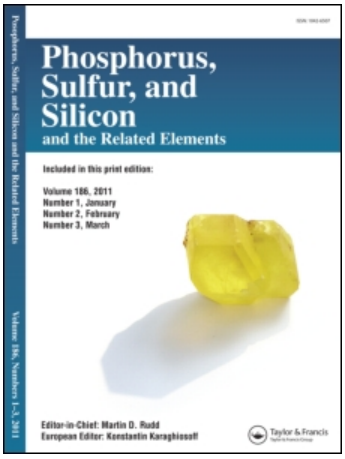

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Synthetic, Structural and Biological Studies on Divalent Tin Complexes of Sixteen to Twenty-Four Membered Tetraaza Macrocycles

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SYNTHETIC, STRUCTURAL AND BIOLOGICAL STUDIES ON DIVALENT TIN COMPLEXES OF SIXTEEN TO TWENTY-FOUR MEMBERED TETRAAZA MACROCYCLES

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A new series of 16- to 24-membered macrocycles of tin(II) containing tetraaza groups has been prepared by the template condensation reaction of glutaric acid and phthalic acid with 1,2-phenylenediamine, 2,6-diaminopyridine, and diethylenetriamine in 1:2:2 molar ratios. The reaction products were characterized by elemental analyses, molecular weight determinations, infrared, ^{1}H NMR, ^{119}Sn NMR, and mass spectral studies. X-ray powder diffraction spectrum of one representative compound also has been reported. 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 macrocycle. The formulation of the complexes as $[Sn(N_4MaC_n)Cl_2]$ (where N_4MaCn represent the ligand molecule and $n = 1$ to 6 has been established on the basis of the chemical composition. All of the complexes are monomeric. The ligands and their complexes also have been screened for their antimicrobial activities and the results are discussed.

INTRODUCTION

Recent interests have been stimulated by the diagnostic and therapeutic medicinal applications of transition metal complexes of macrocyclic ligands. The amide macrocyclic complexes are of special interest since they can function as catalysts in many organic oxidation reactions. Lindoy and co workers[1] have performed elegant studies on ligand design and metal ion recognition of tetraaza- and mixed polyaza

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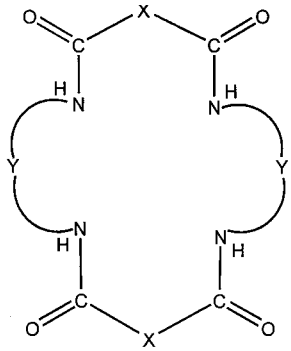

N_4MaC_1; X = $(CH_2)_3$, Y=1,2-C_6H_4

N_4MaC_2; X = (C_6H_4), Y=1,2-C_6H_4

N_4MaC_3; X = $(CH_2)_3$, Y=C_5H_3N

N_4MaC_4; X = (C_6H_4), Y=C_5H_3N

N_4MaC_5; X = $(CH_2)_3$, Y=C_4H_9N

N_4MaC_6; X = (C_6H_4), Y=C_4H_9N

FIGURE 1

marocyclic complexes. One of the most interesting aspects of polyaza macrocyclic complexes is that the ligand can be modified. Some transition metal(II) complexes of polyaza macrocyclic ligands containing coordinated secondary amino groups are chemically oxidized to metal(II) complexes containing a higher degree of unsaturation in the ligand.[2,3] Macrocyclic complexes are thermodynamically quite stable and are involved in a variety of catalytic, biochemical, and industrial processes.[4–6] Interestingly, few reports[7,8] have appeared in the literature where azacyclans have been shown to act as effective and selective catalysts for the electro and photochemical reduction of carbon dioxide. Macrocyclic complexes of tin(II) containing tetraoxotetraaza group are not yet widely explored. Therefore, the present communication deals with the synthesis, spectroscopic characterization and biocidal studies of some new 16- to 24-membered macrocyclic complexes of tin(II) having a tetraoxotetraaza ligand, formed by the template condensation of glutaric acid or phthalic acid with 1,2-phenylenediamine, 2,6-diaminopyridine, and diethylenetriamine in the presence of tin dichloride. The ligands used are:

EXPERIMENTAL

All the glass apparatus used during the experimental work was fitted with quick fit interchangeable standard ground joints. Methanol (E. Merck) was refluxed over magnesium methoxide and distilled (b.p. 65.4°C). The chemicals including glutaric acid (99% pure), phthalic acid (99% pure), 1,2-diaminoethane, 2,6-diaminopyridine, and diethylenetriamine (99% pure) were used as obtained from E. Merck. $SnCl_2 \cdot 2H_2O$ (B.D.H.) was used without further purification.

Synthesis of 2,3,11,12-Dibenzo-5,9,14,18-tetraoxo-1,4,10,13-tetraazacyclooctadecane Tin(II) Chloride [$Sn(N_4MaC_1)Cl_2$]

$SnCl_2{\cdot}2H_2O$ (1.0 g, 4.43 mmol) was dissolved in methanol (25 mL) and cooled in an ice bath. To this was added 1,2-phenylenediamine (0.96 g, 8.88 mmol) solution in methanol (25 mL) and put in magnetically stirred 100 mL round bottom flask. The reaction is followed by addition of glutaric acid (1.17 g, 8.86 mmol) in MeOH (25 mL). The resulting mixture was stirred for 24–25 h. The solid product was isolated by filtration, repeatedly washed with same solvent, and dried in vacuo (yield, 53%). The compound was recrystallized in DMF and dried in vacuo.

Synthesis of 2,3,6,7,10,11,14,15 Tetraazabenzo-5,8,13,16-tetraoxo-1,4,9,12-tetraazahexa-decane Tin(II) Chloride [$Sn(N_4MaC_2)Cl_2$]

$SnCl_2{\cdot}2H_2O$ (1.01 g, 4.48 mmol) in methanol (25 mL) and 1,2-phenylenediamine (0.97 g, 8.97 mmol) in methanol (25 mL) were added in a solution of phthalic acid (1.04 g, 6.02 mmol) in methanol. This mixture was stirred continuously at room temperature for 24–25 h. The product obtained was washed with MeOH and dried in vacuo (yield, 65%). The compound was recrystallized in DMF.

Synthesis of 2,4,12,14-Dipyrido-6,10,16,20-tetraoxo-1,5,11,15-tetraazacyclodode-cane Tin(II) Chloride [$Sn(N_4MaC_3)Cl_2$]

The compound was synthesized by the above method, using $SnCl_2{\cdot}2H_2O$ (1.00 g, 4.43 mmol), 2,6-diaminopyridine (0.97 g, 8.89 mmol), and glutaric acid (1.17 g, 8.86 mmol). The compound was recrystallized in DMF.

Synthesis of 2,4,11,13-Dipyrido-6,9,15,18-tetraoxo-1,5,10,14-tetraazacyclo-octadecane Tin(II) Chloride [$Sn(N_4MaC_4)Cl_2$]

The procedure is same as described above. The reagents used were $SnCl_2{\cdot}2H_2O$ (1.00 g, 4.43 mmol), 2,6-diaminopyridine (0.97 g, 8.89 mmol), and phthalic acid (1.45 g, 8.73 mmol). The compound was recrystallized in DMF.

Synthesis of 8,12,2,24-Tetraoxo-1,7,13,19-tetraazacyclotetradodecane Tin(II) Chloride [$Sn(N_4MaC_5)Cl_2$]

This compound was isolated by the procedure as detailed former. The reagents used were $SnCl_2{\cdot}2H_2O$ (1.00 g, 4.43 mmol), diethylenetriamine

(0.91 g, 8.82 mmol), and glutaric acid (1.17 g, 8.86 mmol). The compound was recrystallized in DMF.

Synthesis of 9,10,20,21-Dibenzo-8,12,19,22-tetraoxo-1,7,12,18, Tetraazacyclodido-decane Tin(II) Chloride [$Sn(N_4MaC_6)Cl_2$]

This preparation was analogous to the above. Phthalic acid. (1.48 g, 8.91 mmol) was used in place of glutaric acid. The compound was recrystallized in DMF.

The purity of the compounds was checked by TLC on silica Gel-G using anhydrous methanol and tetrahydrofuran (1:1) as a solvent. Each of the compound moves as a single spot indicating the presence of only one component and hence their purity. Conductivity measurements were made with a Systronic model 305 conductivity bridge in dry dimethyl formamide. Molecular weights were determined by the Rast camphor method. IR spectra of the solid samples were recorded as KBr discs on a Nicolet magna FT-IR 550 spectrophotometer. 1H NMR spectra were recorded on a FX 90 Q spectrometer in DMSO-d_6 using TMS as internal standard. Nitrogen and chlorine were determined by Kjeldahls or and Volhard's method respectively. Tin was determined gravimetrically as tin oxide.

RESULTS AND DISCUSSION

A series of 16- to 24-membered tetraazamacrocyclic complexes of tin(II) were derived by the template condensation of glutaric or phthalic acid with 1,2-phenylenediamine, 2,6-diaminopyridine, or diethylenetriamine as shown by the following equation with N_4MaC_1 as a ligand:

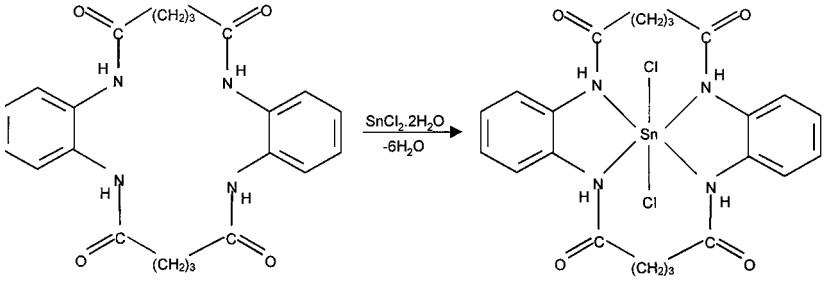

TABLE I Physical Properties and Analytical Data of Tin(II) Macrocyclic Complexes

Compound	Colour	m.p. (°C)	Yield (%)	Analysis found (calcd.) % N	Cl	Sn	Mol. Wt. Found (calcd.)
$[Sn(N_4MaC_1)Cl_2]$	Peach	103	53	8.9 (9.3)	11.2 (11.9)	19.3 (19.9)	581 (598)
$[Sn(N_4MaC_2)Cl_2]$	Peach	174	65	8.8 (8.4)	10.0 (10.7)	17.3 (17.8)	561 (666)
$[Sn(MaC_3)Cl_2]$	Greenish gray	186	48	13.8 (14.0)	19.2 (19.3)	19.3 (19.8)	587 (600)
$[Sn(N_4MaC_4)Cl_2]$	Greenish gray	205	62	11.6 (12.6)	10.0 (10.6)	17.3 (17.8)	646 (668)
$[Sn(N_4MaC_5)Cl_2]$	Cream	203	50	13.2 (14.3)	11.5 (12.0)	19.7 (20.2)	569 (588)
$[Sn(N_4MaC_6)Cl_2]$	Cream	177	41	12.6 (12.9)	10.2 (10.8)	17.5 (18.1)	629 (656)

The resulting macrocyclic complexes are coloured solids. They are soluble in DMSO and DMF. The conductivity values measured for 10^{-3} M solutions in anhydrous DMF are in the range 15–29 ohm^{-1} cm^2 mol^{-1}, showing them to be nonelectrolytes. Molecular weights of the complexes indicated the monomeric nature of the complexes. Elemental analyses agree well with the stoichiometry and chemical formula of the compounds $[Sn(N_4MaC_n)Cl_2]$. The physical properties and analytical data of the complexes are given in Table I.

Infrared Spectra

The absence of $-NH_2$ and $-OH$ stretching vibrations of the amine and $-OH$ groups of the dicarboxylic acids, in the IR spectra of the complexes implying their involvement in the formation of tetraazamacrocycles. The spectra of all of the complexes show a medium intensity band at 3230–3280 cm^{-1} which is assigned to υ(NH) mode of the amide group[9] or the secondary amino group of diethylenetriamine. The amide I, amide II, amide III, and amide IV bands are present at 1670–1717, 1483–1530, 1230–1269 cm^{-1}, and 631–678 respectively.[10] The spectra of the complexes derived from 2,6-diaminopyridine do not show any change in pyridine ring which confirms that the nitrogen does not participate in coordination.[11] The bands in the region 441–477 cm^{-1} in the spectra of all of the complexes may be attributed to the Sn-N stretching vibrations[12]. The Sn-Cl stretching vibrations have been assigned at 480–499 cm^{-1} (Table II) as reported by others[13,14] also.

TABLE II IR Spectral Data (in cm^{-1}) of Tin(II) Macrocyclic Complexes

Compound	ν(N—H)	Amide (I)	Amide (II)	Amide (III)	Amide (IV)	νC—N	νSn—Cl	νSn—N
$[Sn(N_4MaC_1)Cl_2]$	3253 bs	1673 s	1513 s	1230 s	659 s	—	467	480
$[Sn(N_4MaC_2)Cl_2]$	3278 bs	1711 s	1489 s	1239 s	647 s	—	441	492
$[Sn(MaC_3)Cl_2]$	3230 bs	1705 s	1530 s	1244 s	661 s	849 m	463 m	487 m
$[Sn(N_4MaC_4)Cl_2]$	3242 bs	1670 s	1496 s	1261 s	678 s	832 m	471 m	499 m
$[Sn(N_4MaC_5)Cl_2]$	3267 bs	1686 s	1521 s	1253 s	640 s	—	477 m	482 m
$[Sn(N_4MaC_6)Cl_2]$	3280 bs	1717 s	1483 s	1269 s	631 s	—	468 m	493 m

bs = Broad and sharp, m = medium.

^{1}H NMR Spectra

In the ^{1}H NMR spectra of all of the complexes, no signal could be assigned for hydroxyl and amino groups, suggesting that the proposed macrocyclic complexes are formed by the template condensation. A broad signal is observed in the region δ 8.22–8.45 ppm for amide protons.[15,16] The complexes derived from glutaric acid give a multiplet at δ 3.21–3.27 ppm. The complexes show an additional multiplet at δ 7.01–7.26 ppm attributed to phenyl protons of phthalic acid.[16] A multiplet showed in the region δ 2.93–3.09 ppm is attributed to the methylene protons (C—CH_2—N—C) nearest to the secondary amino protons of diethylenetriamine. Furthermore, another multiplet observed in the region δ 6.23–6.39 ppm is assigned to the secondary amino protons C—NH—C of the amine moiety. Chemical shift values of all the complexes are listed in Table III.

Mass Spectra

The mass spectrum of the $[Sn(C_{26}H_{18}N_6O_4)Cl_2]$ complex shows the molecular ion peak at m/z 668 $[M]^+$. The one and two coordinated chloride ions are remove with a mass loss of m/z 35 and 70 The molecular cations during fragmentation process loss the coordinated exocyclic ligands under FAB conditions to give species such as: 592 $[Sn(C_{20}H_{14}N_6O_4)Cl_2]^+$; 516 $[Sn(C_{14}H_{10}N_6O_4)Cl_2]^+$; 536 $[Sn(C_{18}H_{14}N_6O_2)Cl_2]^+$ and 567 $[Sn(C_{22}H_7N_3O_4)Cl_2]^+$ from the loss of the C_6H_4, $C_{12}H_8$, $C_8H_4O_2$ and $C_4H_{11}N_3$ fragments respectively.

X-Ray Diffraction

The possible geometry of the powdered product $[Sn(N_4MaC_6)Cl_2]$ has been deduced on the basis of x-ray powder diffraction studies. The observed interplanar spacing values ("d" in A°), have been measured from

TABLE III ^{1}H NMR Spectral Data (δ, ppm) of Macrocyclic Complexes of Tin(II)

Compound	(CO—NH)	CO—$(CH_2)_3$—CO	Phenyl of phthalic acid	Aromatic	C—CH_2—N—C	C—NH—C
$[Sn(N_4MaC_1)Cl_2]$	8.22	3.23	—	6.75–7.87	—	—
$[Sn(N_4MaC_2)Cl_2]$	8.47	—	7.01	7.06–7.94	—	—
$[Sn(N_4MaC_3)Cl_2]$	8.25	3.27	—	6.89–7.81	—	—
$[Sn(N_4MaC_4)Cl_2]$	8.36	—	7.08	7.11–7.99	—	—
$[Sn(N_4MaC_5)Cl_2]$	8.54	3.21	—	—	3.09	6.23
$[Sn(N_4MaC_6)Cl_2]$	8.51	—	7.26	—	2.93	6.39

TABLE IV X-Ray Diffraction Data of the Compound $[Sn(N_4MaC_6)Cl_2]$

Peak no.	2θ obs	2θ Calcd.	d obs	h	k	L
1	17.90	17.86	6.227	5	0	1
2	17.90	18.04	6.227	0	2	1
3	19.10	19.01	5.839	5	1	0
4	19.10	19.29	5.839	2	2	1
5	21.60	21.50	5.170	3	1	3
6	22.40	22.51	4.987	0	0	4
7	26.10	25.97	4.290	7	1	1
8	26.90	26.73	4.165	7	1	1
9	28.60	28.43	3.922	0	2	4
10	32.20	32.22	3.493	8	0	3
11	34.70	34.53	3.248	0	3	4
12	34.70	34.76	3.248	10	0	1
13	34.70	34.70	3.248	1	3	4
14	42.50	42.34	2.673	1	2	2

Refined values: a = 32.872; b = 13.001; c = 19.851, max dev. of $2\theta = 0.2$ and $\alpha = \beta = \gamma = 90^\circ$.

the diffractogram of the compound and the miller indices h, k, and l have been assigned to each d value and 2θ angles are reported in Table IV. The results suggest that the compound belongs to orthorhombic crystal system having unit cell parameters as: a = 32.872, b = 13.001, c = 19.851, $\alpha = \beta = \gamma = 90^\circ$, max. dev. of $2\theta = 0.2$.

^{119}Sn NMR Spectra

The ^{119}Sn NMR spectrum of the $[Sn(N_4MaC_5)Cl_2]$ complex gives signal at δ −591.6 ppm, indicating coordination number six in the complexes around tin atom.[17]

On the basis of above studies, we can say that the ligands are behaving as tetradentate chelating agents having four coordinating sites. Secondly, the Cl- ion remains bonded to the metal atom. Therefore, a hexa coordinated environment around the tin atom seems to be reasonable.

MICROBIAL ASSAY

Antifungal Screening

The antifungal activity of tin(II) macrocyclic complexes has been evaluated against *Fusarium oxysporum*, *Aspergillus niger*, and *Alternaria*

alternata. Fungicidal activity was measured by the Radial Growth Method[18] using Czapek's agar medium having the composition glucose; 20 g, starch 20 g, agar-agar −20 g and distill water 1000 mL. The compounds were mixed directly with the medium in different concentrations. The spores of fungi were placed on the medium with the help of an inoculum needle. The petri dishes were wrapped in polythene bags containing a few drops of alcohol and were placed in an incubator at $30 \pm 1^{\circ}C$. 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 4 days. The amount of growth inhibition was calculated by the equation: Percent Inhibition = (C-T) × 100/C, where, C is the diameter of the fungal colony in the control plate and T is the diameter of the fungal colony in the test plate.

Antibacterial Screening

The activity against bacteria was evaluated by the paper disc plate method.[19] For this purpose, pure cultures of the organisms were dissolved in peptone-water (1:1) and then uniformly seeded on the nutrient agar plates having the composition; peptone 5 g, beaf extract 5 g, NaCl 5 g, agar-agar 20 g, and distilled water 1000 mL. The compounds were dissolved in 500 and 1000 ppm concentrations. Paper discs of Whatman No. 1 with a diameter of 5 mm were soaked in these solutions. These discs were placed on the medium previously seeded with organisms in petri dishes at suitable distances. The petri dishes were stored in an incubator at $30 \pm 2^{\circ}C$ for 24 h. The zone of inhibition thus formed around each disc containing the test compound was measured accurately in mm. The organisms used in the present investigations included *Pseudomonas cepacicola*, *Escherichia coli*, and *Staphylococcus aureus*.

TABLE V Antifungal Activity of Tin(II) Macrocyclic Complexes (Percent Growth Inhibition after 4 Days at $25 \pm 2^{\circ}C$, Concentration in ppm)

	Fusarium oxysporum			*Aspergillus niger*			*Alternaria alternata*		
Compound	50	100	200	50	100	200	50	100	200
Bavistin (standard)	85	88	100	85	87	100	82	85	100
$[Sn(N_4MaC_1)Cl_2]$	72	80	88	71	81	88	73	82	90
$[Sn(N_4MaC_2)Cl_2]$	69	87	89	81	89	92	78	86	88
$[Sn(N_4MaC_3)Cl_2]$	52	73	89	52	73	91	47	74	90
$[Sn(N_4MaC_4)Cl_2]$	78	87	94	82	90	96	82	91	97
$[Sn(N_4MaC_5)Cl_2]$	64	76	86	74	81	87	73	79	86
$[Sn(N_4MaC_6)Cl_2]$	60	69	79	61	88	80	58	66	78

TABLE VI Antibacterial Activity of Tin(II) Macrocyclic Complexes (Percent Growth Inhibition after 24 hours at $30 \pm 2^{\circ}C$, Concentration in ppm)

	Pseudomonas cepacicola (–)		*Escherichia coli (–)*		*Staphylococcus aureus (+)*	
Compound	500	1000	500	1000	500	1000
$[Sn(N_4MaC_1)Cl_2]$	6	9	7	11	9	3
$[Sn(N_4MaC_2)Cl_2]$	7	10	9	11	7	11
$[Sn(N_4MaC_3)Cl_2]$	8	9	8	10	10	12
$[Sn(N_4MaC_4)Cl_2]$	8	12	6	9	9	13
$[Sn(MaC_5)Cl_2]$	7	8	4	6	6	8
$[Sn(N_4MaC_6)Cl_2]$	5	9	5	8	6	11
Standard (streptomycin)	15	17	17	18	15	17

Mode of Action

Chelation theory[20] accounts for the increased activity of the metal complexes. Chelation reduces the polarity of the metal atom mainly because of partial sharing of its positive charge with the donor groups and possible π electron delocalization within the whole chelate ring. The chelation increases the lipophilic nature of the central atom which subsequently favors its permeation through the lipid layer of the cell membrane.

The results of fungicidal and bactericidal screening of the metal complexes against some pathogenic fungi and bacteria are recorded in Tables V and VI. The results show that the activity is enhanced on undergoing chelation. It is a well known fact that concentration plays a vital role in increasing the degree of inhibition. As the concentration increases, the activity increases. The fungicidal activity was better as compared to the bactericidal activity. It in interesting to note that similar coordination compounds of tin, synthesized with other ligands like heterocylic thosemicarbazones, benzothiazolines, S-benzyldithiocarbazales, or S-methyldithiocarbazates have more activity than the present complexes. This may be due to presence of sulfur atoms in such ligands.

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