

## SYNTHESIS, SPECTRAL STUDIES, AND ANTIMICROBIAL ACTIVITY OF METAL COMPLEXES OF SCHIFF BASES

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### Abstract:

Microwave-assisted synthesis and characterization of the tin and cadmium complexes are reported. Octahedral complexes was synthesized by the reaction of (E)-N-(8,9-dihydropyrazolo[4,3-b]carbazol-6(1H,5H,7H)-ylidene)thiazole. The complexes so formed were characterized by various physicochemical studies i.e. elemental analysis, conductance measurements, magnetic susceptibility and molecular weight determinations. Bonding of complexes is discussed in terms of their UV, IR, XRD, <sup>1</sup>H NMR and TGA studies. Ligands acts as bidentate towards metal ion via nitrogen donor sites. Elemental analysis and NMR spectral data of the ligands with their complexes agree with their proposed structures. The anti-microbial activities of the ligands and their corresponding tin(II) complexes have been screened against various strains of bacteria and fungi.

**Keywords:** Spectroscopic, medicinally, potent, carbazole.

### Introduction:

Heterocyclic ligands and their metal complexes have received considerable attention in chemistry and biology, primarily because of their marked and various biological properties<sup>[i-vii]</sup>. Schiff bases derived from thiazoleheterocycles were reported to possess cytotoxic, anticonvulsant, anticancer and antifungal actives<sup>[viii-x]</sup>. Thiazoles (-N=C-S) containing moiety has been employed as antipsychotic and antibacterial. Thiazole derivative, particularly amino thiazoles, play vital role in pharmaceutical practice owing to their wide biological activities<sup>[xi-xiv]</sup> like fungicidal, antimicrobial, anti-tuberculosis, anti-cancer and anti-inflammatory<sup>[xv-xvi]</sup>. For example, ritonavir an anti-HIV drug contains a 5-substituted oxymethylthiazole moiety, and an isostere of the important insecticide, imidacloprid has 2-chloro-5-substituted methylthiazole as part of the molecule. The substituted thiazoles compounds have a number of characteristic pharmacological features such as relative stability and ease of starting materials, built in biocidal unit, enhanced lipid solubility with hydrophilicity, easy metabolism of compounds. Complexes of schiff base ligands have potential applications in organic synthesis, catalysis, medicinal chemistry and biotechnology<sup>[xvii]</sup>. Tin complexes are well known for their innumerable applications as antifungal, antibacterial, biocidal and cytotoxic agents<sup>[xviii-xix]</sup> but are often very

toxic. Therefore, the syntheses of tin complexes with thiazole could be a strategy of preparation of new drug candidates in which the metal and ligand could act synergistically. In recent years, the structural and biological properties of heterocyclic thiazole and their metal complexes have attracted considerable interest of scientific community [xx-xxi].

## **Experimental Section**

### **Materials and Measurements**

Reagents and solvents were dried and purified by standard methods. The metal salts were obtained from Merck. All the chemicals employed for syntheses were of analytical grade and were used as supplied without further purification. Microwave assisted procedure was carried out in a domestic oven. FT-IR spectra with KBr pellets were recorded on FTIR-8400 S infrared spectrometer (SHIMADZU) in the 4000–400  $\text{cm}^{-1}$  range. Electronic spectra were recorded in DMF solutions double beam spectrophotometer-2101 (SYSTRONICS) with quartz cells of 0.5 cm path length.  $^1\text{H}$  NMR spectra were obtained using a Bruker FT-NMR spectrometer at 300 MHz with the samples dissolved in  $\text{DMSO-}d_6$  mixture using TMS as internal standard. Melting points were recorded on microtech instrument of advanced melting point apparatus and are uncorrected. Molecular weight of complexes was determined by “Rast Camphor method. Molar conductance of the ligands and their complexes were measured by freshly prepared  $10^{-3}$  M solutions in DMF at room temperature with model-1601 microprocessor based conductivity meter with a dip type cell. The magnetic susceptibilities measurements on powder form of the complexes with magnetic susceptibility balance (Mk1) of Sherwood Scientific Corporation, UK using  $\text{MgSO}_4$  as a celebrant at room temperature. X-ray powder diffraction spectra of the compound were obtained on the Bruker diffractometer using Cu ( $K\alpha$ ) target with Ni filter at room temperature. The wavelength used was 1.540600 Å and the reflections from 20–80° was recorded from Department of physics, University of Delhi, Delhi-110007. Biological studies were carried out at Department of basic science, IP University, Dwarka Delhi.

### **Anti-microbial studies**

#### **Anti-fungal studies**

Bio efficacies of the synthesized compounds were checked *in vitro*. The *in vitro* anti-fungal activities of the ligands and their complexes was evaluated against two pathogenic fungi, *Aspergillusniger* and *Aspergillusflavus* using fluconazole as standard by disc diffusion technique. The discs were stored in an incubator at  $35 \pm 2$  °C. The inhibition zone around each disc was measured (in mm) after 48 hours

#### **Anti-bacterial activity**

For the evaluation of degree of inhibitory effects on the growth of a wide spectrum of microorganisms antibacterial activity was performed against (*Bacillus subtilis* and *Escherichia Coli*) bacteria and the results are summarized. In order to compare the results obtained the ciprofloxacin was used as standard drug. Determination of the antibacterial activity was carried out by the paper-disc plate method. The compounds were dissolved in DMF at 200 and 500 ppm concentrations. All the Whatman No. 1 paper with a diameter 5 mm were soaked in these solutions. These discs were placed on the appropriate nutrient medium previously seeded organisms in petri dishes and stored in an incubator at  $35 \pm 2$  °C. The inhibition zone around each disc was measured (in mm) after 24-30 hours

## Synthesis of ligands

A solution of carbazole (0.005 mol) in dry methanol was added to a solution of 2-aminothiazole/ benzothiazole (0.005 mol) in dry methanol and irradiated under microwave irradiations for 4-8 mins at 720 MW power and completion of reaction was checked by TLC. Yellow precipitate of Schiff base was obtained, filtered, washed, dried and recrystallized with absolute ethanol.

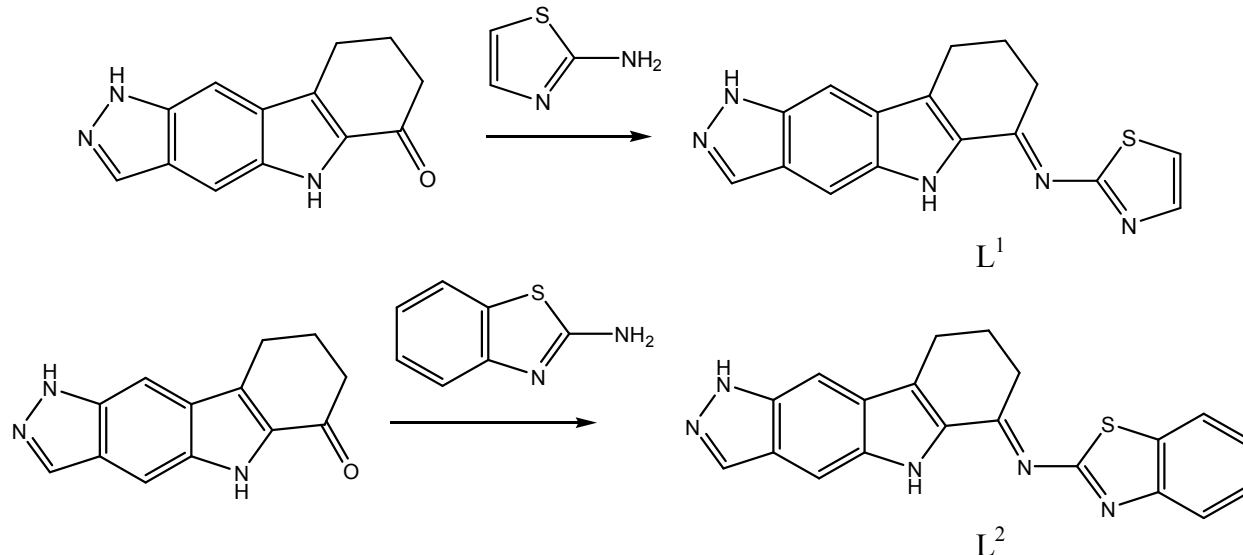


Fig. 1 Synthesis of ligands

## Synthesis of metal complexes

### Preparation of tin(II) complexes

Weighed amounts of hydrated SnCl<sub>2</sub> (0.015 mol) in dry methanol were added to the methanolic solution of the above synthesized thiazole (0.003 mol) (L<sup>1</sup>) and benzothiazole (0.003 mol) (L<sup>2</sup>) ligands in 1:2 stoichiometric ratios. These reaction mixtures were subjected to energy source of microwave for 4-7 mins. The precipitated complexes were filtered and washed with a mixture of methanol and petroleum ether and recrystallized with ethanol and finally dried.

### Preparation of cadmium(II) complexes

To a weighted quantity of synthesized ligands (0.002 mol) (L<sup>1</sup>) and (L<sup>2</sup>) in dry methanol were added to the methanolic monohydrated CdCl<sub>2</sub> solution of (0.001 mol). In different reaction vessels mixture were irradiated under microwave till the completion of reaction and completion of reaction were checked by TLC plates. Small quantities of petroleum ether (60-80 °C) were then added whereupon new complexes were separate out. They were filtered off washed with petroleum ether and finally dried.

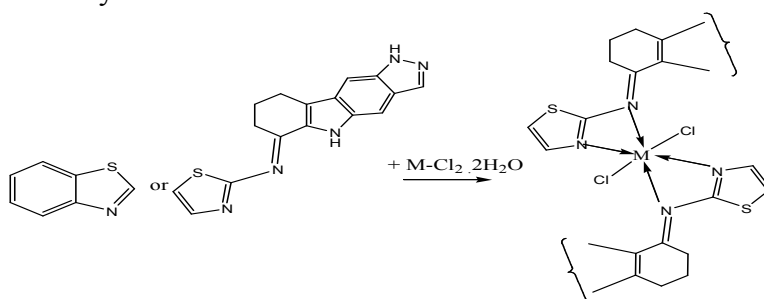


Fig. 2 Structure of synthesized complexes

## Results and Discussion

### Elemental analysis and conductance measurements

Elemental analyses of complexes of Schiff base ligands (**Table-1**) indicate 1:2, M:L stoichiometry denoting the formation of mononuclear complexes in which ligands behaves as bidentate towards the metal ions. The resulting complexes are solids and are soluble in dimethylformamide. The conductivity values measured for  $10^{-3}$ M solution in anhydrous DMF is in the range  $13\text{--}22 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , to be non-electrolytes.

**Table-1. Physical and analytical data of the ligand and its metal complexes**

Compound	Color	m.p. (°C)	yield (%)	M. cond. $\text{m}^2 \text{mol}^{-1}$	M.wt Calc (found)	Microwave irradiation (Time/min)	Analysis (%): Found/(Calcd)			
							C	H	N	S
L <sup>1</sup>	Brown	268-70	89	15	307 (314)	4	62.5 (62.7)	4.2 (4.4)	22.7 (22.9)	10.4 (10.1)
L <sup>2</sup>	grey	255-60	89	22	357.4 (363.2)	8	67.2 (67.7)	4.2 (4.4)	22.5 (22.9)	8.9 (8.1)
Sn(L <sup>1</sup> ) <sub>2</sub> Cl <sub>2</sub>	Brick-red	>300	85	20	804 (817)	7	47.7 (47.9)	3.2 (3.5)	17.4 (17.8)	7.9 (7.5)
Sn(L <sup>2</sup> ) <sub>2</sub> Cl <sub>2</sub>	Brown	278-80	92	18	904 (922)	4	53.1 (53.4)	3.3 (3.4)	15.4 (15.1)	7.0 (7.2)
Cd(L <sup>1</sup> ) <sub>2</sub> Cl <sub>2</sub>	Green	287-90	83	21	798 (802)	7	48.1 (48.4)	3.2 (3.6)	17.5 (17.7)	8.0 (8.5)
Cd(L <sup>2</sup> ) <sub>2</sub> Cl <sub>2</sub>	Cream	>300	92	19	898 (890)	4	53.4 (53.8)	3.3 (3.6)	15.5 (15.1)	7.1 (7.2)

### Metal estimations

#### Cadmium

Cadmium hydroxide was precipitated from an aliquot of calcium chloride stock solution by adding a slight excess of sodium hydroxide. To free it from chlorides and excess sodium hydroxide, the precipitated was washed with hot water in a sintered-glass funnel by applying suction. The wet, purified precipitate of cadmium hydroxide was completely transferred to a glass-stoppered Erlenmeyer flask. About 10 mL of saturated, carefully neutralized solution of sodium thiosulfate were then added, the mixture was vigorously shaken, and the liberated alkali was titrated with 0.1 N hydrochloric acid should be carried out as gradually as possible using methyl orange as an indicator.

#### Tin

A weighed amount of the compound was digested with 2 mL of fuming sulphuric acid and 2 mL of fuming nitric acid in a pre-weighed silica crucible. When the evolution of NO<sub>2</sub> fumes ceased, it was heated strongly and weighed as SnO<sub>2</sub>.

## Magnetic susceptibility

Complexes are diamagnetic in nature at room temperature.

## Electronic Spectral studies

The natures of the ligand field around the metal complexes were deduced from the electronic spectra of the complexes. In the electronic spectra of the ligand, a band arise from the >C=N chromophore at ~370 nm [xxx] shifted to a shorter wavelength for the complexes. Such a shift in the n- $\pi^*$  band was probably due to the donation of lone pair of electron by nitrogen of the ligand to the central metal atom. The bands of medium intensity at ~270 and 300 nm arising from the  $\pi$ - $\pi^*$  transition of the ligand remained almost unchanged in the spectra of tin complexes.

**Table.2 Vibrational ( $\nu$   $\text{cm}^{-1}$ ) spectral data of Schiff bases and their complexes**

Compound	C=C <sub>str.</sub>	C=N <sub>str.</sub>	NH <sub>str.</sub>	M-N <sub>str.</sub>	M-Cl	C=N <sub>str.</sub> (thiazole)
L <sup>1</sup>	1545	1683	3350	-	-	1578
L <sup>2</sup>	1578	1685	3350	-	-	1559
[Sn(L <sup>1</sup> ) <sub>2</sub> Cl <sub>2</sub> ]	1455,1559	1652	3350	525	490	1545
[Sn(L <sup>2</sup> ) <sub>2</sub> Cl <sub>2</sub> ]	1468, 1540	1658	3348	529	495	1538
[Cd(L <sup>1</sup> ) <sub>2</sub> Cl <sub>2</sub> ]	1487, 1578	1638	3311	525	487	1543
[Cd(L <sup>2</sup> ) <sub>2</sub> Cl <sub>2</sub> ]	1478,1549	1642	3317	527	486	1543

## Infrared Spectral studies

In the IR spectra of Schiff bases shows the appearance of >C=N- (azomethines) [xxii] functional group peak indicates that the expected imino compound was formed by the condensation of thiazole derived amines and substituted aromatic ketones and it was also shown that there is no residual starting materials left as well. The IR spectra showed the band at 1683  $\text{cm}^{-1}$  assigned [xxiii] to the >C=N- vibration of ligands which were shifted to the lower frequency by 15 - 20  $\text{cm}^{-1}$  [xxiv] after complexation at 1652  $\text{cm}^{-1}$ . The band appear at 1578 -1550  $\text{cm}^{-1}$  [xxv-xxvii] assigned to the benzothiazole ring nitrogen  $\nu_{\text{C=N}}$  also shifts to the lower frequency which indicates the involvement of ring nitrogen of benzothiazole moiety in chelation. This shift indicates the coordination of ligand to metal atom by the nitrogen of the azomethine and the practically unchanged band of  $\nu_{\text{C-S}}$  appeared at 685  $\text{cm}^{-1}$  [xxii] of the thiazole ring confirmed that the thiazole group itself does not coordinate to metal center by sulfur atoms. Further conclusive evidence of the coordination of these Schiff bases with the metal ions were shown by the appearance of a new frequency band at 525  $\text{cm}^{-1}$  and ~490  $\text{cm}^{-1}$  due to  $\nu(\text{M}\leftarrow\text{N})$  and  $\nu(\text{M}\leftarrow\text{Cl})$  respectively [xxviii-xxix].

## X-Ray Studies

The X-ray diffraction spectrum of the complex, Sn(L<sup>1</sup>)<sub>2</sub>Cl<sub>2</sub> has been recorded in order to have an idea about the lattice dynamics of the compounds. The observed inter planar spacing values ('d' in  $\text{\AA}$ ) have been measured from the diffractogram of the compound and the Miller Indices h, k and l have been assigned to each d value and  $2\theta$  angles are reported in **Table-4** The results show that the compound, belongs to 'Tetragonal' crystal system having unit cell parameters as a = 15.859, b = 15.859, c = 15.95  $\alpha = \beta = \gamma = 90^\circ$ , respectively, max deviation of  $2\theta = 0.043$ . On the basis of the said spectral analyses, suitable structures have been suggested for new complexes.

**Table-4.X-ray powder diffraction data of [Sn(L<sup>1</sup>)<sub>2</sub>Cl<sub>2</sub>] complex**

S. No.	2θ (Obs)	2θ (Calcd)	Intensity	h	K	l	d-spacing °A(Obs)
1	26.353	26.310	558.44	3	3	2	3.379
2	30.795	30.833	516.74	5	1	2	2.901
3	32.346	32.312	422.56	4	1	4	2.765
4	33.721	33.688	1136.37	0	0	6	2.655
5	36.568	36.566	730.77	4	1	5	2.455
6	37.812	37.852	480.82	3	0	6	2.377
7	43.221	43.201	511.71	3	0	7	2.091
8	46.015	46.001	650.85	6	2	5	1.970
9	54.269	54.239	371.54	2	2	9	1.688
10	57.092	57.100	269.76	9	0	4	1.611
11	63.555	63.567	261.81	9	1	6	1.462
12	66.809	66.799	217.61	8	4	7	1.399
13	70.322	70.364	228.56	10	4	5	1.337
14	71.674	71.667	205.07	9	1	8	1.315
15	73.380	73.393	220.30	3	0	12	1.289
16	76.008	76.015	262.44	10	6	5	1.251
17	80.002	79.985	248.28	2	3	13	1.198

Refined Values of a = 15.859; b = 15.859; c = 15.95  $\alpha = \beta = \gamma = 90^\circ$  (Tetragonal lattice).

These values suggest the octahedral geometry around the tin metal and these are in agreement with the previously reported values

### <sup>1</sup>H NMR Spectral studies

The proton magnetic resonance spectra of the Schiff bases and their paramagnetic ruthenium complexes were taken in the DMSO-*d*<sub>6</sub>. The chemical shift values related to the TMS peak are listed in **Table-3**. The Schiff bases exhibited signals due to all expected protons in their expected region. Comparison of the chemical shifts of the uncomplexed Schiff bases with those of the corresponding complexes shows that some of the resonance signals underwent a shift upon complexation. In each case the protons assigned to the aromatic (thiazole/ benzothiazole moiety) were found at ~7.3 -8.0 ppm in the spectra of Schiff bases. The protons due to aromatic groups underwent a downfield shift to 0.9-1.0 ppm in the complexes indicating coordination of these groups with metal ions. Thus <sup>1</sup>H NMR and IR spectral observations are complimentary with one another with respect to ligating behavior of the ligands.

**Table-3.<sup>1</sup>H NMR spectral data (δ ppm) of the ligands and their complexes**

Compound	δ (N-H) pyrole(s)	δ (C-H) pyrole(s)	δ (N-H) indole(s)	δ (CH <sub>2</sub> ) (m)	δ (Ar-CH) (m)	δ (CH <sub>2</sub> ) thiazole (d)
L <sup>1</sup>	12.1	8.30	10.1	1.3-2.4	7.0-7.3	7.4-8.2
L <sup>2</sup>	12.4	8.2	10.1	1.3-2.4	7.3-8.0	-
[Sn(L <sup>1</sup> ) <sub>2</sub> Cl <sub>2</sub> ]	12.1	8.3	10.3	1.8-3.3	7.6-7.8	8.3-9.1

[Sn(L <sup>2</sup> ) <sub>2</sub> Cl <sub>2</sub> ]	12.4	8.30	10.2	1.8-3.3	7.4-8.1	-
[Cd(L <sup>1</sup> ) <sub>2</sub> Cl <sub>2</sub> ]	12.2	8.3	10.1	1.5-2.4	7.0-7.3	8.3-8.9
[Cd(L <sup>2</sup> ) <sub>2</sub> Cl <sub>2</sub> ]	12.4	8.20	10.1	1.8-3.1	7.4-8.1	-

### Mass spectra

Mass spectra provide a vital clue for elucidating the structure of compounds. The electronic impact mass spectrum of the L<sup>2</sup> ligand showed a molecular ion (M<sup>+</sup>) peak at m/z = 363 corresponding to [C<sub>20</sub>H<sub>15</sub>N<sub>5</sub>S], which confirmed the proposed formula. The different competitive fragmentation pathways of ligand gave peaks at m/z 166, 195, 239, 254, 266, 270. The intensities of these peaks give the stability and abundance of the fragments.

### Thermogravimetric analysis

The preliminary studies on thermal stability of Schiff base complexes were carried out by TGA in air. It has been seen that all these materials exhibit quite high thermal stability. Complex begins to decompose around 200-300 °C range suggests that the loss in weight in all complexes corresponds to the evaporation of ligand. Then loses weight rapidly up to 500 °C is due to the loss in the weight of remaining organic ligand molecule. In all cases remaining residues are metal oxides. These results are according to the composition of the complexes.

### Pharmacological results

#### In vitro antibacterial and antifungal activities

The antibacterial and antifungal studies suggests that the both the Schiff bases were found to be biologically active and their metal complexes showed significantly enhanced antibacterial and antifungal activities. It is, however, known that, chelating tends to make the Schiff bases acts as more powerful and potent and bacteriostatic agents, thus inhibiting the growth of bacteria and fungi more than the Schiff bases.

In case of antibacterial studies it was observed that both the Schiff bases were found to be potentially active *E. Coli* and *B. Subtilis*. Metal complexes showed much enhanced activity (Table-5).

**Table-5. Antibacterial and antifungal data of ligands and complexes investigated.**

S. No.	Compound	Bacteria		Fungi	
		B. Subtilis	E. Coli	A. Niger	A. Flavus
1.	L <sup>1</sup>	25	23	10	16
2.	L <sup>2</sup>	23	25	15	14
3.	[Sn(L <sup>1</sup> ) <sub>2</sub> Cl <sub>2</sub> ]	27	31	39	32
4.	[Sn(L <sup>2</sup> ) <sub>2</sub> Cl <sub>2</sub> ]	35	35	50	35
5.	[Cd(L <sup>1</sup> ) <sub>2</sub> Cl <sub>2</sub> ]	32	34	36	34
6.	[Cd(L <sup>2</sup> ) <sub>2</sub> Cl <sub>2</sub> ]	25	28	19	24

inhibition zone diameter mm (% inhibition)

Both the Schiff bases and complexes showed high antifungal activity than the antibacterial activity. Antifungal activity of synthesized Schiff bases and some of their complexes is almost nearer to the standard drug fluconazole.

The ligands showed moderate antibacterial activity, however they showed good antifungal activity. It is evident from data that the activity significantly increased on coordination. This enhancement in the activity of the both may be rationalized on the basis that their structures mainly possess  $>C=N-$  bond. It has been suggested that the ligand with the nitrogen donor systems inhibit enzyme activity. Since the enzymes which require these groups for their activity appears to be especially more susceptible to the deactivation by metal ion on coordination. Moreover, coordination reduces the polarity of metal ion mainly because of the partial sharing of its positive charge with the donor groups within the chelate ring <sup>[31]</sup> system formed during coordination.

### Antifertility activity

No significant change in the body weights of the rats were observed after the treatment with the starting materials, ligands and their tin complexes. However, significant decrease in the weight of the testes, epididymis and seminal vesicles were observed in tested animals (**Table-6**).

**Table-6. Effects of synthesized compounds on body and reproductive organ weights of the male rat.**

S. No.	Treatment	Body weight (g)			Organ weight (mg)	
		Initial	Final	Testes	Epididymis	Seminal vesicle
1.	Control	225 ± 22.5	238 ± 21.5	1390 ± 30.5	450 ± 18.9	485 ± 22.5
2.	L <sup>1</sup>	228.6 ± 13.4	240 ± 12.5	620.6 ± 20.4	242.6 ± 15.6	232.6 ± 13.4
3.	[Sn(L <sup>1</sup> ) <sub>2</sub> Cl <sub>2</sub> ]	210 ± 13.4	227 ± 15.4	740 ± 27.4	310 ± 13.4	325 ± 11.4

### Sperm mortality and density

Oral administration of starting materials and tin complexes results in a significant decline in the sperm mortality in cauda epididymis and sperm density in the testes and cauda epididymis (**Table-7**).

**Table-7. Sperm dynamics of ligand and its tin(II) complex on treated rats**

S. No.	Treatment	Sperm mortality (Cauda epididymis) (%)	Sperm density (million/cm <sup>3</sup> )		Fertility tests (%)
			Testis	Epididymis	
1.	Control	85.0 ± 4.9	5.1 ± 0.30	57.5 ± 4.5	100
2.	L <sup>1</sup>	28.5 ± 4.5	4.1 ± 0.11	27.3 ± 1.5	74
3.	[Sn(L <sup>1</sup> ) <sub>2</sub> Cl <sub>2</sub> ]	32.5 ± 7.1	4.8 ± 0.13	45 ± 3.4	98



## Fertility

The sluggish motile sperm were unable to fertile normal cyclic females. The test was 74 to 90 percent negative in the treated animals (**Table-7**).

## Conclusions:

This paper reports the synthesis and characterization of two new Sn(II) and Cd(II) complexes with thiazole derived ligand and investigating their spectral studies. The procedure is simple and efficient towards various aryl ketones. Physico-chemical characterization revealed that the ligand coordinates to metal ions in a bidentate manner with NN donor sites. Octahedral stereochemistry around the metal ions has also been proposed on the basis of above-mentioned studies. The complexes showed enhanced pharmacological activity compared with the ligand. Complex  $[Cd(L^2)Cl_2]$  exhibited low activity while the remaining complexes showed very good activity. Enhanced activity of the complexes was due to the increased lipophilic character owing to metal coordination.

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## References :

- i. S. Kumar, D. N. Dhar, P. N. Saxena, J. Sci. Ind. Res.68, 181 (2009).
- ii. T. Nguyen, A. D. Sutton, M. Brynda, J. C. Fettinger, G. J. Long, P. P. Power, *Science* 4, 844 (2005).
- iii. E. P. Balskus, C. T. Walsh, *Science* 24, 1653 (2010).
- iv. D. Sriram, P. Yogeeswari, N. S. Myneedu, V. Saraswat, *Bioorg. & Med. Chem. Lett.* 16, 2127 (2006).
- v. M. Nath, R. Yadav, M. Gielen, H. Dalil, D. de Vos, G. Eng, *Appl. Organometal. Chem.* 11, 727 (1997).
- vi. C.K. Modia and D.H. Janib, *Appl. Organometal. Chem.* 25, 429 (2011).
- vii. R. S. Hunoora, B. R. Patila, D. S. Badigera, R. S. Vadavia, K. B. Gudasia, V. M. Chandrashekar, I. S. Muchchandib, *Appl. Organometal. Chem.* 25, 476 (2011).
- viii. M. T. H. Tarafder, K. T. Jin, K. A. Crouse, *Polyhedron* 21, 2547 (2002).
- ix. A. H. Pathan, G. N. Naik, R. P. Bakale, S. S. Machakanur, K. B. Gudsai, *Appl. Organometal. Chem.* 26, 148 (2012).
- x. U. El-Ayaan, A. A. M. Abdel-Aziz, *Eur. J. Med. Chem.* 40, 1214 (2005).
- xi. K. B. Gudasi, S. A. Patil, R. S. Vadavi, R. V. Shenoy, M. S. Patil, *Transition Met. Chem.* 30, 1014 (2005).
- xii. M. A. Ali, M. H. Mirza, G. A. Fong, *Transition Met. Chem.* 29, 613 (2004).
- xiii. T. O. Shmakova, D. A. Garnovskii, K. A. Lysenko, E. P. Lvakhnenko, V. I. Simakov, I. S. Vasilchenko, A. I. Uraev, A. S. Burlov, M. Y. Antipin, A. D. Garnovskii, I. E. Uflyand, *Russ. J. Coord. Chem.* 35, 657 (2009).
- xiv. N. Patel, H. H. M. Parekh, M. N. Patel, *Transition Met. Chem.* 30, 13 (2005).
- xv. Manju, A. Chaudhary, D. Kumar, *Asian J. Chem. & Environ. Res.* 3, 13 (2010).
- xvi. Manju, D. Kishore, D. Kumar, *J. Coord. Chem.* 64, 2130 (2011).
- xvii. T. A. K. Al-Allaf, L. J. Rshan, A. Stelzner, D. R. Powell, *Appl. Organomet. Chem.* 17,

- 891 (2003).
- xviii. N. A. Oztas, G. Y. Ehirli, N. Ancin, S. G. Oztas, Y. Ozcan, S. Ide, *Spectro. Chem. Acta*, part A.72, 929 (2009).
- xix. E. Labisbal, L. R. Guez, A. S. Pedrares, M. Alonso, A. Vizoso, J. Romero, J. A. G. Vazquez, A. Sousa, , *J. Organomet. Chem.* 691, 1321 (2006).
- xx. N. K.obakhidze, N. Farfan, M. Romero, J. M. M. Stivalet, M. G. B. Lopez, H. G. Ortega, O. Dominguez, R. Santillan, F. S. Bartz, I. G. Mora, *J. Organomet. Chem.*695, 1189 (2010).
- xxi. M. X. Li, D. Zhang, L. Z. Zhang, J. Y. Niu, B. S. Ji, *J. Organomet. Chem.*696, 852 (2011).
- xxii. L. J. Bellamy, *Infrared spectra of complex molecules*, 3<sup>rd</sup> Ed, Methuen: London (1966).
- xxiii. M. A. Neelakantan, S. S. Marriappan, J. Dharmaraja, T. Jeyakumar, K. Muthukumaran, *SpectrochimicaActa Part A.*71, 628 (2008).
- xxiv. K. Nakamoto, *Infrared Spectra of Inorganic and coordination compounds Part A: Theory and Applications in Inorganic Chemistry*, 6<sup>th</sup> Ed., Wiley, John Wiley & Sons, Inc., Hoboken, New Jersey (2009).
- xxv. C. A. Bolos, P. V. Fanourgakis, P. C. Christidis, G. S. Nikolov, *Polyhedron*18, 1661 (1999).
- xxvi. N. L. D. Filho, *Polyhedron*18, 2241 (1999).
- xxvii. Q. F. Yin, B. Z. Ju, S. F. Zhang, X. B. Wang, J. Z. Yang, *Carbohydr. Polym.*72, 326 (2008).
- xxviii. L. J. Bellamy, *The Infrared spectra of complex molecules*, 2<sup>nd</sup> Ed., Chapman & Hall, Metheum, London (1958).
- xxix. Z. H. Chauhan, C. T. Surpan, *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*32, 1445 (2002).
- xxx. S. Gaur, N. Fahmi, R. V. Singh, *Phosphorus, Sulphur and Silicon.*182, 853 (2007).
- xxxi. Z. H. Chohan, H. A. Shad, F. H. Nasim, *Appl. Organomet. Chem.*23, 319 (2009).

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