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Synthesis, Characterization and Biological Studies of Organotin(IV) Thiocarbamates

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Organotin(IV) derivatives of dithiocarbamic acid having the general formula R_2SnL_2 and R_3SnL have been prepared by reacting 1-(2-pyridyl)piperazinedithiocarbamic acid and organotin(IV) chloride in stoichiometric amount in dry ethanol. These compounds have been characterized by IR, multinuclear NMR (^1H, ^{13}C, ^{119}Sn) spectral analyses. The spectroscopic data revealed that triorganotin(IV) derivatives are four-coordinated in non-coordinating solvent and have five-coordinated polymeric geometry around the tin in solid state. Diorganotin dithiocarbamates are found to be penta-coordinating in non-coordinating solvent. While in solid state geometry around tin may be hexa-coordinated. These compounds have also been screened for bactericidal and fungicidal activities. LD_{50} data have also been collected by Brine-Shrimp lethality bioassay method.

Key Words: Thiocarboxylates, Organotins, Biological activity.

INTRODUCTION

Organotin thiocarboxylates interact strongly with biological substrate and have catalytic applications[1-3]. Thiocarboxylic acid and their transition metal complexes have attracted much attention due to their interesting structural properties[4-6]. Thiocarboxylic acid ligand has been used as fungicides, pesticides, vulcanization accelerator, floating agent, lubricant additives and in thin film deposition by chemical vapour deposition method (CVD)[7]. Organotin(IV) thiocarboxylate is a subject of investigation due to their interesting structural behaviour and biological activity[8-10].

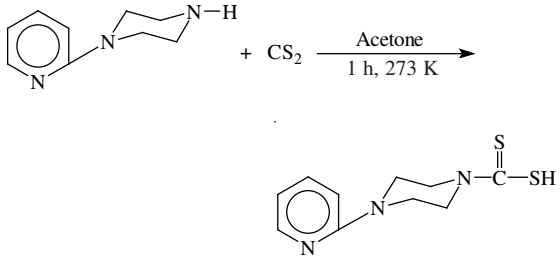
In view of the interesting results reported for organotin thiocarboxylates, it is considered worthwhile to synthesize the organotin(IV) thiocarbamate derivatives and investigate their nature of bonding with tin. Therefore, as a part of our group investigations on organotin compounds[11-15], we attempt to synthesize new complexes of organotin(IV) with 1-(2-pyridyl) piperazinedithiocarbamic acid and are characterized by different spectroscopic techniques. In this paper we are reporting the synthesis, characterization and biological activity of organotin(IV) thiocarbamates.

EXPERIMENTAL

Melting points were determined in a capillary tube using electrothermal melting point apparatus model MP-D Mitamura Ricken Kogyo (Japan). The infrared absorption spectra were recorded as KBr pallets on a Bio-Rad Spectrometer (USA). ^1H and ^{13}C NMR were recorded on Bruker 300 FT-NMR, using $CDCl_3$ as internal reference, (δ ^1H $CDCl_3$-7.24 ppm) and (δ ^{13}C $CDCl_3$-77.6 ppm).

Analytical grade organotin(IV) chlorides were purchased from Aldrich Chemical Company. 1-(2-Pyridyl) piperazine was procured from ACROS and CS_2 was obtained from Riedel-de-Haen. Organic solvents used such as acetone, ethanol, tetrahydrofuran (THF), methanol, chloroform, *n*-hexane, toluene and dimethyl sulfoxide (DMSO) were of E-Merck and Fluka and dried *in situ* by the reported methods[16].

Synthesis of 1-(2-pyridyl)piperazinedithiocarbamic acid: A solution of 1-(2-pyridyl)piperazine (1 mmol) in acetone (50 mL) was added dropwise to carbon disulfide (1 mmol) in a round bottom two necked flask (250 mL) equipped with water condenser (**Scheme-I**). The solution was stirred at 273 K for 1 h and than allowed to stand overnight at room

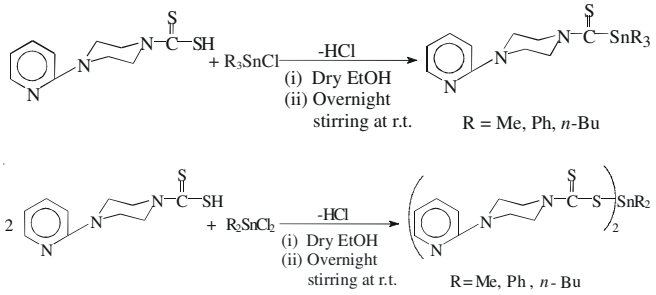


1-(2-Pyridyl)piperazine 1-(2-Pyridyl)piperazine-dithiocarbamic acid

Scheme-I: Synthesis of ligand

temperature. Solvent was evaporated under reduced pressure by rotary evaporator. Solid product obtained was recrystallized from chloroform.

General procedure for synthesis of organotin(IV) thiocarbamate: Di- and triorganotin(IV) chloride reacts with 1-(2-pyridyl)piperazinedithiocarbamic acid as depicted in the following **Scheme-II**.

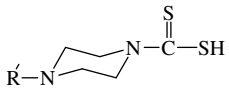


Scheme-II: Synthesis of organotin(IV) thiocarbamates

Ethanolic solution containing stoichiometric amount of 1-(2-pyridyl)piperazinedithiocarbamic acid (1 g, 4.18 mmol) was added dropwise to an ethanolic solution of R_2SnCl_2 (0.5 mmol) or R_3SnCl (1 mmol). The mixture was stirred for 24 h at room temperature. The solid product obtained was collected by filtration and recrystallized from chloroform.

RESULTS AND DISCUSSION

The ligand 1-(2-pyridyl)piperazinedithiocarbamic acid was synthesized by following procedure as shown in **Scheme-I** with all the necessary conditions[17]. The yield obtained is 80 %. The synthesized ligand acid is a crystalline solid, having high melting point.

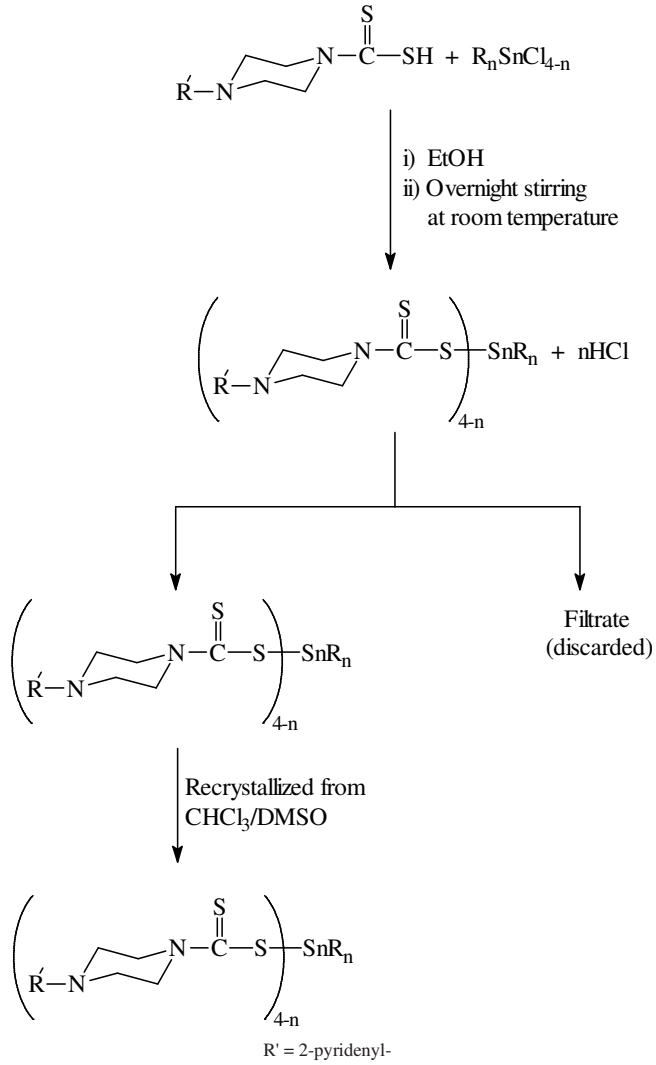
Complexes of di- and triorganotin(IV) were synthesized by stirring the stoichiometric amount of the ligand acid,  with the corresponding organotin(IV) chloride in dry ethanol for 24 h (**Scheme-III**).

The physical properties of the synthesized compounds are given in Table-1. All the compounds are stable and soluble in common organic solvents.

TABLE-1
PHYSICAL DATA OF ORGANOTIN(IV) DERIVATIVES OF DITHIOCARBAMIC ACID

Comp. No.	General Formula	m.f.	m.w.	m.p. (°C)	Solubility
HL	HL	$C_{10}H_{13}N_3S_2$	239	180-82	$CHCl_3$, DMSO
I	Me_2SnL_2	$C_{22}H_{30}N_6S_4Sn$	625	104-06	$CHCl_3$
II	Me_3SnL	$C_{13}H_{21}N_3S_2Sn$	402	185-87	$CHCl_3$, DMSO
III	Bu_2SnL_2	$C_{28}H_{42}N_6S_4Sn$	709	156-58	$CHCl_3$
IV	Bu_3SnL	$C_{22}H_{39}N_3S_2Sn$	528	190-92	$CHCl_3$
V	Ph_2SnL_2	$C_{32}H_{34}N_6S_4Sn$	749	170-72	DMSO
VI	Ph_3SnL	$C_{28}H_{27}N_3S_2Sn$	588	225-27	$CHCl_3$

Infrared spectroscopy: Infrared spectra of organotin(IV) derivatives of 1-(2-pyridyl)piperazinedithiocarbamic acid

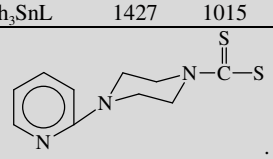


Scheme-III: Synthesis of organotin(IV) thiocarbamates

have been recorded in the range of 4000-400 cm^{-1} as KBr discs and the most important bands of investigated complexes are given in Table-2.

TABLE-2
IR DATA (cm^{-1}) FOR ORGANOTIN(IV) DERIVATIVES OF DITHIOCARBAMIC ACID[a]

Sample Number	ν(C-N)	ν(C-S)	ν(C=S)	ν(S-H)	ν(Sn-C)	ν(Sn-S)
HL	1480	1011	932	2716	–	–
Me_2SnL_2	1427	1011	976	–	552	409
Me_3SnL	1435	1011	932	–	563	408
n-Bu_2SnL_2	1435	1011	934	–	575	408
n-Bu_3SnL	1459	1024	876	–	560	–
Ph_2SnL_2	1431	1012	989	–	594	450
Ph_3SnL	1427	1015	934	–	583	445

a 

In organotin(IV) dithiocarbamates, comparison was made between the spectra of complexes and their precursors. The N-H bond in 1-(2-pyridyl)piperazine (secondary amine)

stretching at 3200 cm^{-1} disappeared when it is reacted with carbon disulfide, indicating the formation of ligand acid. The disappearance of S-H bond stretching frequency of the free ligand nearly at 2550 cm^{-1} and appearance of Sn-S bond stretching in the range of 445-408 cm^{-1}, indicates the formation of complexes[17].

Bands in the range of 594-552 and 445-408 cm^{-1} indicate the presence of Sn-C and Sn-S bonds in the synthesized compounds, respectively[18]. In organotin(IV) derivatives of 1-(2-pyridyl)piperazinedithiocarbamic acid, appearance of single bands for C-N and C=S bonds at 1480-1431 cm^{-1} and 989-876 cm^{-1}, respectively show the bidentate nature of ligand acid[19] and suggest trigonal bipyramidal structure (Fig. 1c) or bridged polymeric structure for the triorganotin compounds (Fig. 1b), while diorganotin(IV) compounds support the distorted octahedral geometry.

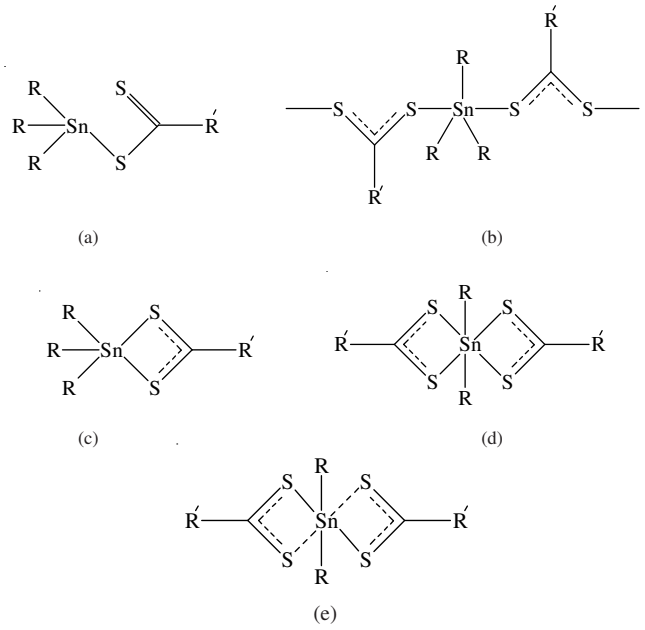


Fig. 1. Proposed structures (a), (b) and (c) for triorganotin(IV) dithiocarbamates and (d) and (e) for diorganotin(IV) dithiocarbamates

Multinuclear NMR spectroscopy: The ^1H NMR spectral data for the synthesized compounds and free acids have been recorded in $CDCl_3$ or DMSO solutions and are reported in Table-3. In the spectrum of the ligand, SH proton resonates at 1.26 ppm as a singlet, while the signals at 3.11 and 3.60 ppm with their distinct multiplicities and *J* values have been assigned to piperazine protons and at 6.63, 7.49, 6.66 and 8.20 ppm to protons of pyridyl moieties of the ligand (Table-3). The analogous pattern of the signals at rather similar positions has been observed for the investigated compounds (Table-3).

The absence of SH proton resonance in all of the compounds confirm the formation of organotin(IV) dithiocarbamates. In diphenyl- and triphenyltin(IV) derivatives (compounds **V** and **VI**), a complex pattern is observed in the range of 7.36-7.54 and 7.56-7.77 ppm due to the aromatic protons of the ligand and phenyl groups of the complexes. However, for di- and trimethyltin(IV) derivatives, the methyl protons appeared as sharp singlets at 1.32 and 0.65 ppm with well resolved $^2J[^{119}Sn, ^1H]$ = 73.6 and 59.6 Hz, respectively. The coupling constants and C-Sn-C bond angle (Table-5) 109º and 111º, calculated by Lockhart's equation, support five-coordinated geometry for the dimethyl- and a four-coordinated one for the trimethyltin(IV) dithiocarbamates in non-coordinating solvent[20]. The protons of the *n*-butyl moieties of the di- and tri-*n*-butyltin(IV) also show a complex pattern and were assigned according to the literature[21-24].

Despite the complex pattern of ^1H NMR spectra of *n*-butyltin(IV) derivatives (compound **III** and **IV**), a clear triplet due to the terminal methyl group appears in both at 0.95 and 0.94 ppm, respectively with $^3J[^1H, ^1H]$ = 7.4 and 7.2 Hz. Here again the coupling constant and the calculated C-Sn-C bond angle in solution, based on $^2J[^{119}Sn,^1H]$ value as given in Table-5, support the four-coordinated geometry for the tri-*n*-butyltin(IV) dithiocarbamate in non-coordinating solvent[25].

^{13}C NMR spectral data in $CDCl_3$ or DMSO solutions of ligand acid (HL) and their respective di- and triorganotin(IV) derivatives are given in Table-4. The number of signals observed for the ligand acid corresponds to the presence of

TABLE-3
^1H NMR DATA OF ORGANOTIN(IV) DERIVATIVES OF DITHIOCARBAMIC ACID[a,b,c]

^1H No.	Compound						
	Ligand	**I** Me_2SnL_2	**II** Me_3SnL	**III** *n*-Bu_2SnL_2	**IV** *n*-Bu_3SnL	**V** Ph_2SnL_2	**V** Ph_3SnL
SH	1.27 (s)	–	–	–	–	–	–
2,2'	3.11 (t, 5.4)	3.80 (t, 5.4)	3.80 (t, 5.4)	3.71 (t, 5.4)	3.26 (t, 5.4)	3.17 (t, 5.4)	3.70 (t, 5.4)
3,3'	3.60 (t, 5.1)	4.10 (t, 5.1)	3.64 (t, 5.4)	4.22 (t, 5.4)	3.79 (t, 5.1)	3.71 (t, 5.1)	4.22 (t, 5.1)
5	6.63 (t, 6.0)	6.60 (t, 6.9)	6.64 (t, 6.9)	6.70 (t, 6.9)	6.68 (t, 6.3)	6.74 (t, 6.9)	6.71 (t, 7.2)
6	7.49 (t, 7.2)	7.57 (t, 7.5)	7.50 (t, 7.8)	7.51 (t, 7.2)	7.53 (t, 7.2)	7.95 (t, 7.2)	7.55 (t, 7.2)
7	6.66 (d, 8.4)	6.70 (d, 8.4)	6.67 (d, 8.4)	6.64 (d, 8.4)	6.70 (d, 8.7)	6.91 (d, 8.7)	6.64 (d, 8.4)
8	8.20 (d, 3.9)	8.23 (d, 3.3)	8.19 (d, 3.9)	8.22 (d, 3.3)	8.19 (d, 2.7)	8.13 (d, 3.0)	8.21 (d, 3.0)
α	–	1.32 [73.6]	0.65 [59.6]	1.91 (m)	1.59 (m) [54.3]	–	–
β	–	–	–	1.42 (m)	1.37 (m)	7.49 (m)	7.74 (m) [57.3]
γ	–	–	–	1.28 (m)	1.31 (m)	7.36 (m)	7.56 (m)
δ	–	–	–	0.94 (t) [12.9]	0.94 [12.2]	7.54 (m)	7.77 (m)

[a]Chemical shifts (δ) in ppm. ^nJ [^{119}Sn, ^1H] are listed in square brackets.

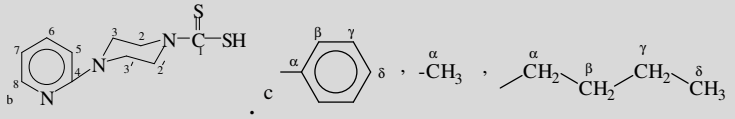


TABLE-4
^{13}C NMR DATA OF ORGANOTIN(IV) DERIVATIVES OF DITHIOCARBAMIC ACID[a,b]

^{13}C No.	Compound						
	Ligand	**I** Me_2SnL_2	**II** Me_3SnL	**III** n-Bu_2SnL_2	**IV** n-Bu_3SnL	**V** Ph_2SnL_2	**V** Ph_3SnL
1	180.10	196.89	197.90	200.76	198.20	192.98	196.52
2,2'	49.23	51.04	49.21	50.59	51.08	52.21	51.75
3,3'	44.83	44.33	44.84	44.45	44.47	43.80	44.37
4	158.67	158.12	158.68	158.60	158.66	158.58	158.44
5	107.43	107.22	107.43	107.22	107.30	107.65	107.00
6	137.96	137.97	137.95	137.72	137.79	138.30	136.16
7	114.49	114.47	114.48	113.95	114.37	114.55	114.04
8	148.05	148.03	148.05	148.07	148.05	148.05	148.06
α	–	10.09	14.00	18.10 [322]	17.80 [319]	144.0	138.9 [632]
β	–	–	–	28.50 [19]	28.88 [21]	135.64	136.1 [45]
γ	–	–	–	26.42 [62]	27.10 [65]	128.03	128.20
δ	–	–	–	13.80	13.70	130.57	129.10
^{119}Sn	–	+187.5	-167.2	–	+32.4	+57.5	-178.9

[a]Chemical shifts (δ) in ppm. [b]See footnote of Table-3 for numbering and α, β, γ, δ.

expected magnetically non-equivalent carbon atoms. The positions of aromatic (pyridyl) and aliphatic (piperazine) moieties, carbon signals undergo minor changes in the complexes as compared to that in the ligand. However, dithioate carbonyl (C=S) involvement in bonding to tin atom is confirmed by the resonance ascribed to C=S carbon, which exhibits large shift upon coordination[26].

The signals of the R groups attached to Sn atom, where R is Me, *n*-Bu and Ph, were assigned by comparison with their homologous, combined with the $^{n}J[^{119}Sn, ^{13}C]$ coupling constants[27-29]. The magnitude for $^{n}J[^{119}Sn, ^{13}C]$ coupling in compound (**I**)-(**VI**) are observed as given in Table-4.

In addition to $^{n}J[^{119}Sn, ^{1}H]$ the coupling constants, $^{n}J[^{119}Sn, ^{13}C]$ are also quite agreeable for making predictions about the geometry around the tin atom.

For the tri-*n*-butyltin(IV) derivative with the $^{1}J[^{119}Sn, ^{13}C]$ value being 319 Hz and by the use of Holecek *et al.*, equation[30,31] C-Sn-C value of 108.7º was calculated, which corresponds to a tetrahedral geometry in $CDCl_3$ solution (Table-4). For the diorganotin(IV) species for which earlier results indicate five-coordination, the calculated C-Sn-C angles are consistent with the bipyramidal geometries[26].

^{119}Sn NMR spectroscopy plays an important role in determining structures of organotin compounds. All the ^{119}Sn NMR spectra were recorded in $CDCl_3$ or DMSO solution as shown in Table-5 which shows ^{119}Sn NMR data for all the synthesized complexes with only exception of complex (III) because of its limited solubility in common organic solvents. In each case the ^{119}Sn spectrum shows only a sharp singlet indicating the formation of a single species with the ^{119}Sn resonance appearing at low frequency than that of its organotin chloride precursor. In general ^{119}Sn chemical shifts move to lower frequency with increasing coordination number[26]. Although the shift ranges are somewhat dependent on the nature of substituents at the tin atom, the following ranges have been proposed for some organotin(IV) dithiocarbamates, +200 to +45 ppm for four-coordinated compounds, -150 to 250 ppm for five coordinated compounds and -300 to -500 ppm for six-coordinated compounds[32]. On the basis of ^{119}Sn NMR data, it appears that compound (**I**) and (**V**) show tetrahedral geometry, whereas compounds (**II**), (**IV**) and (**VI**) show coordination number more than four.

TABLE-5
C-Sn-C ANGLES (º) CALCULATED FROM NMR PARAMETERS

Compound	$^{1}J[^{119}Sn, ^{13}C]$(Hz)	$^{2}J[^{119}Sn, ^{1}H]$ (Hz)	C-Sn-C Angles (º) calculated from	
			^{1}J	^{2}J
Me_2SnL_2	–	73.6	–	123.5
Me_3SnL	–	59.6	–	119.6
n-Bu_2SnL	322	–	109.0	–
n-Bu_3SnL	319	54.3	108.7	109.2
Ph_3SnL	632	57.3	115.4	110.6

Biological activty

Antifungal activity: Stock solution of the pure compounds (200 µg/mL) were prepared in sterile DMSO. Sabouraud dextrose agar was prepared by mixing sabouraud (35.5 g), glucose agar (4 %) and agar-agar (4 g) in 500 mL distilled water at 90-95 ºC on a water bath. 4 mL of media was dispensed into screw-capped tubes and autoclaved at 121 ºC for 15 min. The test compound (66.6 µL) was added from the stock solution to the non-solidify at room temperature and inoculated with 4 mm diameter of inoculums derived from a seven-day old respective fungal culture. For non-mycelial growth, an agar surface streak was employed. The tubes were incubated at 27-29 ºC for 7-10 days and the growth in the compound-containing media was determined by measuring the linear growth (mm) and growth inhibition with reference to the respective control[22].

The ligand acid, 1-(2-pyridyl)piperazine dithiocarbamic acid (HL) shows significant activity against *Trichophyton longifusus* and *Microsporum canis* while compounds (**I**), (**V**) and (**VI**) exhibit low activity against the said bacteria. Similarly, compound (**II**) shows significant activity against *Trichophyton longifusus*, *Aspergillus flavus*, *Microsporum canis* and *Fusarium solani*, while compound (**III**) gives moderate activity against *Microsporum canis*. However, compound (**IV**) was found to have significant activity against all the tested fungi, as shown in Table-6.

Antibacterial activity: The synthesized compounds were screened for antibacterial activity against a number of bacteria using imipenem as standard drug. Wells were dug in the media with the help of a sterile metallic borer with centres at least 24 mm apart. Two to eight hour old bacterial inoculums containing approximately 10^4-10^6 colony-forming units (CFU)/mL were

TABLE-6
ANTIFUNGAL ACTIVITY DATA[a,b,c] OF ORGANOTIN(IV) 1-(2-PYRIDYL)PIPERAZINE DITHIOCARBAMATES

Name of fungus	Inhibition (%)							Standard drug (μg/mL)	MIC (μg/mL)
	HL	I	II	III	IV	V	VI		
Trichlophyton longifusus	80	0	80	20	90	0	0	Miconazole	70
Candida albicans	0	0	0	0	80	0	0	Miconazole	110.8
As pergillus flavus	0	20	80	0	80	0	20	Miconazole	20
Microsporum canis	80	20	80	50	80	0	20	Miconazole	98.4
Fusarium solani	0	0	80	0	80	0	0	Miconazole	73.2
Candida glabrata	0	0	0	0	80	0	0	Miconazole	110.8

[a]MIC = Minimum inhibitory concentration. [b]Incubation period = 7 days. [c]Concentration = 200 μg/mL of DMSO.

spread on the surface of nutrient agar with the help of a sterile cotton swab. The recommended concentration of the test sample (1 mg/mL in DMSO) was introduced in the respective wells. Other wells supplemented with DMSO and reference antibacterial drugs serving as negative and positive controls, respectively. The plates were incubated immediately at 37 ºC for 20 h. The activity was determined by measuring the diameter of zones showing complete inhibition (mm). Growth inhibition was calculated with reference to positive control. LD_{50} values were also determined by a brine-shrimp method[18].

All the synthesized compounds were also subjected to screening test for their antibacterial activity, using the agar well diffusion method[23] and the results are summarized in Table-7.

TABLE-7
ANTIBACTERIAL ACTIVITY DATA[a,b,c] OF ORGANOTIN(IV) 1-(2-PYRIDYL)PIPERAZINE DITHIOCARBAMATES

Name of bacterium	Zone of inhibition (nm)							Ref. drug
	L	I	II	III	IV	V	VI	
Escherichia coli	–	–	–	–	30	14	18	25
Bacillus subtilis	10	11	9	10	40	19	22	26
Shigella flexenari	–	15	12	11	–	12	–	24
Staphylococcus aureus	13	12	12	12	–	16	–	17
Pseudomonas aeruginosa	15	18	12	10	14	11	19	17
Salmonella typhi	11	12	11	10	–	17	20	21

[a] – = Show no activity. [b]Concentration = 100 μg/mL of DMSO. [c]Standard drug = imipenem.

The ligand acid (HL) shows good activity against *Pseudomonas aeruginosa*, low activity against *Staphylococcus aureus* and non-significant activity against *Bacillus subtilis* and *Salmonella typhi*. Compound (**I**) shows significant activity against *Pseudomonas aeruginosa*, good activity against *Shigella flexenari* and low activity against *Staphylococcus aureus*, *Salmonella typhi* and *Bacillus subtilis*.

Similarly, compounds (**II** and **III**) show low activity against most of the bacteria (Table-7). Compound (**IV**) shows significant activity against *Escherichia coli* and *Bacillus subtilis* and low activity against *Pseudomonas aeruginosa*. Compound (**V**) shows good activity against *Bacillus subtilis*, *Staphylococcus aureus* and *Salmonella typhi*, while low activity against *Escherichia coli*, *Shigella flexenari* and *Pseudodomonas aeruginosa*.

The compound (**VI**) was observed to have significant activity against *Escherichia coli*, *Bacillus subtilis*, *Pseudomonas aeruginosa* and *Salmonella typhi*.

Cytotoxicity: LD_{50} data for synthesized compounds have been determined by brine-shrimp bioassay lethality method[24] and the results are summarized in Table-8. It has been observed that (**I**), (**III**) and (**V**) along with ligand acid (HL) show no cytotoxicity, while the compound (**II**) with LD_{50} value 5.57 μg/mL is the least and (**IV**) and (**VI**) are the most toxic compounds.

TABLE-8
LETHALITY BIOASSAY OF ORGANOTIN(IV) 1-(2-PYRIDYL)PIPERAZINE DITHIOCARBAMATES

Compound No.	Dose (μg/mL)	No. of shrimps	No. of survivors	LD_{50} (μg/mL)
L	100	30	27	–
	10	30	28	
	1	30	30	
I	100	30	23	–
	10	30	24	
	1	30	29	
II	100	30	6	5.5764
	10	30	14	
	1	30	20	
III	100	30	22	–
	10	30	28	
	1	30	29	
IV	100	30	0	0.00
	10	30	0	
	1	30	0	
V	100	30	22	–
	10	30	24	
	1	30	25	
VI	100	30	0	0.00
	10	30	0	
	1	30	0	

[a]Against brine-shrimp = *Artemia slaina*. [b]Standard drug = Etoposide. [c]LD_{50} of standard drug = 7.4625 (μg/mL).

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