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Synthesis, characterization and antimicrobial activities of organotin(IV) complexes with ethylthioglycolate

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ABSTRACT

A series of organotin(IV) complexes have been synthesized by reacting ethylthioglycolate with di- and triorganotin halides in 1:1 M/L ratio in methanol under stirring conditions. The newly synthesized complexes have been characterized by elemental analysis, IR and NMR spectroscopy (^{1}H, ^{13}C). IR results shows that ligand act as monodentate which is also confirmed by semi-empirical study. NMR data reveals four coordinated geometry in solution. Biological activities data demonstrates that complexes show significant activity against various bacterial and fungal strains with few exceptions and are found cidal in their biological action.

Capsule Summary: Organotin(IV) complexes with ethylthioglycolate were prepared, characterized and finally, tested for antimicrobial activities. The ligand act as monodentate and NMR data reveals four coordinated geometry in solution. The prepared organotin(IV) complexes showed a significant antimicrobial activities.

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INTRODUCTION

During the past few decades the chemistry of organotin(IV) complexes has witnessed a quantum leap (Rehman et al., 2009). Because of biomedical and commercial applications, organotin(IV) complexes have been the subject of interest (Jain et al., 2004). The biological importance of organotins has been supported by studies concentrating on structure-activity correlations that deal mainly with structural aspects and antitumour activity, and also linked with possible tumorigenic activity (Shahid et al., 2006). This aspect has been attracting the attention of a number of researchers and a multitude of structural types have been discovered (Affan

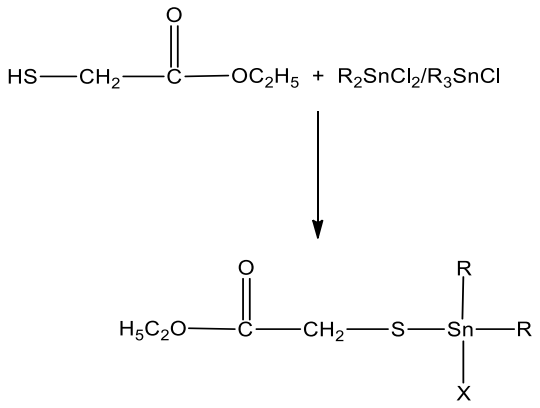
et al., 2009). These compounds have been generally used as agrochemicals (David, et al., 2008) and antifouling paints (Smith et al., 1979) due to their low phytotoxicity and favourable environmental degradation to non-toxic inorganic residues. The objective of the current study is to synthesize organotin(IV) complexes and characterized them with different spectral techniques. Also provide useful insights in the understanding of antimicrobial potency of synthesized complexes and structure activity relationship.

MATERIAL AND METHODS

Ethylthioglycolate, ethanol, acetone, chloroform, triphenyltin chloride, trimethyltin chloride, tributyltin chloride, dibutyltin dichloride and DMSO were purchased from Aldrich sigma-(USA). Sodium carbonate (Na_2CO_3), Na_2HPO_4, KH_2PO_4, 2,2-diphenyl-1-picryl-1-hydrazyl (DPPH) reagent, ethanol and methanol were purchased from Merck (Germany). Nutrient agar, Nutrient broth and Potato dextrose agar were purchased from Oxoid Company (UK). All reagents were of analytical grade and used without further purification. The melting points were determined in an open capillary on an electrothermal melting point apparatus, model Stuart (SMP3) (UK) and are uncorrected. The antimicrobial activities of the ligand and organotin(IV) complexes have been performed in Incubator (Sanyo, Germany) under Laminar air flow (Dalton, Japan) and sterilized in the Autoclave apparatus (Omron, Japan). Infrared spectra were recorded using Perkin-Elmer 1000 FTIR Spectrophotometer as KBr/CsBr discs in range of 4000-250 cm^{-1}. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 MHz FTNMR spectrometer (Germany). The percentage composition of the elements was determined by using CHNS-932 elemental analyzer, Leco (USA). The molecules were modeled by MOPAC 2007 (Stewart, 2007) program in gas phase using PM3 method (Stewart, 2004). The Root Mean Square Gradient for molecules was all less than one. Self Consistent Field was achieved in each case. Vibration analysis showed absence of imaginary frequencies.

General procedure for synthesis of organotin(IV) complexes

Ethylthioglycolate (1 mmol) was suspended in methanol (20 mL) in a round bottom 250 ml flask and treated with R_2SnCl_2/R_3SnCl (R = Me, *n*-Bu, Ph) in 1:1 M/L ratio (Scheme 1). The mixture was stirred for 6 h at room temperature. The solvent was evaporated under reduced pressure through rotary evaporator. The solid product obtained was dried in open air and recrystallized in acetone:*n*-hexane (1:2).



Scheme 1: General procedure for synthesis of organotin(IV) complexes

Antimicrobial activity

Bacterial growth medium, cultures and inoculum preparation: Pure cultures were maintained on nutrient agar medium in the slants and petri plates. For the inoculums preparation 13 gL^{-1} of nutrient broth was suspended in distilled water, mixed well and distributed homogenously and autoclaved. 10 ?L of pure culture of a bacterial strain was mixed in medium and placed in shaker for 24 h at 37 °C. The inocula were stored at 4 °C. The inocula with 1×10^8 spores/mL were used for further analysis.

Fungal growth medium, culture and inoculum preparation: Pure culture of the fungi were maintained on sabouraud dextrose agar (SDA) medium (65 g L^{-1}) in slant and petri plates that were placed in hot air oven at 180 °C for 3 h under presterilized conditions. These culture slants were incubated at 28 °C for 3-4 days for the multiplication of fungal strains.

Antimicrobial assay by disc diffusion method: Antimicrobial activity of compounds was screened by using disc diffusion method (CLSI, 2007). For bacterial and fungal strains assay, nutrient agar (28 g L^{-1}) and potato dextrose agar (39 g L^{-1}), respectively, was dissolved in distilled water. The media was autoclaved at 121 °C for 15 minutes and used to culture bacteria. Before the medium was transferred to petri plates; inoculums (100 ?L/100 mL) was added to the medium and poured in sterilized petri plates. After this, small filter paper discs were laid flat on growth medium containing 100 ?L of sample. The petri plates were then incubated at 37 °C for 24 h and at 28 °C for 48 h, for the growth of bacteria and fungus, respectively. The sample having antimicrobial activity exhibited clear zones around the discs. The zones of inhibition were measured in millimeters using zone reader (Haung et al., 2001). Triplicate of petri plates were prepared. Rifampicin and Fluconazol (20 ?g/disc) were used as positive control for bacteria and fungus, respectively.

RESULTS AND DISCUSSION

Fig. 1: Geometry optimized structure of complex 1

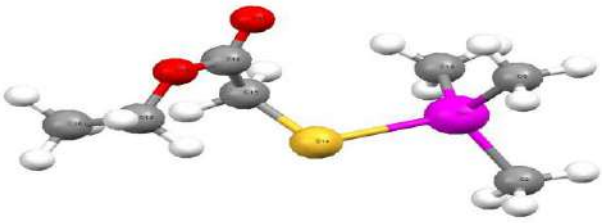


Fig. 2: Geometry optimized structure of complex 2

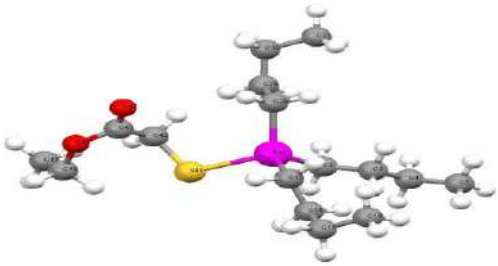


Fig. 3: Geometry optimized structure of complex 3

Fig. 4: Geometry optimized structure of complex 4

The synthesized complexes are solid and stable in air. They have sharp melting points and are soluble in common organic solvents. The physical data is given in Table 1.

Infrared spectroscopy

The IR spectra of the ethylthioglycolate and organotin(IV) complexes were recorded as KB/CsBr discs in the range of 4000-250 cm^{-1}. The IR spectrum of the free ligand shows band with medium intensity at 2754 cm^{-1}, attributed to the ν(S–H) vibration. The explicit feature in the spectra of complexes is the absence of the –SH stretching vibration which indicates the complexation (Jabeen et al., 2012). The metal-sulfur bond formation was supported by appearance of new band in the range of 425–452 cm^{-1} for *ν*(Sn-S). A strong band at 316 cm^{-1} has been observed due to *ν*(M-Cl) for compound 1. The data is given in Table 2. New bands appear in the range 507-573 cm^{-1} were assigned to *ν*(Sn-C) (Shahzadi et al., 2005; Pellerito et al., 2006; Khan et al., 2012).

^{1}H NMR spectroscopy

^{1}H NMR data is given in Table 3. The assignment of every signal has been made by comparing the spectra of the complexes with that of the ligand. The ^{1}H NMR spectra of organotin(IV) complexes did not display any signal due to –SH proton at 1.21 ppm, which confirmed the deprotonation (Kalinowski et al., 1984). The disappearance of the -SH signal of ligand indicates coordination of the S to the Sn atom. In compound 2, methyl protons give sharp singlet at 0.64 pm, while in compound 4, the ortho protons were observed at lower field (7.31-7.36 m) and those for meta and para protons at 7.40-7.41 m and 7.72-7.75m, respectively.

^{13}C NMR spectroscopy

The ^{13}C NMR data of ethylthioglycolate and organotin(IV) complexes are given in Table 4. The signal due to the carbon atom attached to the S atom in ethylthioglycolate appeared at δ171.13 ppm. However, in the spectra of the complexes, the signal show downfield shift in the range 172.15-172.50 ppm. This considerable shift in the spectra of metal complexes indicates the coordination of sulphur to the central metal atom in complexes (Javed et al., 2014; Jamil et al., 2009; Hussain et al., 2011). R group attached to tin appeared in the expected range (Jabeen et al., 2012; Shahzadi et al., 2005; Khan et al., 2012).

Antibacterial activity

The ethylthioglycolate and organotin(IV) complexes were screened for antibacterial activity by the disc diffusion method (CLSI, 2007) and zone of inhibition is measured in millimeters (Haung et al., 2001). The antibacterial activity of the ligand HL and complexes were recorded against four bacterial strains e.g., *P. multocida, E. coli, B. subtilis and S. aureus*. The results are given in Table 5. The antibacterial studies show that the complexes exhibit high activity towards all tested bacteria as compared to free ligand with exception of complex 2 (Rehman et al., 2006). Dibutyltin and triphenyltin complexes show more activity against all strains than other organotin compounds (Rehman et al., 2011).

Table 1: Physical data of ethylthioglycolate and organotin(IV) complexes

Compound No.	Molecular formula	M.W (g/mol)	M.P (°C)	Elemental analysis Calculated (found)		
				%C	%H	%S
HL	$C_4H_8O_2S$	120.07	-	-	-	-
				37.2	6.5	8.25
1	$C_{12}H_{25}O_2ClSSn$	387.45	102-103			
				-37.16	-6.46	-8.21
				29.72	5.7	11.3
2	$C_7H_{16}O_2SSn$	282.87	192-193			
				-29.68	-5.66	-11.34
				46.97	8.38	7.82
3	$C_{16}H_{34}O_2SSn$	409.11	162-163			
				-46.93	-8.34	-7.86
				56.33	4.73	6.82
4	$C_{22}H_{22}O_2SSn$	469.09	174-175			
				-56.29	-4.69	-6.86

Table 2: IR data (cm^{-1}) of organotin(IV) complexes with ethylthioglycolate

Compound No.	$\nu(COO)_{asym}$	$\nu(COO)_{sym}$	ν(S-H)	ν(Sn-C)	ν(Sn-S)	ν(Sn-Cl)
HL	1655	1466	2754	-	-	-
1	1656	1460	-	573	425	316
2	1653	1465	-	507	437	-
3	1653	1460	-	565	452	-
4	1655	1469	-	551	447	-

Table 3: ^{1}H NMR data[a-c] (ppm) of organotin(IV) complexes with ethylthioglycolate

Proton No	HL	1	2	3	4
1	1.18t (3.7)	1.17t (3.7)	1.18t (3.7)	1.18t (3.7)	1.17t (3.7)
2	2.86-2.89m	2.86-2.88m	2.85-2.90m	2.86-2.90m	2.87-2.88m
4	3.70-3.75m	3.71-3.75m	3.72-3.75m	3.70-3.74m	3.71-3.75m
SH	1.21 s	-	-	-	-

[a]Compound (1) Sn-$CH_2CH_2CH_2CH_3Cl$; 0.87t, 1.50–1.69m; Compound (2) Sn-CH_3; 0.64s [57]; Compound (3) Sn-CH_2-$CH_2CH_2CH_3$; 0.89t(7.2), 1.23–1.65m; Compound (4) Sn-C_6H_5; 7.72-7.75m, 7.31-7.36m, 7.40-7.41m [b]Chemical shifts (δ) in ppm. ^nJ[^{119}Sn, ^{1}H] and ^nJ(^{1}H, ^{1}H) are listed in square brackets and parenthesis, respectively; [c]Multiplicity is given as: s = singlet, t = triplet, m = multiplet $^1CH_3$-$^2CH_2$-O-^{3}C(=O)-$^4CH_2$-S

In fact, the butyltin complexes 1 and 3 are detected as broad-spectrum antibiotic compounds, they inhibit the growth of several Gram positive and Gram negative bacteria and in several cases their growth inhibitory effect is better than that of the free ligand (Garrod et al., 1981). The compound 3 show slightly better activity against *B. subtilus* as compared to positive control. Ethylthioglycolate HL shows activity against *E. coli* with zone diameter 18.9 mm and it is found inactive against *P. multocida*, *S. aureus* and *B. subtilis*. The order of increasing activity of complexes is *S. aureus* < *E. coli* < *P. multocida* < *B. subtilis.*

Antifungal activity

The antifungal activity of ligand HL and complexes was recorded against four fungal strains, *A. niger, A. flavus, G. lucidum and A. alternata* using disc diffusion method (CLSI, 2007).

Table 4: ^{13}C NMR data[a] (ppm) of organotin(IV) complexes with ethylthioglycolate

Carbon No.	HL	1	2	3	4
1	14.35	14.32	14.32	14.31	14.36
2	26.12	26.12	26.12	26.13	29.14
3	169.47	169.47	169.48	169.47	169.47
4	171.13	171.31	172.15	172.31	172.5

[a]Compound (1); Sn-$CH_2CH_2CH_2CH_3Cl$; (C-α) 26.30 [541], (C-β) 28.14 [39], (C-γ) 27.84 [117], (C-δ) 14.22; Compound (2); Sn-CH_3; -2.0 [395] Compound (3); Sn-$CH_2CH_2CH_2CH_3$; (C-α) 21.48 [539], (C-β) 28.21 [38], (C-γ) 27.62 [116], (C-δ) 14.12; Compound (4) Sn-C_6H_5; 135.49, 129.02, 128.79, 128.04

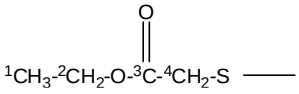


Table 5: Antibacterial data[a] (mm) of organotin(IV) complexes with ethylthioglycolate

Comp. No.	Bacterial zone size (mm)			
	E. coli	*B. subtilus*	*S. aureus*	*P. multocida*
HL	$18.9^{bc} \pm 0.7$	$0.0^{c} \pm 0.0$	$0.0^{c} \pm 0.0$	$0.0^{c} \pm 0.0$
1	$22.8^{b} \pm 1.0$	$18.7^{bc} \pm 0.9$	$23.1^{b} \pm 0.6$	$22.8^{b} \pm 0.7$
2	$24.7^{ab} \pm 1.1$	$19.7^{b} \pm 1.0$	$23.1^{b} \pm 0.6$	$26.7^{ab} \pm 0.6$
3	$0.0^{c} \pm 0.0$	$50.0^{a} \pm 1.0$	$0.0^{c} \pm 0.0$	$19.8^{bc} \pm 0.8$
4	$23.2^{b} \pm 0.8$	$20.6^{b} \pm 0.8$	$22.5^{b} \pm 1.0$	$22.5^{b} \pm 1.0$
Rifampicin	$36.1^{a} \pm 1.3$	$32.5^{ab} \pm 1.2$	$30.5^{a} \pm 1.2$	$40.4^{a} \pm 1.2$

[a]Values are mean ± SD of five samples analyzed individually in triplicate at $p<0.05$

Table 6: Antifungal activity data[a] of organotin(IV) complexes with ethylthioglycolate

Complex No.	Fungal zone size (mm)			
	A. niger	*A. flavus*	*A. alternata*	*G. lucidum*
HL	$50.5^{a} \pm 1.0$	$24.1^{bc} \pm 0.6$	$20.4^{bc} \pm 1.0$	$28.5^{ab} \pm 1.0$
1	$0.0^{c} \pm 0.0$	$24.9^{b} \pm 1.0$	$0.0^{c} \pm 0.0$	$0.0^{c} \pm 0.0$
2	$0.0^{c} \pm 0.0$	$0.0^{c} \pm 0.0$	$0.0^{c} \pm 0.0$	$0.0^{c} \pm 0.0$
3	$35.6^{b} \pm 1.0$	$36.3^{ab} \pm 0.2$	$22.6^{b} \pm 0.8$	$22.6^{bc} \pm 0.8$
4	$50.1^{ab} \pm 1.0$	$49.0^{a} \pm 1.1$	$26.1a^{b} \pm 0.6$	$30.0^{a} \pm 0.7$
Fluconazole	$28.3^{bc} \pm 1.2$	$27.7^{b} \pm 1.2$	$28.5^{a} \pm 1.3$	$26.4^{b} \pm 1.1$

[a]Values are mean ± SD of five samples analyzed individually in triplicate at $p<0.05$

In comparison to ligand, the complexes were found more active towards fungal strains with few exceptions and in some cases their activity is equal to or even greater than the positive control which suggests that metal coordination increases the activity as compare to free ligand (Rehman et al., 2006; Rehman et al., 2011). Compounds 3 and 4 show 100 % growth inhibition against all fungal strains whereas compound 2 shows growth inhibition against only one fungal strain (Table 6). The compound 4 was found to be the best antifungal agent that completely inhibited the growth of all the four test fungi.

It has been proposed that probably the organotin(IV) complexes inhibited the growth of micro-organisms by affecting the production of an enzyme and hence the micro-organisms were not able to metabolize nutrients efficiently and consequently, growth cease, as those enzymes that require free sulfhydral group (-SH) for activity, appeared to be especially susceptible to deactivation by ions of complexes (Rehman et al., 2011).

Ethylthioglycolate HL was less active against *A. alternata* with zone diameter 20.4 mm, and active against *G. lucidum* and *A. flavus* with zone diameter 28.5 mm and 24.1 mm, respectively and strongly active against *A. niger* with diameter 50.5 mm. Complex 2 is inactive against all fungal strains while complex 1 is only active against *A. flavus* with zone diameter of 24.9 mm.

Table 7: Selected bond lengths [Å] for compound 1-4

Compound No.	Sn-C	Sn-S	S-C	Sn-Cl	C-O
1	2.17, 2.17	2.53	1.82	2.38	1.21, 1.36, 1.42
2	2.14, 2.1, 2.15	2.55	1.82	-	1.21, 1.36, 1.42
3	2.19, 2.19, 2.19	2.55	1.82	-	1.21, 1.36, 1.42
4	2.08, 2.08, 2.08	2.56	1.82	-	1.23, 1.36, 1.42

Table 8: Selected bond angles (°) for compound 1-4

Compound No.	C-Sn-C	Sn-S-C	C-Sn-S	Cl-Sn-S	Cl-Sn-C
1	116.8	107	109.7, 111.5	106.3	105.5, 106.3
2	111.3, 111.0, 112.0	107.7	109.1, 104.9, 107.9	-	-
3	112.1, 113.0, 110.4	107.5	105.9,107.4, 109.9	-	-
4	110.1, 116.3, 111.3	106.3	109.5, 104.1, 105.0	-	-

The order of increasing activity of complexes is *A. nigar* < *A. flavus* < *G. lucidum* < *A. alternate*. The results are compared with *Fluconazol* used as positive control which shows good activity against *A. niger* and *A. alternata* with zone diameter 28.3 and 28.5 mm, respectively. It shows moderate activity against *A. flavus* and *G. lucidum* with zone diameter 27.7 and 26.4 mm, respectively.

Structure-activity relationship

Although, it is difficult to make out an exact structure activity relationship between the microbial activity and the structure of the complexes, it can possibly be concluded that the chelation as well as addition of a substrate enhance the activity of the complexes. The variation in the toxicity of different antibacterial agents against different organisms as suggested by Garrod et al., (Garrod et al., 1981) depends either on the impermeability of the cell or differences in ribosomes to the antimicrobial agent. Though the results suggest that the ligand has remarkable toxic property and organotin complexes inhibit the growth of organisms to a greater extent. This is in accordance with the earlier reports (Singh et al., 2001; Rehman et al., 2011).

Semi-empirical study

Compounds 1-4 are four-coordinated with distorted tetrahedral geometry, in which Sn atom is attached to S atom of ethylthioglycolate. All bond angles and bond lengths are closer to those reported in literature (Shahzadi and Ali. 2008). Selected bond angles and bond lengths are given in the Table 7 and 8. Geometry optimized structure are given in Figs. 1-4.

CONCLUSIONS

The organotin(IV) complexes have been synthesized employing efficient synthetic procedure affording quantitative yield. IR data shows the monodentate nature of ligand which is also confirmed by semi-empirical study. NMR data shows 4-coordinated geometry in solution. Biological activity data revealed that complexes were more active with few exceptions and found cidal in their biological action.

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REFERENCES

Affan, A.M., Fasihuddin, B.A., Liew, Y.Z., Foo, S.W., Ismail, J., 2009. Synthesis, Spectroscopic Characterization and Antibacterial Activity of Organotin(IV) Complexes Containing Hydrazone Ligand: X-ray Single Crystal Structure of [*n*-$Bu_2Sn(H_2PAI).H_2O$]. Journal of Scientific Research 1(2), 306-316.

Bacchi, A., Carcelli, M., Pelagatti, P., Pellizzi, G., Arguelles, M.C.R., Solinas, C., Zani, F., 2005. Antimicrobial and mutagenic properties of organotin(IV) complexes with isatin and N-alkylisatin bisthiocarbonohydrazones. Journal of Inorganic Biochemistry 99(2), 397-408.

CLSI (The Clinical Laboratory Standards Institute). 2007. Agar dilution and disc diffusion susceptibility of Campylobacter spp. Journal of Clinical Microbiology 45(8), 2758-2759.

David, A., Gielen, M., Pannell, K., Tiekink, E., 2008. Tin Chemistry, John Wiley, UK.

Garrod, L.P., Lambert, H.P., Grady, F.O., 1981. Antibiotic and Chemotherapy, 5th Ed., Edinburgh, Scotland: Churchill Livingstone, 1981.

Huang, G., Moore, S., Jiaxin, J., Dehui, D., 2001. Antioxidant and antibacterial activity of methanol extract of *Artemisia.* Journal of Food Science and Technology 11, 25-32.

Hussain, S., Ali, S., Shahzadi, S., Sharma, S.K., Qanungo, K., Altaf M., Evans, H.S., 2011. Synthesis, Characterization and Semi-empirical Study of Organotin(IV) Complexes with 4-(Hydroxymethyl)piperidine-1-carbodithioic Acid: X-Ray Structure of Chlorodimethyl(4-hydroxymethyl piperidine-1-carbodithioato-S,S`)tin(IV). Phosphorus, Sulphur and Silicon and Related Elements 186(3), 542-551.

Jabeen, M., Ali, S., Shahzadi, S., Shahid, M., Khan, Q.M., Sharma, S.K., Qanungo, K., 2012. Homobimetallic Complexes of Ligand Having O- and S-Donor Sites With Same and Different Di- and Trialkyl/aryltin(IV) Moiety: Their Synthesis, Spectral Characterization and Biological Activities. Journal of Iranian Chemical Society 9, 307-320.

Jain, M., Singh, V., Singh, V.R., 2004. Biologically Potent Sulphonamide Imine Complexes of Organotin(IV): Synthesis, Spectroscopic Characterization and Biological Screening. Journal of Iranian Chemical Society 1(1), 20-27.

Jamil, K., Bakhtiar, M., Khan, A.R., Rubina, F., Rehana, R., Wajid, R., Qaisar, M., Khan, A.F., Khan, A.K., Danish, M., Bhatti, A.A., Rizwan, M., Naveed, A., Hussain, M., Pervez, A., 2009. Synthesis characterization and antimicrobial activities of noval organotin compounds. African Journal of Pure and Applied Chemistry 3, 66-71.

Javed, F., Ali, S., Shah, M.W., Munawar, K.S., Shahzadi, S., Hameed Ullah, Fatima, H., Ahmed, M., Sharma S.K., Qanungo, K., 2014. Synthesis, Characterization, Semi-empirical Study and Biological Activities of Organotin(IV) and Transition Metal Complexes with *o*-Methyl carbonodithioate. Journal of Coordination Chemistry 67, 2795-2808.

Kalinowski, H.O., Berger, S., Braun, S., 1984. ^{13}C-NMR Spektroskopie, Georg ThiemeVerlag, Stuttgart.

Khan, H.N., Ali, S., Shahzadi, S., Helliwell, M., 2012. Synthesis, Spectroscopy and Antimicrobial Activity of Chloro-organotin(IV) Complexes of S-Donor Ligand: Crystal Structure of Chloro-*t*-dibutyltin[4-methyl-1-piperidine]thiocarboxylate. Russian Journal of Inorganic Chemistry 57(5), 665-670.

Pellerito, C., Scopelliti, M., Fiore, T., Nagy, L., Barone, G., Abbate, M., Stocco, G.C., Pellerito, L., 2006. Structural investigations on diorgano- and triorganotin(IV) derivatives of [meso-tetra(4-sulfonatophenyl)porphine] metal chlorides. Journal of Organometallic Chemistry 691, 1573-1583.

Rehman, W., Badshah, A., Khan, S., Ahmad, I., 2009. Synthesis, Structural Investigations and Biological Screening of Diorganotin(IV) Complexes Derived from 5, 5-Diethyl Sodium Barbital. Chinese Journal of Structural Chemistry 28(9), 419-426.

Rehman, W., Baloch, K.M., Badshah, A., Ali, S., 2006. Synthesis, characterization and biological study of diorganotin(IV) complexes of monomethyl phthalate Spectrochimica Acta Part A 65, 689-694.

Rehman, Z., Muhammad, N., Ali, S., Butler, S.I., Meetsma, A., 2011. New mononuclear organotin(IV) 4-benzhydrylpiperazine-1-carbodithioates: Synthesis, spectroscopic characterization, X-ray structures and in vitro antimicrobial activities Inorganica Chimica Acta 373(1), 187-194.

Shahid, K., Shahzadi, S., Ali, S., Mazhar, M., 2006. Synthesis, Spectroscopic Studies and Biological Applications of Organotin(IV) Derivatives of 3-[N-(4-Nitrophenyl)-amido]propenoic Acid and 3-[N-(4-Nitrophenyl)-amido]propanoic Acid. Bulletin of Korean Chemical Society 27(1), 44-52.

Shahzadi, S., Shahid, K., Ali, S., Mazhar, M., Khan, M.K., 2005. Organotin(IV) Derivatives as Biocides: An Investigation of Structure by IR, Solution NMR, Electron Impact MS and Assessment of Structure Correlation with Biocidal Activity. Journal of Iranian Chemical Society 2(4), 277-288.

Shahzadi, S., Ali, S., 2008. Structural Chemistry of Organotin(IV) Complexes:A Review. Journal of Iranian Chemical Society 5(1), 16-28

Singh, H.L., Khungar, B., Tripaati, U.D., Varshney, A.K., 2001. Spectral and Antimicrobial Studies of Organotin(IV) Complexes of Bidentate Schiff Bases having Nitrogen and Sulphur Donor Systems. Main Group Metal Chemistry 24, 5-12.

Smith, P.J., Crow, A.J., Hill, R., 1979. Laboratory Evaluation of Tributyltin(IV) Compounds as Wood Preservatives. Publication 559, International Tin Research Institute, London.

Stewart, J.J.P., 2007. MOPAC, Stewart Computational, Chemistry, Version: 7.334W.

Stewart, J.J.P., 2004. Optimization of parameters for semi-empirical methods IV: extension of MNDO, AM1 and PM3 to more main group elements. Journal of Molecular Modeling 10, 155-164.