Journal of Chemical Health Risks

www.jchr.org

JCHR (2023) 13(4), 1606-1615 | ISSN:2251-6727

Synthesis, characterization and structure activity relationship of novel biologically active heteroleptic complexes of tin (IV) with N, O and S donor ligands

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(Received: 02 September 2023 Revised: 14 October Accepted: 07 November)

KEYWORDS

Pyrazoline, Dithiophosphate, Tin(IV), Antimicrobial, Heteroleotic complexes

Abstract

A series of new heteroleptic complexes of Sn (IV) have been prepared by the reaction of $SnCl_4$ with nitrogen and oxygen donor 3(2'-hydroxyphenyl)5-(4-substitutedphenyl)Pyrazolines and sulfur donor O,O'-Dialkyl and alkylene Dithiophosphate under inert atmosphere. These newly synthesized complexes have been characterized by using elemental analysis, molecular weight measurements, FTIR, ^{1}HNMR, ^{13}CNMR, ^{119}SnNMR and ^{31}PNMR. These investigations suggest that, both ligands (pyrazoline and dithiophosphate) show monoanionic bidentate behavior and coordinate through $O_{phenolic}$, $N_{azomethine}$ and $S_{dithiphosphoric}$ donor groups. The bonding mode of Sn(IV) with both ligands in heteroleptic complexes have been discussed and tentative structure have also been proposed. All these complexes have been screened for antibacterial as well as antifungal activity. Structure activity relationship have also been discussed and these heteroleptic complexes were showing promising activity as compared to standards taken.

1. Introduction

Now a days, emergence of antimicrobial drug resistance is a serious threat to the global public health [1]. However, plenty of compounds as antimicrobial drug have been prepared since 1930 and most of them are from traditional sources (Organic Origin) which have limited structural variations and mode of actions [2]. So, these drugs may only target on genomic systems of the pathogens, as a result, microbes get evolved and become resistant to that drugs over the period of time easily [3]. Thus, there is a dire need to design new strategies for the development of potential compounds that could target both biochemical as well as multiple cellular processes for effective antimicrobial treatment. In order to achieve this goal, lots of studies have been carried out for developing new metal containing compounds with good biological activity as these compounds have wide range of three dimensional geometries and unique mode of action [4, 5]. According to literature survey, it was demonstrated that the pyrazoline compounds play a significant role in medicinal chemistry due to its variety of application in biological fields (such as anti-inflammatory, antidepressant, and antipyretic activities) as well as its structural diversity by incorporating electron donating and electron withdrawing groups in parent pyrazoline moiety [6]. Thus, pyrazoline metal complexes may offer remarkable activity as antimicrobial agents.

In spite of having biological properties, the uses of metal complexes for therapeutic purposes are limited due to the toxicity towards healthy cells. Despite this shortcomings, several researcher have reported many transition, organometallic and lanthanide complexes which are extensively investigated for their biological activity [7-10]. So that the syntheses of bioactive metal complexes with positive, limited or no side effects is considered reasonable. However, reports available on non-transition metal complexes are very few especially on inorganic tin due to its highly hygroscopic nature, despite of that its complexes with bioactive ligands may exhibit significant activity [11]. Thus, we wish to continue with less investigated inorganic tin (IV) complexes as it has well-known bioactive tin center. It has also been revealed that the combination of different ligands with metal (heteroleptic complexes) may enhance the biological activity [12]. Thus, in continuation of our previous work, we have chosen dithiophophates as sulfur containing ligands since they display high potency in metal chelation therapy [13] and have high efficacy as fungicides [14] and pesticides [15] as well as wide variety of coordination modes [16] that allowed to produce potential coordination

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JCHR (2023) 13(4), 1606-1615 | ISSN:2251-6727

compounds with most of the metals. Therefore, the syntheses of heteroleptic complexes of tin (IV) complexes with bioactive ligands could be a strategy of preparation of new compound with promising biological activity.

So, based on the above literature survey and the work carried out by our lab on pure homoleptic metal complexes and their activity. We are reporting here with the Synthesis, characterization, bioactivity and structure activity relationship in heteroleptic complexes of Tin (IV) with Pyrazoline and dithiophosphate.

2. Experimental

2.1. Material and Methods

All the solvents (benzene, methanol, ethanol etc.) were dried and purified by standard methods [17]. Chemicals used were of analytical grade quality. Tin tetrachloride (HPLC), Phosphorus pentasulfide (S.D.Fine), o-hydroxyacetophenone (CDH), benzaldehydes (E.Merk), sodium hydroxide (Glaxo), hydrochloric acid (Ranbaxy), acetic acid (CDH), and hydrazine hydrate (Ranbaxy) were used as received. Pyrazolines and ammonium dithiophosphate were prepared by the reported methods [18-20].

The complexes of Sn(IV) with 3(2'-hydroxyphenyl)5-(4-substitutedphenyl)Pyrazolines and O,O'-Dialkyl and alkylene Dithiophosphate of general formula $SnCl_2(C_{15}H_{12}N_2OX)[(RO)_2PS_2]$ and $SnCl_2(C_{15}H_{12}N_2OX)[S_2POGO]$ were prepared as following reaction scheme in a 1:1:1 molar ratio, where X= H, CH_3, OCH_3, Cl, R= $-CH_2CH_2CH_3$ and G = $-CH_2CMe_2CH_2-$.

Step 1:

$$SnCl_4 + C_{15}H_{12}N_2OX \xrightarrow{\text{Dry Benzene}} SnCl_3(C_{15}H_{12}N_2OX) + HCl$$

Step 2:

$$SnCl_3(C_{15}H_{12}N_2OX) + [(RO)_2PS_2]NH_4 \xrightarrow{\text{Methanol/Benzene}} SnCl_2(C_{15}H_{12}N_2OX)[(RO)_2PS_2] + NH_4Cl$$

$$SnCl_3(C_{15}H_{12}N_2OX) + [S_2\overline{POGO}]NH_4 \xrightarrow{\text{Methanol/Benzene}} SnCl_2(C_{15}H_{12}N_2OX)[S_2\overline{POGO}] + NH_4Cl$$

2.2. General Procedure

Under inert atmosphere, a benzene solution of $SnCl_4$ was added drop wise to the benzene solution of pyrazoline and stirred the content for 5-6 h until the visible color change was observed. The solution was cooled at low temperature (18˚C) and a methanolic solution of ammonium salt of dithiophosphate was added with constant stirring. The reaction mixture was further stirred for about 6 h. The by product was filtered off through alkoxy funnel and the solvent was removed under vacuum. A blackish brown colored solid was obtained. The newly synthesized compound was washed with ethanol and dried under the vacuum. Compound 1-8 were prepared by using this method. The physical details were given in table 1.

Table 1: Physical Characterization

S. No.	Complexes	Mol. Wt. found (calculated)	Yield	M. p.	State
1	$SnCl_2(C_{15}H_{12}N_2OH)[(C_3H_7O)_2PS_2]$	638.0438 (640.1714)	85	148	Amorphous solid
2	$SnCl_2(C_{15}H_{12}N_2OCH_3)[(C_3H_7O)_2PS_2]$	654.0012 (654.1979)	87	168	Amorphous solid
3	$SnCl_2(C_{15}H_{12}N_2O.OCH_3)[(C_3H_7O)_2PS_2]$	669.9100 (670.1973)	80	235	Amorphous solid
4	$SnCl_2(C_{15}H_{12}N_2OCl)[(C_3H_7O)_2PS_2]$	710.1758 (710.0705)	75	197	Amorphous solid
5	$SnCl_2(C_{15}H_{12}N_2OH)[S_2\overline{POCH_2C(CH_3)_2CH_2O}]$	625.1021 (624.1291)	83	174	Amorphous solid
6	$SnCl_2(C_{15}H_{12}N_2OCH_3)[S_2\overline{POCH_2C(CH_3)_2CH_2O}]$	638.0077 (638.1556)	78	194	Amorphous solid

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7	$SnCl_2(C_{15}H_{12}N_2O.OCH_3)[S_2POCH_2C(CH_3)_2CH_2($	654.3166 (654.1556)	88	270	Amorphous solid
8	$SnCl_2(C_{15}H_{12}N_2OCl)[S_2POCH_2C(CH_3)_2CH_2O]$	659.0017 (658.5750)	70	231	Amorphous solid

2.3. Physical measurements

Elemental analysis (C, H, and N) was carried out on a Coleman CHN analyzer. Chlorine and sulfur was estimated using Volhard's method and Messenger's method respectively [21]. Tin was estimated as tin oxide (SnO_2) using an analytical method [21]. IR spectra were recorded on a model 6700 spectrophotometer (Thermo Nicolet) in the range of 4000–100 cm^{-1}. NMR spectra were recorded at room temperature on a Bruker DRX-300 spectrometer, operated at 300.1, 75.45 and 111.95 MHz for ^{1}H, ^{13}C, and ^{119}Sn, using TMS (tetramethyl silane) and TMT (tetramethyl tin) as internal standards, respectively. Molecular weights were determined on a Knauer Vapour pressure osmometer in $CHCl_3$ at 45˚C.

2.4. Antimicrobial Assay

The antibacterial and antifungal activities of the complexes were investigated and compared with standards (Tetracycline and Terbinafine respectively) and ligands. The antibacterial studies were performed using a 2.5 $mgmL^{-1}$ concentrated solution by disc diffusion method [22, 23]. The pathogens, against which antibacterial activity was determined, were B. subtillis & S. aureus and antifungal activity was observed against C. albicans & A. niger.

Table 2: Elemental analysis data

S. No.	Compound	Mol. Wt. Found (Calculated)	Elemental Analysis Found (Calculated)					
			Sn	S	C	H	N	Cl
1	$SnCl_2(C_{15}H_{12}N_2OH)[(C_3H_7O)_2PS_2]$	638.0438 -640.1714	18.142 - 18.5435	10.11 - 10.0177	38.9222 - 39.3995	4.2 - 4.2509	3.9882 - 4.3759	11.2101 - 11.0761
2	$SnCl_2(C_{15}H_{12}N_2OCH_3)[(C_3H_7O)_2PS_2]$	654.0012 -654.1979	18.0107 - 18.1451	9.9902 -9.8024	41.0309 - 40.3907	5.6738 - 4.4679	3.8623 -4.282	9.6732 - 10.8386
3	$SnCl_2(C_{15}H_{12}N_2O.OCH_3)[(C_3H_7O)_2PS_2]$	669.91 -670.1973	17.7031 - 17.7127	8.9562 -9.5689	40.4432 - 39.4264	4.1106 - 4.3612	4.001 - 4.1798	10.5193 - 10.5799
4	$SnCl_2(C_{15}H_{12}N_2OCl)[(C_3H_7O)_2PS_2]$	710.1758 -710.0705	16.592 - 16.7181	10.1332 -9.0316	36.521 -35.521	3.0117 - 3.6905	4.3212 - 3.9451	15.0002 - 14.9787
5	$SnCl_2(C_{15}H_{12}N_2OH)[S_2POCH_2C(CH_3)_2CH_2O]$	625.1021	20.0022	10.1012	39.01	3.8164	4.0192	10.4598

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JCHR (2023) 13(4), 1606-1615 | ISSN:2251-6727

		-624.1291	-19.0202	-10.2752	-38.4878	-3.7142	-4.4883	-11.3608
6	$SnCl_2(C_{15}H_{12}N_2OCH_3)[S_2POCH_2C(CH_3)_2CH_2O]$	638.0077 -638.1556	18.5082 -18.6021	9.9871 -10.0494	38.8808 -39.524	3.9003 -3.9484	3.9737 -4.3897	11.8372 -11.1111
7	$SnCl_2(C_{15}H_{12}N_2O.OCH_3)[S_2POCH_2C(CH_3)_2CH_2O]$	654.3166 -654.1556	18.202 -18.1471	10.7818 -9.8036	37.1017 -38.5572	3.9901 -3.8519	4.3008 -4.2823	11.1037 -10.8393
8	$SnCl_2(C_{15}H_{12}N_2OCl)[S_2POCH_2C(CH_3)_2CH_2O]$	659.0017 -658.575	18.112 -18.0253	9.977 -9.7378	36.8872 -36.4748	3.5669 -3.3669	4.3017 -4.2536	15.9422 -16.1499

3. Results and Discussion

All these hybrid complexes were prepared by the reaction of tin tetrachloride with substituted pyrazoline and dithiophosphate in the inert atmosphere. They all are blackish brown in color, non-hygroscopic in nature, stable at room temperature. All the complexes were soluble in chloroform and other coordinating solvents such as DMSO, DMF etc. The elemental analysis data are summarized in table 2. Monomeric nature of all the complexes were explained by molecular weight measurements data (Osmometric method).

3.1. Infrared Spectral Analysis

The infrared spectra of the complexes are recorded in the range 4000-100 cm^{-1} and summarized in Table 3. A medium intensity band due to ν[N-H] stretching in the region 3309-3408 cm^{-1} is observed in all the complexes. The vibrations attributed to ν[C=N] at 1680-1654 cm^{-1} in the infrared spectra of the free pyrazolines shifted to 1647-1520 cm^{-1} in the spectra of complexes 1-8, in agreement with coordination of the azomethine nitrogen [24-31]. The bands in the region 1090-1035 cm^{-1} and 887-860 cm^{-1} may be ascribed to ν[(P)-O-C] and [P-O-(C)] of dithiophosphate moiety respectively [32-38]. The ν[P=S] absorption laying at 710-660 cm^{-1} in the spectra of complexes which shifted approx. 50 cm^{-1} with respect to free ligand, indicating the bidentate behavior of dithiophosphate ligand moiety [32-36]. The bands in the region 618-572 cm^{-1} has been assigned to ν [P-S] stretching mode [38]. In the free pyrazoline ligand, the signal due to ν [O-H] stretching is found at ~ 3080 cm^{-1} is completely missing from the spectra of the complexes and the new absorptions at 575-549 cm^{-1} were assigned to ν [Sn-O], those at 425-395 to ν [Sn-N] [39]. The appearance of bands at 375-285 cm^{-1} and 330-280 cm^{-1} is attributed to ν [Sn-S] and ν [Sn-Cl] respectively [40].

Table 3: Infra-Red Spectral band of Sn(IV) complexes

S. No.	Complexes	ν [N-H]	ν[C=N]	ν[(P)-O-C]	ν[P-O-(C)]	ν[P=S]	ν[P-S]	ν[Sn-O]	ν[Sn-N]	ν[Sn-S]	ν[Sn-Cl]
1	$SnCl_2(C_{15}H_{12}N_2OH)[(C_3H_7O)_2PS_2]$	3388	1610	1090	860	660	560	561	418	368	290
2	$SnCl_2(C_{15}H_{12}N_2OCH_3)[(C_3H_7O)_2PS_2]$	3375	1647	1042	868	690	595	545	405	295	270

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3	$SnCl_2(C_{15}H_{12}N_2O.OCH_3)[(C_3H_7O)_2PS_2]$	3363	1590	1046	887	678	598	568	412	348	330
4	$SnCl_2(C_{15}H_{12}N_2OCl)[(C_3H_7O)_2PS_2]$	3379	1608	1082	879	710	550	549	402	285	280
5	$SnCl_2(C_{15}H_{12}N_2OH)[S_2PO$	3408	1605	1035	880	669	618	565	408	360	322
6	$SnCl_2(C_{15}H_{12}N_2OCH_3)[S_2$	3350	1635	1085	875	690	572	562	395	390	300
7	$SnCl_2(C_{15}H_{12}N_2O.OCH_3)[$	3342	1520	1047	870	685	594	560	425	375	310
8	$SnCl_2(C_{15}H_{12}N_2OCl)[S_2PC$	3309	1600	1039	878	681	609	575	422	310	302

3.2. Multinuclear NMR spectroscopy

The NMR spectra (^1H, ^{13}C, ^{31}P and ^{119}Sn) of all complexes were run in DMSO-d_6 and listed in table 4. The ^{1}HNMR spectra of complexes show multiplet at δ7.85-6.50 ppm due the presence of aromatic protons of pyrazoline [24-31]. Disappearance of the signal of phenolic O-H, which was present at δ11 ppm in the spectra of pyrazoline ligand, indicating the deprotonation of phenolic O-H proton and formation of [Sn-O] bond in the all complexes [24-31, 38]. A broad singlet appeared at δ 5.72-5.0 ppm could be assigned to N-H proton, which was approximately resembled to the peak (at δ5.72-5.0 ppm) found in free ligands, suggesting that the [N-H] group probably did not participated in coordination to the metal [27-34, 41]. The signal observed in the range δ 3.81-3.05 ppm as triplet and δ 2.32-2.13 ppm as doublet could be attributed to the >CH- and -CH_2- group of five membered ring of pyrazoline respectively [24-31, 41]. The chemical shift due to the protons present in dithiophosphate ligand in the complexes are observed in the range δ 1.04-0.93 ppm as triplet, δ 5.28- 4.15 ppm as multiplet, and δ 1.65-1.45 ppm as multiplet may be assigned to -CH_3, -OCH_2-, and -CH_2- groups respectively [36-38]. The ^{13}C spectra show all the important signals present in the complexes with reference to free ligands and the comparison with these ligands have been made to explain the coordination behavior of metal and structure of complexes. The signal for imino (C=N) carbon was observed at δ 143.3-141.8 ppm in the free ligands, which show large shift upon complexation. This reveals the inference about the coordination of azomethine nitrogen with metal in the complexes. The signal observed in the region 137.12-136.21 ppm as multiplet could be attributed to the aromatic carbon [24-31]. The peak due to –OCH_2 group of dithiophosphate is observed at δ 77.49-76.85 ppm [38, 41]. The signals in the region δ 43.14-42.15 ppm and 27.53-26.70 ppm are observed due to the >CH and –CH_2 groups [36, 37].

^{31}P NMR spectra of complexes show only one signal at δ107.70- 91.50 ppm for phosphorus atom. The downfield shift was observed in comparison to free ligand indicates bidentate nature of ligand [36-38].

^{119}Sn NMR spectra were recorded to determine the coordination mode and geometry of tin(IV) complexes. The only one signal obtained at δ (-530) – (-597) ppm in ^{119}Sn NMR spectra of all the complexes in agreement with the one type of tin site and octahedral geometry around tin (IV) complexes [42]. Recently, a few reports demonstrated that the ^{119}Sn NMR chemical shifts are very sensitive to the electronegativity of groups or atom directly attached to the tin. Thus, it is worthy to refer that the chemical shift value of ^{119}Sn NMR increases as electronegativity of atom increases, which is result of dπ –dπ and dπ-pπ back donation [43].

Table 4: NMR data for Sn(IV) Complexes

S. No.	Complexes	^{1}HNMR	^{13}CNMR	^{31}PNMR	^{119}SnNMR
1	$SnCl_2(C_{15}H_{12}N_2OH)[(C_3H_7O)_2PS_2]$	7.45-6.85(m,9H,Ar-H) 0.98(t,6H,-CH_3) 5.28(m,4H,-OCH_2) 1.65(m,4H,-CH_2) 5.72(s,1H,-NH)	-	106.10	-530.3

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		3.45(t,1H,-CH) 2.17(d,2H,-CH_2)			
2	$SnCl_2(C_{15}H_{12}N_2OCH_3)[(C_3H_7O)_2PS_2]$	7.59-6.72(m,8H,Ar-H) 0.99(t,6H,-CH_3) 5.45(m,4H,-OCH_2) 1.62(m,4H,-CH_2) 4.97(s,1H,-NH) 3.48(t,1H,-CH) 2.13(d,2H,-CH_2) 0.95(s,3H,-CH_3)	-	105.82	-542.5
3	$SnCl_2(C_{15}H_{12}N_2O.OCH_3)[(C_3H_7O)_2PS_2]$	7.50-6.82(m,8H,Ar-H) 0.93(t,6H,-OCH_3) 5.30(m,4H,-OCH_2) 1.45(m,4H,-CH_2) 5.13(s,1H,-NH) 3.75(t,1H,-CH) 2.15(d,2H,-CH_2) 3.65(s,3H,-OCH_3)	-	105.95	-555.7
4	$SnCl_2(C_{15}H_{12}N_2OCl)[(C_3H_7O)_2PS_2]$	7.43-6.70(m,8H,Ar-H) 0.97(t,6H,-CH_3) 5.33(m,4H,-OCH_2) 1.60(m,4H,-CH_2) 5.15(s,1H,-NH) 3.81(t,1H,-CH) 2.21(d,2H,-CH_2)	-	106.20	-538.9
5	$SnCl_2(C_{15}H_{12}N_2OH)[S_2POCH_2C(CH_3)$	7.56-6.93(m,9H,Ar-H) 0.99(s,6H,-CH_3) 4.16(d,4H,-OCH_2) 5.15(s,1H,-NH) 3.05(t,1H, -CH) 2.19(d,2H,-CH_2)	26.28(C H_3, dtp) 30.03(C, dtp) 77.42(-OCH_2, dtp) 137.08(Ar-C) 165.69(C=N) 42.98(C H) 27.53(C H_2)	91.50	-550.6
6	$SnCl_2(C_{15}H_{12}N_2OCH_3)[S_2POCH_2C(CH$	7.85-6.50(m,8H,Ar-H) 1.02(s,6H,-CH_3) 5.42(s,1H,-NH) 3.73(t,1H,-CH) 2.20(d,2H,-CH_2) 0.97(s,3H,-CH_3)	25.32(C H_3) 77.49(-OCH_2, dtp)	91.82	-580.3

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			136.31(Ar-C) 165.32(C=N) 42.15(CH) 26.76(CH_2)		
7	$SnCl_2(C_{15}H_{12}N_2O.OCH_3)[S_2POCH_2C($	7.54-6.80(m,8H,Ar-H) 0.94(s,6H,-CH_3) 4.18(d,4H,-OCH_2) 5.33(s,1H,-NH) 3.23(t,1H,-CH) 2.32(d,2H,-CH_2) 3.69(s,3H,-OCH_3)	25.51(CH_3, dtp) 30.12(C, dtp) 76.85(-OCH_2, dtp) 136.92(Ar-C) 165.52(C=N) 42.65(CH) 26.70(CH_2)	94.72	-597.9
8	$SnCl_2(C_{15}H_{12}N_2OCl)[S_2POCH_2C(CH_3$	7.45-6.70(m,8H,Ar-H) 1.04(s,6H,-CH_3) 5.09(d,4H,-OCH_2) 4.91(s,1H,-NH) 3.43(t,1H,-CH) 2.13(d,2H,-CH_2)	26.01(CH_3, dtp) 30.34(C, dtp) 77.15(-OCH_2, dtp) 137.12(Ar-C) 165.35(C=N) 43.14(CH) 27.19(CH_2)	107.70	-565.2

5.3. Biological Studies

The antibacterial activity of heteroleptic tin(IV) complexes were tested against the bacterial species, B. subtillis and S. aureus. Antibiotic (Tetracycline) was used as standard and data were summarized in table 5. The results infer that the complexes of Sn (IV) with 3-(2'-hydroxy phenyl)-5-(4'- substituted phenyl) pyrazoline and O'O-alkylene dithiophosphate (complex 7) gives maximum inhibition of growth (18.8mm against B. subtillis, and 20.0 mm against S. aureus) in comparison to the other mixed ligand complexes of Sn(IV), respective ligands and standard tetracycline. However, complex 3

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shows moderate inhibition of growth (15.7 mm against B. subtillis, and 13.5 mm against S. aureus) and ligand 3-(2'-hydroxy phenyl)-5-(4'- substituted phenyl) pyrazoline, and O'O'- dialkyl and alkylene dithiophosphate show minimum inhibition of growth. Overall it is found that the complex 7 exhibit better antibacterial activity as compared to tetracycline and can be used as antibacterial drug.

Antifungal activity of the complexes were tested against C. albicans and A. niger. Results were compared with terbinafine drug. Data (listed in table 6) show that the mixed ligand complexe of Sn (IV) with 3-(2'-hydroxy phenyl)-5-(4'- substituted phenyl) pyrazoline and O'O-alkylene dithiophosphate (complex 7) gives maximum ~ almost similar antifungal activity (18.9 mm zone of inhibition) against C albicans in comparison to respective ligands, complexes and antifungal drug terbinafine. Against A niger somewhat lower antifungal activity was found (17.5 mm zone of inhibition). Therefore, it can be noted that all these ligand and complexes show somewhat lower or similar antifungal activity as compared to terbinafine (antifungal drug).

Enhanced activity of complex 7 in comparison to others against tested bacterial strain could be explained by the structure activity relationship according to following points:

1. The presence of electron donating functional groups as polar component and ring system in the complexes may improve the activity as polar and electron rich groups may form H-bonding interaction with nitrogen and hydrogen of amino acid of bacteria which could destroy its enzyme responsible for particular function, which may lead to death of bacteria [44].
2. The sulfur containing compound present in complexes shows dynamic impact on antibacterial activity as these compound may inhibit the formation of enzyme which is responsible for metabolism of bacteria [44].
3. Tin tetrachloride on complexation may improve the activity against tested bacterial strain, because entry of tin moiety with in the cell through hydrophobic membrane may only possible due to the encapsulation by the ligands.

Table 5: Antibacterial Activity of Sn(IV) complexes

		Zone of inhibition (mm)					
S. No.	Pathogen	Pyrazoline[a]	Dtp[b]1	Dtp[c]2	Complex 3	Complex 7	Tetracycline
1	S. aureus	6.5 mm	7.0 mm	10.2 mm	15.7 mm	20.0 mm	17.0 mm
2	B. subtillis	6.0 mm	9.4 mm	9.0 mm	13.5 mm	18.8 mm	15.0 mm

a: $(C_{15}H_{13}N_2O.OCH_3)$, b: $[(C_3H_7O)_2PS_2]$, c: $S_2POCH_2C(CH_3)_2CH_2O$

Table 6: Antifungal Activity of Sn(IV) complexes

Zone of Inhibition (mm)							
S. No.	Pathogen	Pyrazoline[a]	Dtp[b]1	Dtp[c]2	Complex 3	Complex 7	Terbinafine
1	A. niger	3.0 mm	9.0 mm	11.0 mm	12.0 mm	17.5 mm	18.0mm
2	C.albicans	2.25 mm	7.5 mm	8.2 mm	9.7 mm	18.0 mm	18.5 mm

a: $(C_{15}H_{13}N_2O.OCH_3)$, b: $[(C_3H_7O)_2PS_2]$, c: $S_2POCH_2C(CH_3)_2CH_2O$

4. Conclusion

The new heteroleptic complexes of tin with pyrazoline and dithiophosphate ligands have been synthesized and characterized by elemental analysis, IR, multinuclear NMR (^1H, ^{13}C, ^{31}P, ^{119}Sn). According to above studies, an octahedral geometry around Sn(IV) center can be

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proposed with mono-anionic bidentate ligand. Formation of mononuclear complexes have also been confirmed by molecular weight data and ^{119}Sn NMR. Biological studies, according to structure activity relationship reveals that these heteroleptic complexes containing electron donating functional groups are incredibly active as antibacterial and antifungal drugs in comparison to ligands and homoleptic complexes.

5. Acknowledgements

The authors are thankful to SAIF CDRI, India, IIT Bombay, STIC Cochin, India for providing necessary analytical and spectral data. We are also grateful to the department of chemistry, D.D.U. Gorakhpur University, Gorakhpur, (U.P.) India for providing library facility and laboratory.

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