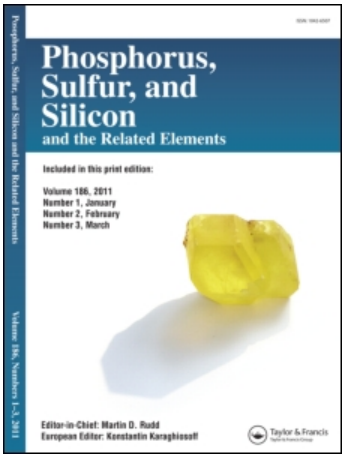

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STUDIES ON BIOLOGICALLY POTENT TETRAAZAMACROCYCLIC COMPLEXES OF BIVALENT TIN

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Fourteen- to eighteen-membered tetraamide macrocyclic ligands N_4L^1-N_4L^4 have been prepared by the condensation of 1,2-diaminoethane or 1,3-diaminopropane with malonic or succinic acid in the presence of condensing reagents dicyclohexylcarbodiimide and 4-dimethylaminopyridine. On reduction, these macrocyclic ligands give a new series of tetraazamacrocycles $MacL^1$-$MacL^4$ which form complexes with tin(II) chloride. The ligands and their complexes were characterized by elemental analyses, molecular weight determinations, infrared and ^1H NMR spectral studies. The hexacoordinated state for tin has been confirmed by spectral studies. An octahedral geometry for these complexes has been proposed as the binding sites are the nitrogen atoms of the macrocycles. On the basis of the chemical composition the representation of the complexes as $[Sn(MacL^n)Cl_2]$ (n = 1–4) has been established. The ligands and their complexes also have been screened for their antifungal and antibacterial activities and the findings have been reported and explained.

Keywords: Antibacterial activity; antifungal activity; biologically potent ligands; bivalent tin complexes; tetraamides

INTRODUCTION

Macrocyclic polyamine complexes of bivalent transition metals have been of great interest due to their importance as an essential metalloenzyme active site.[1] Typically the 14-membered tetraamine macrocyclic complexes of cyclen (1,4,8,11-tetrazacyclotetradecane) are well recognized as an example among the macrocyclic polyamines in coordination

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chemistry.[2] Therefore, the physical and chemical properties of the metal complexes are closely related to the structural features of the corresponding macrocyclic ligands. Numerous efforts in this area have been directed toward the synthesis of new types of cyclen analogues. These include in the variation of the ring size, functionalization of the cyclen skeleton,[3] attachment of pendant donors to tetraamines,[4] introduction of variable degree of unsaturation, and introduction of substituents to the methylene carbon skeleton.[4–9] Metalloporphyrins are being explored for the use as photosensitizers [10,11] and for treating pathologies in which the superoxide radical and its progeny are suspected of playing important roles.[12–15] The multifarious roles played by the naturally occurring macrocycles in the functioning of biological systems are now well know.[16–19] Their role in the physiology and biochemistry in the life forms is of paramount importance.

The chemistry of macrocyclic complexes also is of significant interest due to the use of such complexes as dyes and pigments as well as MRI contrast agents and models for naturally occurring macrocyclic systems. The design of host molecules as receptors for the recognition of substrate anion guest molecules in aqueous solution is a very important target from an environmental, industrial, and health-related point of view with multiple potential applications.[20,21] Polyazamacrocyclic ligands also have been reported to catalyze biologically significant reactions of their bounded guests[22] such as ATP hydrolysis and formation. Mostly, the polyamide macrocycles formed on reduction with B_2H_6 or $LiAlH_4$ lead to the formation of their corresponding polyazamacrocycles, which may be used to construct of various macropolycyclic systems. Keeping theses facts in mind, we have synthesized and characterized the tetraazamacrocyclic complexes of tin(II) in which dicyclohexylcarbodiimide and 4-dimethylamino-pyridine act as good condensing reagents for the condensation of primary amine and carboxylic acid. This article deals with the striking structural features, synthesis, and appreciable biological applications of these complexes.

EXPERIMENTAL

All the apparatus used during the experimental work were fitted with quick fit interchangeable standard ground joints. Melting points were determined in sealed capillary tubes. The solvents and volatile fractions were removed under reduced pressure using traps of convential design dipped in ice. Fused calcium chloride towers were used to prevent the back diffusion of moisture from the vacuum pump. The chemicals including dicyclohexylcarbodiimide, 1,2-diaminoethane,

1,3-diaminopropane, and $LiAlH_4$ were used as obtained from E. Merck. $SnCl_2$(BDH) was used without further purification.

Synthesis of the Ligands (N_4L^1-N_4L^4)

The reaction is carried out in 2:2 molar ratio. The appropriate amount of dicyclohexylcarbodiimide (1.5624 g) and catalytic amount of 4-dimethylaminopyridine in minimum amount of dichloromethane at 0°C, put on in magnetically stirred two-nacked round-bottom flask. The reaction is followed by the addition of 1,2-diaminoethane or 1,3-diaminopropane (corresponding to the dicyclohexylcarbodiimide) in dichloromethane and malonic or succinic acid (corresponding to the dicyclohexylcarbodiimide) in dichloromethane. The resulting mixture was stirred for 10–12 h at 0°C. The solid product was isolated by filtration and washed several times with the solvent and dried in vacuo. The solid products were recrystalized from benzene and dried in vacuo.

Synthesis of $MacL^1$-$MacL^4$

The reaction is carried out in 1:2 molar ratio. The ligands N_4L^1-N_4L^4 (1.0 g) were dissolved in tetrahydrofuran and cooled at 0°C. Lithium aluminium hydride (corresponding to ligands) in tetrahydrofuran was stirred for about 10 h in an ice bath. The reaction is followed by mixing the solution of ligand and $LiAlH_4$. The reaction mixture was stirred under reflux for 72 h. After cooling, 20 ml of 15% aq. NaOH and then 30 ml water were added to the mixture at 0°C. The solid product was isolated by filtration and the residue repeatedly washed with hot tetrahydrofuran. The filtrate was concentrated under reduced pressure. The liquid thus dried in vacuo.

Synthesis of the Complexes

The reaction is carried out in 1:1 molar ratio. 0.9–0.8 g ligands $MacL^1$-$MacL^4$ were dissolved in methanol. The reaction is followed by the addition of tin(II) chloride (corresponding to ligands $MacL^1$-$MacL^4$) solution. The resulting mixture was stirred for 12 h at 0°C, the solid product was obtained by filtration and washed repeatedly with same solvent and dried in vacuo. The products were recrystallized from benzene.

Thus, a series of 14–18 membered tetraazamacrocyclic ligands and their complexes was derived by the condensation of dicarboxylic acids with primary diamines in the presence of condensing reagents DCC and DMAP as shown in Figure 1.

RESULTS AND DISCUSSION

The resulting macrocyclic complexes are colored solids, soluble in tetrahydrofuran and dimethylformamide. The conductivity values measured for 10^{-3} M solution in anhydrous DMF are in the range 13–22 ohm^{-1} cm^2 mol^{-1}, showing them to be nonelectrolytes. Elemental analyses agree well with the stoichiometry and chemical formula of the compounds [Sn(MacL^n)Cl$_2$]. The physical properties and analytical data of the complexes are given in Table I.

Infrared Spectra

The preliminary identification of the macrocyclic ligands and their complexes have been obtained from their infrared spectra. The first feature of all the complexes that attracts attention is the absence of –NH$_2$ stretching vibrations of the amine and –OH groups of the dicaboxylic acids, implying their involvement in the formulation of tertraamidemacrocycles. A single sharp band observed for amide ligands

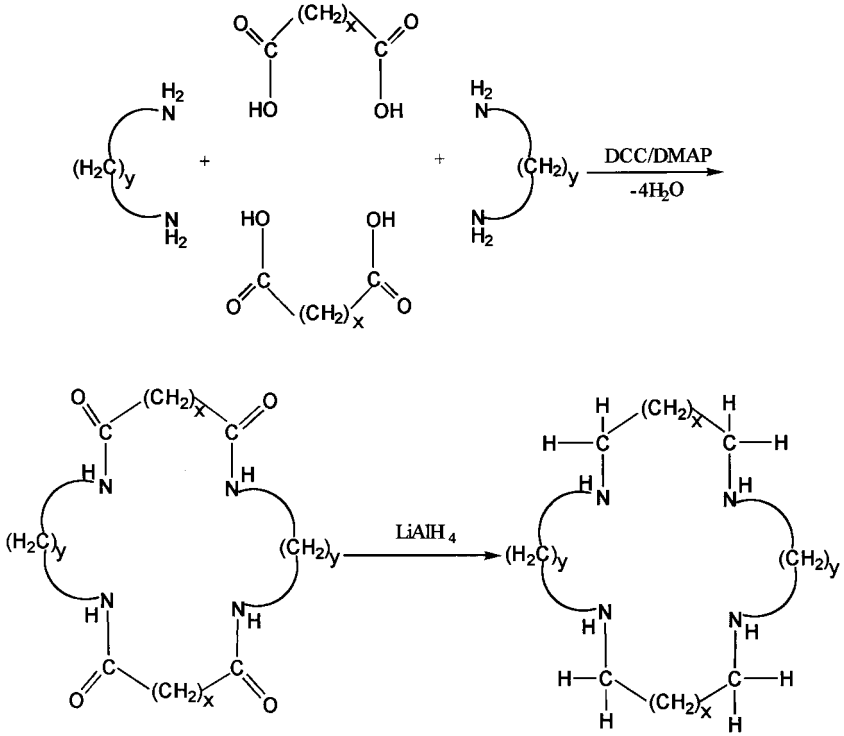
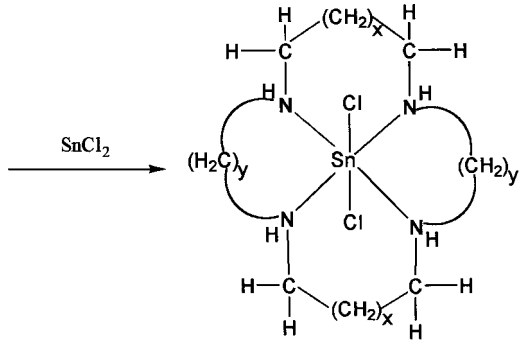


FIGURE 1 Synthesis of Ligands and Complexes. *(Continued)*



N_4L^1	x = 1	y = 2
N_4L^2	x = 1	y = 3
N_4L^3	x = 2	y = 2
N_4L^4	x = 2	y = 3
$MacL^1$	x = 1	y = 2
$MacL^2$	x = 1	y = 3
$MacL^3$	x = 2	y = 2
$MacL^4$	x = 2	y = 3
$[Sn(MacL^1)Cl_2]$	x = 1	y = 2
$[Sn(MacL^2)Cl_2]$	x = 1	y = 3
$[Sn(MacL^3)Cl_2]$	x = 2	y = 2
$[Sn(MacL^4)Cl_2]$	x = 2	y = 3

FIGURE 1 (Continued)

N_4L^1-N_4L^4 in the region 3275–3286 cm^{-1} may be assigned to ν(N—H) of amide group. The amide I, amide II, amide III, and amide IV groups are present at 1648–1707, 1544–1587, 1252–1275, and 626–681 cm^{-1} respectively.[23,24] It provides a strong evidence for the presence of a closed cyclic product. Strong and sharp absorption bands appeared in the regions 2820–3055 and 1405–1460 cm^{-1} in all the complexes are assigned to the C—H stretching and C—H bending vibratinal modes repsectively.[25] It has been noticed that tetraazamacrocyles $MacL^1$-$MacL^4$ do not show amide bands corresponding to tetraamide macrocycles. However, a slight negative shift in the NH stretching vibration has been observed. All other bands do not show appreciable change.

In the spectra of macrocyclic complexes $[Sn(MacL^1)Cl_2]$—$[Sn(MacL^4)Cl_2]$ as compared to their tetraazamacrocycles, the slight negative shift in the ν(N—H) band that appeared in the region

TABLE I Physical Properties and Analytical Data of Tetraamides, Tetraazamacrocylic Ligands, and Their Tin(II) Macrocylic Complexes

Compound	Empirical formula	m.p. (°C) and color	Analysis % found (calcd.)			Mol. wt. found (calcd.)
			N	Cl	Sn	
N_4L^1	$C_{10}H_{16}O_4N_4$	195 White	20.77 (21.86)	—	—	245 (256)
N_4L^2	$C_{12}H_{20}O_4N_4$	209 White	18.06 (19.66)	—	—	251 (285)
N_4L^3	$C_{12}H_{20}O_4N_4$	218 White	18.41 (19.66)	—	—	264 (285)
N_4L^4	$C_{14}H_{24}O_4N_4$	202 White	16.99 (17.96)	—	—	299 (312)
$MacL^1$	$C_{10}H_{24}N_4$	173 Light brown	26.78 (28.01)	—	—	181 (200)
$MacL^2$	$C_{12}H_{28}N_4$	154 Light brown	23.44 (24.57)	—	—	199 (228)
$MacL^3$	$C_{12}H_{28}N_4$	161 Light brown	23.14 (24.57)	—	—	211 (228)
$MacL^4$	$C_{14}H_{32}N_4$	178 Light brown	20.99 (21.89)	—	—	230 (256)
$[Sn(MacL^1)Cl_2]$	$C_{10}H_{24}N_4Cl_2Sn$	196 Off-white	13.52 (14.37)	17.45 (18.18)	29.89 (30.43)	361 (390)
$[Sn(MacL^2)Cl_2]$	$C_{10}H_{28}N_4Cl_2Sn$	217 White	12.41 (13.40)	16.29 (16.96)	27.88 (28.39)	387 (418)
$[Sn(MacL^3)Cl_2]$	$C_{12}H_{28}N_4Cl_2Sn$	162 Off-white	20.05 (13.40)	16.20 (16.96)	27.81 (28.39)	403 (418)
$[Sn(MacL^4)Cl_2]$	$C_{14}H_{32}N_4Cl_2Sn$	261 Off-white	11.04 (12.56)	15.27 (15.90)	26.04 (26.61)	439 (446)

3218–3229 cm^{-1} was noticed. It is ascribed to the coordinated N—H stretching vibration. This is further substantiated by the fact that all the complexes show a medium intensity band in the region 441–459 cm^{-1} which is attributed to the Sn—N stretching vibrations. The Sn—Cl stretching vibrations of compounds have been assigned at 480–488 cm^{-1} as reported earlier also.[26] The infrared spectral data of ligands and their complexes are listed in Table II.

^{1}H NMR Spectra

The ^{1}H NMR spectra of the amide ligands, tetraazamacrocycles and their macrocyclic complexes (Table III) reveal the signals expected for the given Figure 1. In the spectra of all the complexes, no band could be assigned for hydroxyl or amino groups, suggesting that the proposed macrocylic complexes have formed after the condensation. A broad signal is observed in the region δ 7.86–8.16 ppm for amide

TABLE II IR Spectral Data (in cm^{-1}) of Tetraamides, Tetraazamacrocylic Ligands, and Their Tin(II) Complexes

Compound	ν (N—H)	CH		νSn—N	νSn—Cl
		Stretching	Bending		
N_4L^1	3275	3055	1460	—	—
N_4L^2	3278	3018	1447	—	—
N_4L^3	3286	3047	1454	—	—
N_4L^4	3281	3024	1458	—	—
$MacL^1$	3261	2892	1429	—	—
$MacL^2$	3257	2951	1438	—	—
$MacL^3$	3235	2903	1434	—	—
$MacL^4$	3243	2933	1441	—	—
$[Sn(MacL^1)Cl_2]$	3229	2852	1422	441	483
$[Sn(MacL^2)Cl_2]$	3221	2820	1405	459	480
$[Sn(MacL^3)Cl_2]$	3216	2864	1417	443	484
$[Sn(MacL^4)Cl_2]$	3218	2829	1412	446	488

protons[27,28] in macrocyclic ligands N_4L^1-N_4L^4. A multiplet appearing in the region δ 3.25–3.67 ppm could be ascribed to the methylene protons (CO—N—CH_2) adjacent to the nitrogen atom. The spectra of N_4L^2-N_4L^4 show multipletes in the region δ 2.05–2.08 ppm assignable to methylene protons of 1,3-diaminopropane moiety. However, a singlet appearing in the region δ 2.81–2.92 and 3.09–3.11 ppm may be ascribed to the methylene protons of the malonic acid and succinic acid moiety which are adjacent to the nitrogen atoms.

The ^1H NMR spectra of $MacL^1$-$MacL^4$ do not show any signal assignable to amide protons. It confirms the reduction of carboxylic groups. The spectra of tetraazamacrocycles show multiplet in the region δ 6.18-6.31 ppm due to (C—H) secondary amino protons. Another multiplet observed in the regions δ 2.55–2.73 ppm is attributed to the methylene protons (N—CH_2—C) of acid moiety. Tetraazamacrocycles $MacL^1$ and $MacL^3$ show a multiplet in the region δ 3.11–3.13 ppm, indicating the methylene protons of (N—CH_2) amine moiety. $MacL^1$ and $MacL^2$ show a multiplet in the region δ 1.93–2.19 ppm due to the central methylene protons [C—(CH_2)—C]. However, $MacL^3$ and $MacL^4$ show another multiplet in the region δ 1.79–1.89 ppm ascribed to methylene protons of succinic acid portion.

According to the above interpretation we can say that the ligands act as tetradentate chelating agents having four coordination sites. Secondly, since the anions Cl remained bonded with the tin atom, a hexacoordinated environment around the tin metal atom seems to be reasonable.

TABLE III ^{1}H NMR Spectral Data of Tetraamides, Tetraazamacrocylic Ligands, and Their Tin(II) Macrocyclic Complexes

Compound	CO—NH	CO—N—CH_2	C—NH	N—CH_2—C	N—CH_2	C—CH_2—C	N—C—CH_2
N_4L^1	8.16	3.67	—	—	—	—	—
N_4L^2	7.97	3.25	—	—	—	—	—
N_4L^3	7.86	3.48	—	—	—	—	—
N_4L^4	8.11	3.54	—	—	—	—	—
$MacL^1$	—	—	6.18	273	3.13	1.93	—
$MacL^2$	—	—	6.21	259	—	2.19	—
$MacL^3$	—	—	6.29	2.55	3.11	—	1.89
$MacL^4$	—	—	6.31	2.64	—	—	1.79
$[Sn(MacL^1)Cl_2]$	—	—	6.29	2.85	3.26	2.01	—
$[Sn(MacL^2)Cl_2]$	—	—	6.27	2.73	—	2.25	—
$[Sn(MacL^3)Cl_2]$	—	—	6.36	2.64	3.21	—	1.98
$[Sn(MacL^4)Cl_2]$	—	—	6.42	2.79	—	—	2.02

Antifungal Activity

The antifungal activity of tetraazamacrocyclic ligands and their complexes with divalent tin has been evaluated by Radial Growth Method[29] using Czapek's agar medium having the composition, glucose 20 g, starch 20 g, agar-agar 20 g, and distil water 1000 mL. To this medium was added requisite amount of the compounds after being dissolved in dimethylformamide so as to get a certain final concentration (50, 100, and 200 ppm). The medium then was poured into the petri plates and the spores of fungi were placed on the medium with the help of an inoculum needle. These petri plates were wrapped in polythene bags containing a few drops of alcohol and were placed in an incubator at $30 \pm 1^{\circ}$C. The controls were also run and three replicates were used in each case. The linear growth of the fungus was obtained by measuring the fungal colony diameter after four days. The amount of growth inhibition was calculated by the equation:

$$\text{Percent Inhibition} = (C - T) \times 100/C,$$

where C is the diameter of fungal colony in control plate and T is the diameter of fungal colony in test plate.

The organisms used in these investigations included *Collectatrichum capsici* and *Macrophomina phaseolina*.

Antibacterial Activity

The activity against bacteria was evaluated by the Inhibition Zone Technique.[30] The nutrient agar medium having the composition peptone 5 g, beef extract 5 g, NaCl 5 g, agar-agar 20 g, and distil water 1000 mL was pipetted into the petri dish. When it solidified, 5 mL of warm seeded agar was applied. The seeded agar was prepared by cooling the molten agar to 40°C and that added the amount of bacterial suspension. The compounds were dissolved in dimethylformamide in 500 and 1000 ppm concentrations. Paper discs of Whatman No. 1 filter paper measuring diameter of 5 mm were soaked in these solutions of varied concentrations. The discs were dried and placed on the medium previously seeded with organisms in petri plates at suitable distance. The petri plates were stored in an incubator at $28 \pm 2^{\circ}$C for 24 h. The zone of inhibition, thus formed around each disc containing the test compounds was measured accurately in mm. The organisms used in these investigations included *Pseudomonas cepacicola* (−) and *Klebsella aerogenous* (−).

TABLE IV Fungicidal Screening Data of Tetraamides, Tetraazamacrocylic Ligands, and Their Divalent Tin Complexes, Percent Growth Inhibition After 4 days at $30 \pm 1^{\circ}C$

	Collectatrichum capsici			*Macrophomia phaseolina*		
Compounds	50 ppm	100 ppm	200 ppm	50 ppm	100 ppm	200 ppm
N_4L^1	32	49	65	29	51	71
N_4L^2	35	44	51	34	—	60
N_4L^3	51	72	80	49	70	83
N_4L^4	47	65	81	47	68	90
$MacL^1$	32	57	73	32	54	76
$MacL^2$	39	57	77	—	55	76
$MacL^3$	64	76	86	74	81	85
$MacL^4$	60	69	79	58	65	79
$[Sn(MacL^1)Cl_2]$	37	56	79	34	53	74
$[Sn(MacL^2)Cl_2]$	53	75	88	53	76	92
$[Sn(MacL^3)Cl_2]$	79	89	94	82	90	96
$[Sn(MacL^4)Cl_2]$	74	83	91	70	79	91
Bavistin	83	100	100	87	100	100

Mode of Action

The chelation theory[31] accounts for the increased activity of the metal complexes. The chelation reduces the polarity of metal atom mainly because of partial sharing of its positive charge with the donor groups

TABLE V Bactericidal Screening Data of Tetraamides, Tetraazamacrocylic Ligands, and Their Tin(II) Macrocyclic Complexes, Inhibition Zone of I (mm) after 24 h at $28 \pm 2^{\circ}C$

	Pseudomonas cepacicola (–)		*Klebsella aerogenous* (–)	
Compound	500 ppm	1000 ppm	500 ppm	1000 ppm
Streptomycin	2	3	3	5
N_4L^1	6	8	5	8
N_4L^2	6	9	5	7
N_4L^3	4	6	4	7
N_4L^4	8	10	8	11
$MacL^1$	7	11	4	10
$MacL^2$	8	11	7	12
$MacL^3$	5	9	7	9
$MacL^4$	9	12	9	13
$[Sn(MacL^1)Cl_2]$	7	13	6	10
$[Sn(MacL^2)Cl_2]$	9	12	8	13
$[Sn(MacL^3)Cl_2]$	6	11	7	12
$[Sn(MacL^4)Cl_2]$	10	12	10	13

and possible π electron delocalisation within a whole chelating ring. The chelation increases the lipophilic nature of the central atom which subsequently favours its premeation through the lipid layer of the cell membrane.

The results of biological activity have been compared with the conventional fungicide, bavistin, and the conventional bactericide streptomycin used as standards. The results achieved out of these studies have been enlisted in Tables IV and V in which the antifungal activity indicated that the metal chelates are more active than their parent diamines, dicarboxylic acids, metal salts, tetraamides, and tetraazamacrocycles. In case of antibacterial activity the ligands and complexes showed similar type of behaviors as indicated in antifungal activity.

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