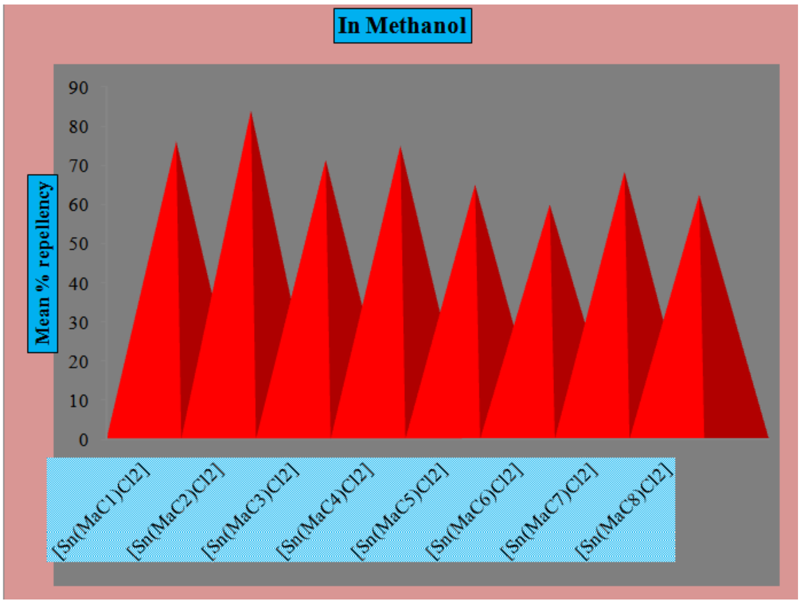


Figure 2: Repellent action of macrocyclic complexes of tin(II) against adult Khapra beetle, Trogoderma granarium (Everls)

Trogoderma granarium exhibited repellent behaviour against compounds. The data given in Fig. 2 reveal that [Sn(MacroC_1)Cl_2] *in* acetone extract exhibited maximum repellency (92.26%) whereas [Sn(MacroC_6)Cl_2] *in methanol* registered minimum repellency (59.97%).

Thus, it can be inferred that the aforementioned macrocyclic compounds of tin act as good repellent which may be suggestive of alternative to chemical/synthetic pesticides.

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