Pakistan Journal of Science (Vol. 73 No. 1 March, 2021)

DFT STUDIES OF TRIPHENYLTIN(IV) 5-CHLOROSALICYLATE: SOLID STATE STRUCTURAL COMPARISON WITH OTHER TRIPHENYLTIN(IV) BENZOATES

S. Hussain[1*], S. Ali[2], S. Shahzadi[2], S.K. Sharma[3] and K. Qanungo[3]

[1]Department of Chemistry, Lahore Garrison University, DHA Phase VI, Lahore, Pakistan
[2]Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan
[3]Department of Applied Science and Humanities, Faculty of Engineering and Technology, Mody Institute of Technology and Science (Deemed University), Lakshmangargh, Sikar, Rajasthan 332311, India
[*]Corresponding author's E-mail: sairashahzadi@hotmail.com

ABSTRACT: DFT calculations were performed for triphenyltin(IV) 5-chlorosalicylate (**1**) in gas phase using Firefly QC package. Quantum mechanical calculations demonstrate that both the carboxylate oxygens of the ligand are connected with tin(IV) center in a bidentate fashion in **1**. The phenyl group of the precursor ligand and the COOSn moiety are coplanar. The calculated E_{LUMO} and E_{HOMO} values describe comparative electron accepting and donating abilities. The structural features of the complex **1** were compared with the solid state single crystal XRD findings of the reported triphenyltin(IV) benzoates **2**-**7**. A direct relation was found between the Sn-O2 bond length and $\Delta_{(Sn-O2)-(Sn-O1).}$ Ionization potential, electron affinity, electrophilicity, chemical potential, global hardness and global softness values were also calculated for the complex **1**.

Key words: DFT, XRD, Triphenyltin(IV) 5-chlorosalicylate, Triphenyltin(IV) benzoates.

(Received 02.11.2020 Accepted 03.02.2021)

INTRODUCTION

Organotin(IV) derivatives are famous for their numerous structural diversities which can be owed to the flexibility in coordination modes (bidentate or monodentate) of the bonded ligands, variations in the coordination numbers and geometries. The triorganotin(IV) products mostly exhibit trigonal bipyramidal or tetrahedral structural arrangements, while diorganotin(IV) complexes have numerous coordination numbers and geometries (Abbas *et al.*, 2013). They may exist in the form of polymers, oligomers, tetramers, dimers or monomers (Hussain *et al.*, 2013). Tin(IV) may change its coordination mode depending upon the difference of electronegativity of the -COO- moiety with the remaining ligand skeleton, nature of solvent, the concentration of solution and the size of organic group bonded with tin(IV) (Vollano *et al.*, 1984). The major structural differences in organotin(IV) complexes occur due to the high coordination ability of tin, especially due its involvement in either strong or weak inter- or intramolecular coordination (Gielen, 2008).

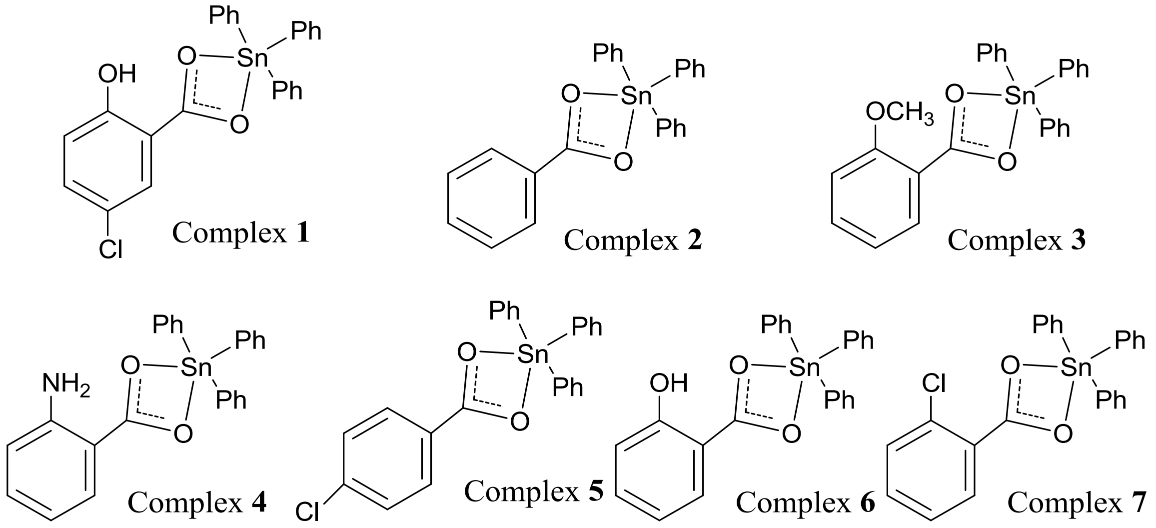
In the past few decades, there had been a greater role of Density Functional Theory (DFT) in the illustration of numerous structural features of organotin compounds. In fact, this theory has revolutionized the quantum chemistry and has offered a computational technique to interpret electron correlation in a better way as compared to the conventional methods (Geerlings *et al.*, 2003). This theory had been successfully applied to validate the organotin structures proposed on the basis of spectroscopic analyses (Dubey *et al.*, 2019). Numerous studies have successfully explained the complex formation, bonding behavior and various structural features of coordinated products by DFT (Dias *et al.*, 2017; Hussain *et al.*, 2012; Hussain *et al.*, 2015; Nitsch *et al.*, 2017; Shujah *et al.*, 2018).

This study aims at application of density functional theory (DFT) to elucidate the structure of triphenyltin(IV) 5-chlorosalicylate. The results obtained from the quantum mechanical calculations were compared with those of the reported triphenyltin(IV) benzoates.

MATERIALS AND METHODS

The investigated compound triphenyltin(IV) 5-chlorosalicylate (**1**) can by prepared by stirring together the equimolar quantities of potassium hydroxide and 5-chloro-2-hydroxybenzoic acid for one hour in 50 ml methanol (50 mL) followed by equimolar addition of Ph_3SnCl (1 mmol) and then stirring at room temperature for 5 h. The reaction mixture is filtered and the solid product is obtained by evaporation of filtrate and then crystallization in methanol and petroleum ether (2:1) (Hussain *et al.*, 2015).

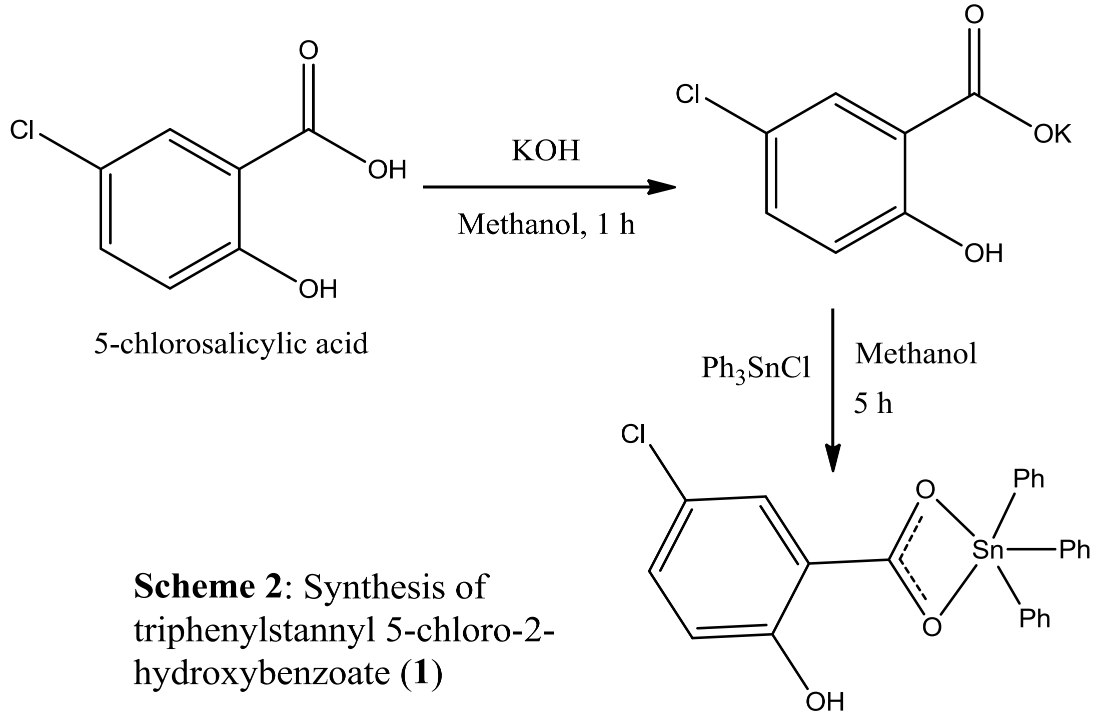
DFT calculations for triphenyltin(IV) 5-chlorosalicylate (**1**) were performed in gas phase using Firefly QC package (Granovsky, 2012), which is partially based on the GAMESS (US) (Schmidt *et al.*, 1993) source code using the BLYP exchange-correlation functional, with the 3-21G basis set. Absence of imaginary frequencies was checked to confirm the global minimum. The structural features of the complex **1** were compared with the solid state single crystal XRD findings of the reported triphenyltin(IV) benzoates which include triphenyltin(IV) benzoate (**2**), triphenyltin(IV) 2-methoxybenzoate (**3**), triphenyltin(IV) 2-aminobenzoate (**4**), triphenyltin(IV) 4-chloorobenzoate (**5**), triphenyltin(IV) 2-hydroxybenzoate (**6**) and triphenyltin(IV) 2-chlorobenzoate (**7**). The individual structures of the complexes **1**-**7** have been displayed in Scheme 1.



Scheme 1. Structures of the complexes 1-7

RESULTS AND DISCUSSION

The synthetic procedure and spectroscopic studies (FTIR, ^{1}H NMR and ^{13}C NMR) for the formation of triphenyltin(IV) 5-chlorosalicylate are reported elsewhere (Hussain *et al.*, 2015). A brief reaction path for the synthesis of this complex has been described below (Scheme 2) (Hussain *et al.*, 2015):



Scheme 2: Synthesis of triphenylstannyl 5-chloro-2-hydroxybenzoate (**1**)

DFT calculations were performed for triphenyltin(IV) 5-chlorosalicylate in gas phase using Firefly QC package. The structural features of the investigated complex **1** were compared with those of similar triphenyltin(IV) carboxylates reported earlier **2**-**7** (Hussain *et al.*, 2016; Smith *et al.*, 1995; Swisher *et al.*, 1984; Vollano *et al.*, 1984).

In the geometry optimized structure of triphenyltin(IV) 5-chlorosalicylate **1** (Figure 1), both the oxygen atoms of the substituted carboxylic acid develop a linkage to the tin atom in a bidentate manner. Bidentate linkage of the carboxylate ligands with organotin(IV) moieties is common as reported earlier (Mariam *et al.*, 2018; Sirajuddin *et al.*, 2019; Sirajuddin *et al.*, 2014). It has also been reported that the geometries of triphenyltin esters of salicylic acids mostly vary from tetrhedron (monodentate behavior of carboxylate ligand) to trigonal bipyramidal (bidentate behavior of carboxylate ligand) (Hussain *et al.*, 2015). In addition to the bidentate linkage of the central tin atom with carboxylate ligand in coordinated product **1**, the other three positions on tin are occupied by the phenyl ligands. The Sn-C (2.18 Å, 2.17 Å, 2.17 Å) and tin-oxgyen (2.60 Å, 2.13 Å) bonds are typical for similarly reported complexes (Shahzadi & Ali, 2008); the two C-O bond lengths (C-O1 and C-O2) are also non-equivalent (C-O1 = 1.36 Å and C-O2 = 1.28 Å). Table 1 shows the comparison of the bond length (Sn-O and C-O) data of the compound **1** with those of triphenyltin(IV) benzoates **2**-**7**.

Table 1. Comparison of the bond length (Å) data of complex 1 with those of complexes 2-7.

Comp. No.	Sn-O1	Sn-O2	$\Delta_{(Sn-O2)-(Sn-O1)}$	C-O1	C-O2	Reference
1	2.13	2.60	0.47	1.36	1.28	-
2	2.074	2.695	0.621	1.313	1.222	(Smith *et al.*, 1995)
3	2.054	2.781	0.727	1.321	1.214	(Vollano *et al.*, 1984)
4	2.043	2.823	0.78	1.310	1.237	(Swisher *et al.*, 1984)
5	2.048	2.861	0.813	1.304	1.216	(Smith *et al.*, 1995)
6	2.083	3.071	0.988	1.301	1.232	(Vollano *et al.*, 1984)
7	2.201	3.649	1.448	1.261	1.250	(Smith *et al.*, 1995)

The O1 and O2 represent the hydroxyl oxygen and the carbonyl oxygen, respectively of the carboxylate group of the coordinated ligand precursor. In organotin(IV) carboxylates, the hydroxyl oxygen of -COOH group is more strongly bonded with tin (reflected from smaller Sn-O1 bond distance) as compared to the carbonyl oxygen (indicated by larger Sn-O2 bond length); more closer the values of Sn-O1 and Sn-O2 bond lengths; more the uniform behavior of both the oxygen atoms (O1 and O2) and hence the bidentate chelation. The non-participation of phenolic -OH in complexation with the metal can be rendered to the presence of -Cl group at para position in 5-chlorosalicylic acid (ligand precursor); the chloro-group due to its electron donating resonance effect increases the electron density at phenolic-OH (para position) as a result the phenolic hydroxyl group is failed to deprotonate and thus remains non-coordinated. However, there may be the chances of interamolecular hydrogen between phenolic -OH and adjacent carbonyl group of -COOH which was also depicted by single crystal XRD structure of a similarly reported compound namely dibutyltin(IV) bis(5-chlorosalicylate) formed with the same ligand. Such kind of bonding is common in many organotin(IV) derivatives of the salicylic acids (Hussain *et al.*, 2015).

A closer look at Table 2 clarifies that there is a direct relation between the values of Sn-O2 bond length and $\Delta_{(Sn-O2)-(Sn-O1)}$. In the investigated triphenyltin(IV) benzoates, the Sn-O2 bond length is increased in the following order: 1<2<3<4<5<6<7, the value of $\Delta_{(Sn-O2)-(Sn-O1)}$ is also increased in the same order (from complex **1** to **7**). Consequently the bidentate chelation mode is varied in the reverse order; it is lowered with the increase of $\Delta_{(Sn-O2)-(Sn-O1)}$ value in going from the complex **1** to **7**. In case of triphenyltin(IV) 5-chlorosalicylate (**1**), the $\Delta_{(Sn-O2)-(Sn-O1)}$ value is the lowest (2.60-2.13 = 0.47 Å) as compared to all other triphenyltin(IV) benzoates **2**-**7** (Table 1). The reason is the simultaneous electron donating resonance effect of both the chloride and hydroxyl groups which increase the electron density at aromatic nucleus. It results in shifting of some electronic charge towards carboxylate ion, which enables both the carbonyl and hydroxyl oxygen atoms to develop a coordination linkage with the tin(IV) ion; thus a bidentate coordination mode is supported in this case. The investigated complex **1** demonstrates the highest bidentate chelation mode among all the complexes. When we move from triphenyltin(IV) 5-chloro-2-hydroxybenzoate (**1**) to triphenyltin(IV) benzoate (**2**), the Sn-O2 bond length is comparatively increased (2.695 Å) to a some extent with a consequent decrease of Sn-O1 bond length (2.074 Å); the overall result is that the $\Delta_{(Sn-O2)-(Sn-O1)}$ of **2** is increased to 0.621 Å (2.695-2.074) as compared to the complex **1**. In contrast to the complexes **1** (tri-substituted phenyl group of the ligand) and **2** (un-substituted phenyl group of the ligand), the phenyl nucleus of the ligand is di-substituted (one substituent is the carboxylate group and the other is 4-chlooro/2-

chloro/2-amino/2-hydroxy/2-methoxy) in complexes **3-7**; it results in an increase of Sn-O2 and $\Delta_{(Sn-O2)-(Sn-O1)}$ values and hence the monodentate behavior. The compound **7** displays the longest Sn-O2 bond length (3.649 Å) among all the triphenyltin(IV) benzoates (**1-7**) and consequently it demonstrates the highest $\Delta_{(Sn-O2)-(Sn-O1)}$ value. In all the triphenyltin(IV) derivatives (**1-7**), the shorter tin-oxygen bond (Sn-O1) is associated with longer carbon-oxygen bond length (C-O1) and *vice versa* (Sn-O2 longer and C-O2 shorter) according to early reported literature (Hussain *et al.*, 2016). An overview of the above Table 1 clarifies that the Sn–O1 bond distances (2.043-2.201 Å) are very close to covalent radii (2.13 Å) which indicates the covalent bonding in the Sn–O1. However, the Sn–O2 bond lengths (2.60-3.649 Å) are significantly lower than the sum of the van der Waal's radii (3.68 Å) and higher than the covalent radii (2.13 Å), demonstrating the coordinate covalent bonding in Sn–O2 linkage (Hussain *et al.*, 2016).

The calculated LUMO and HOMO orbitals of the molecules **1** are displayed in Figure 2 (a-c). Notice that both the HOMO and LUMO orbitals lie primarily on phenyl group attached to the carboxylate ligands. The calculated LUMO and HOMO energies are displayed in Table 2. It has been well established that a small HOMO-LUMO gap indicates an unstable molecule with high chemical reactivity whereas a large HOMO-LUMO gap demonstrates a stable molecule with low chemical reactivity. The value of E_{LUMO} displays the ability of a molecule to accept electrons (-electron affinity) whereas its ability to donate electrons (-ionization potential) is reflected by E_{HOMO}. The calculated E_{LUMO} and E_{HOMO} values (Table 2) describe comparative electron accepting and donating abilities of the investigated molecule **1**. Table 2 also displays the calculated global softness values ($S=1/2\eta$) (Yang & Parr, 1985), global hardness (η = I-A/2) values (Parr & Pearson, 1983), chemical potential values $\mu = -(I+A)/2$ (Parr *et al.*, 1978) and electrophilicity values ($\omega = \mu^2/2\eta$) (Parr *et al.*, 1999).

In compound **1**, the COOSn and the phenyl group (of ligand) are coplanar (inter planar angle is only 0.63 deg). The two phenyl groups on either side of the third phenyl group (which is diametrically opposite to the ligand) are symmetrically placed at 61.5^0 and 62.5^0 to the COOSn plane. The O-C-O bond angles are 118.33^0, while the O-Sn-O bond angles are 56.2^0. The computed partial charges (mulliken) of the atoms in the investigated molecule **1** show that the tin atom bears positive charges while the coordinating oxygen atoms have negative charges (Figure 3). The molecular electrostatic potential map shows the presence of more electron density on the oxygen atom (Figure 4). The direction of computed dipole moment (3.29 D) is shown in (Figure 5).

Table 2. Computed Molecular Descriptors by DFT.

HOMO energy (eV)	**-5.5211**	**Global Softness (S, eV^{-1})**	**0.3039**
LUMO energy(eV)	-2.2311	Chemical Potential (μ, eV)	-3.8761
HOMO-LUMO (eV)	3.29	Electrophilicity (ω, eV)	4.5666
Global Hardness (η, eV)	1.645	Dipole Moment (Debye)	3.29

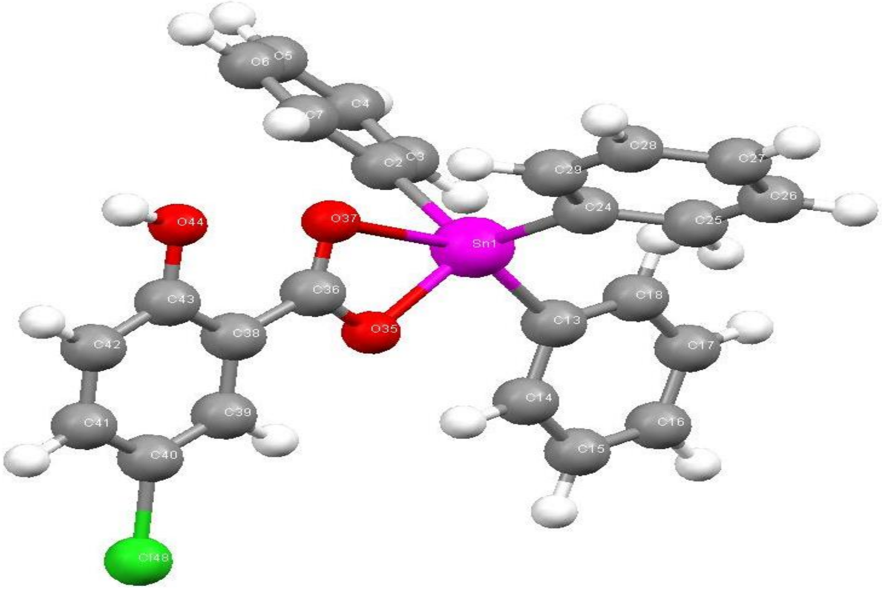


Figure-1. Geometry optimized structure of complex 1 (DFT 3-21G).

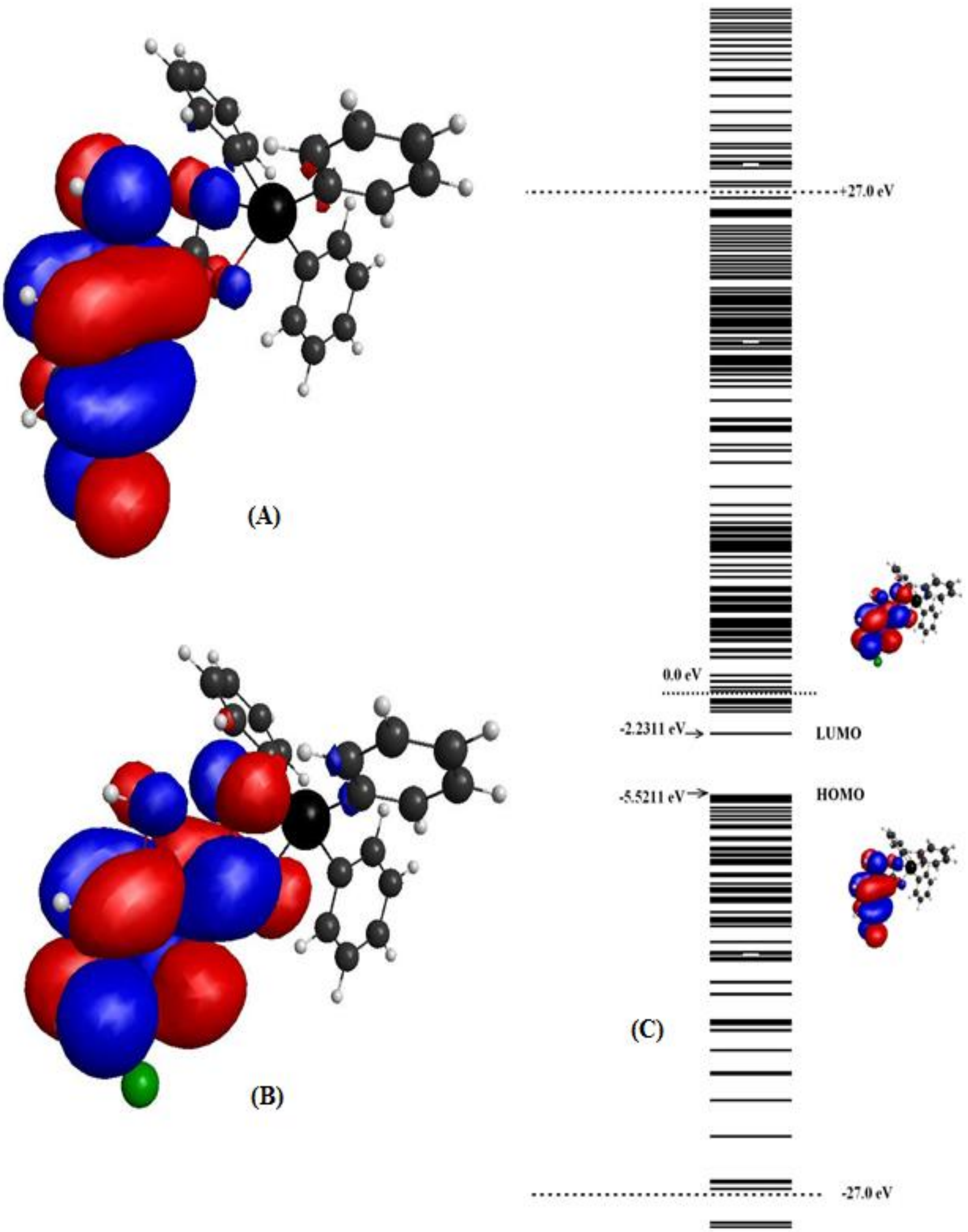


Figure-2. (a) HOMO orbital of 1 (DFT 3-21 G) (b) LUMO orbital of 1 (DFT 3-21 G) (c) Energy level diagram of molecular orbitals of 1 (DFT 3-21 G).

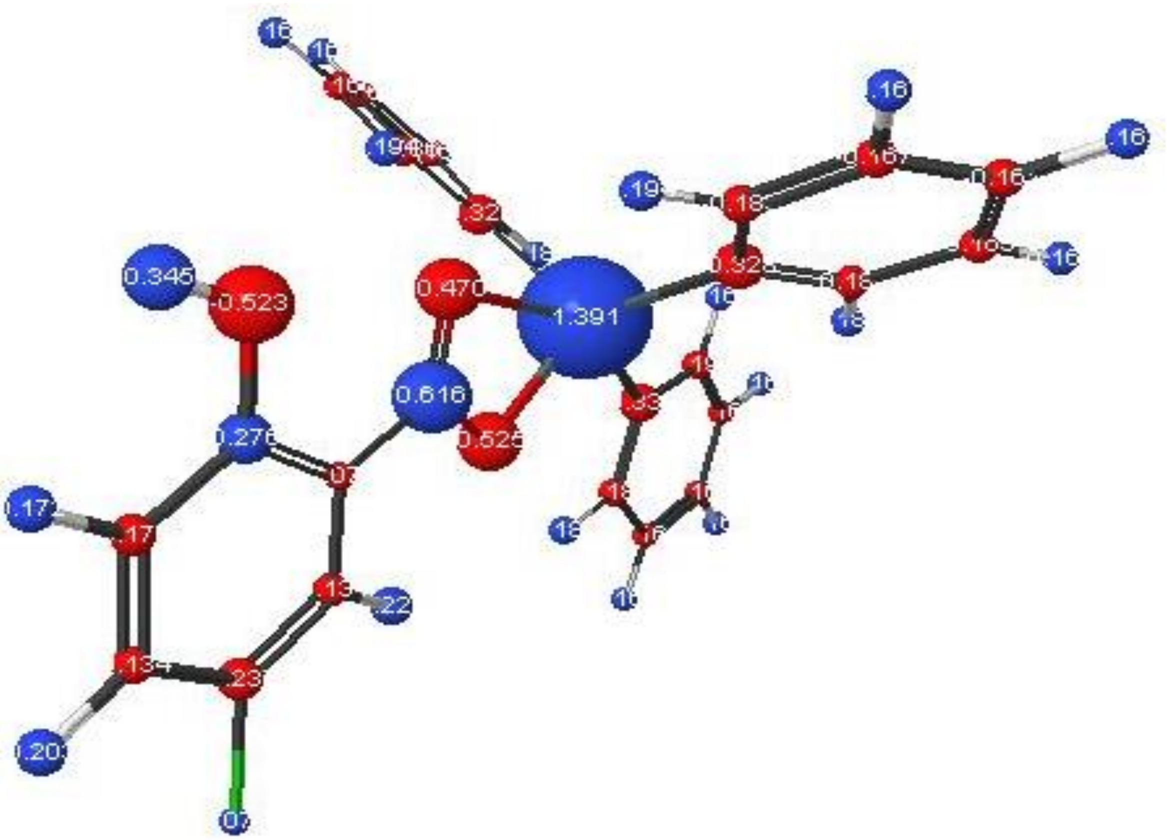


Figure 3. Charge description in the molecules.

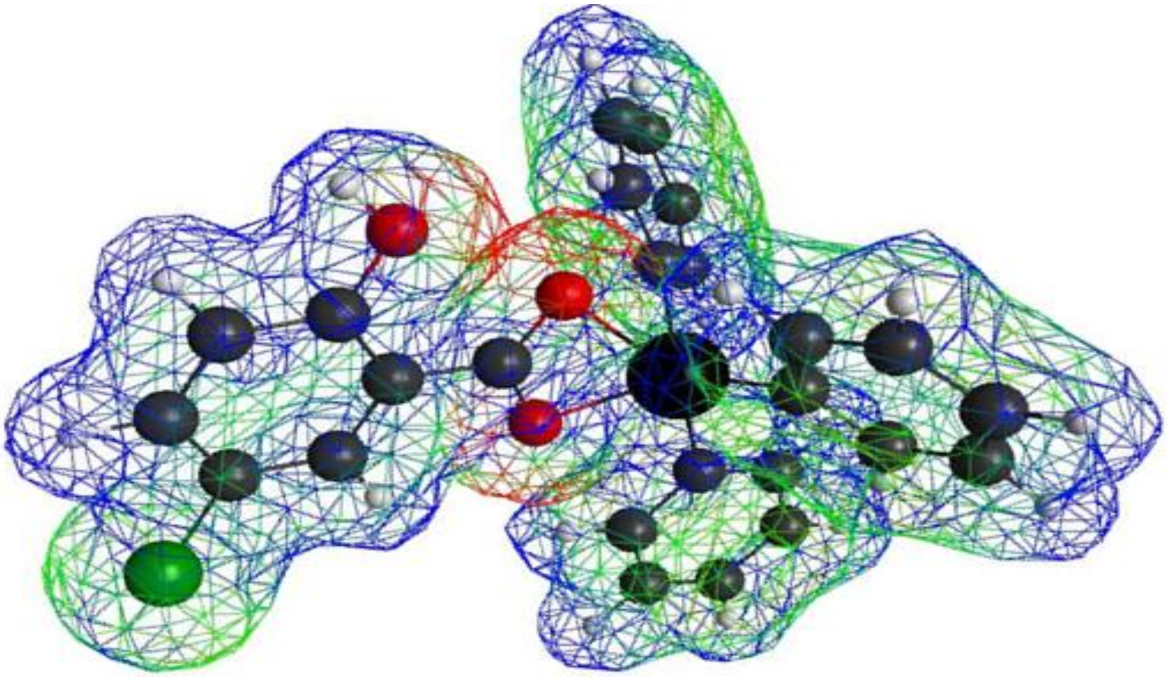


Figure 4. Molecular electrostatic surface potential mapped on total electron density map for the complex (red negative, green neutral, blue positive) (DFT 3-21G).

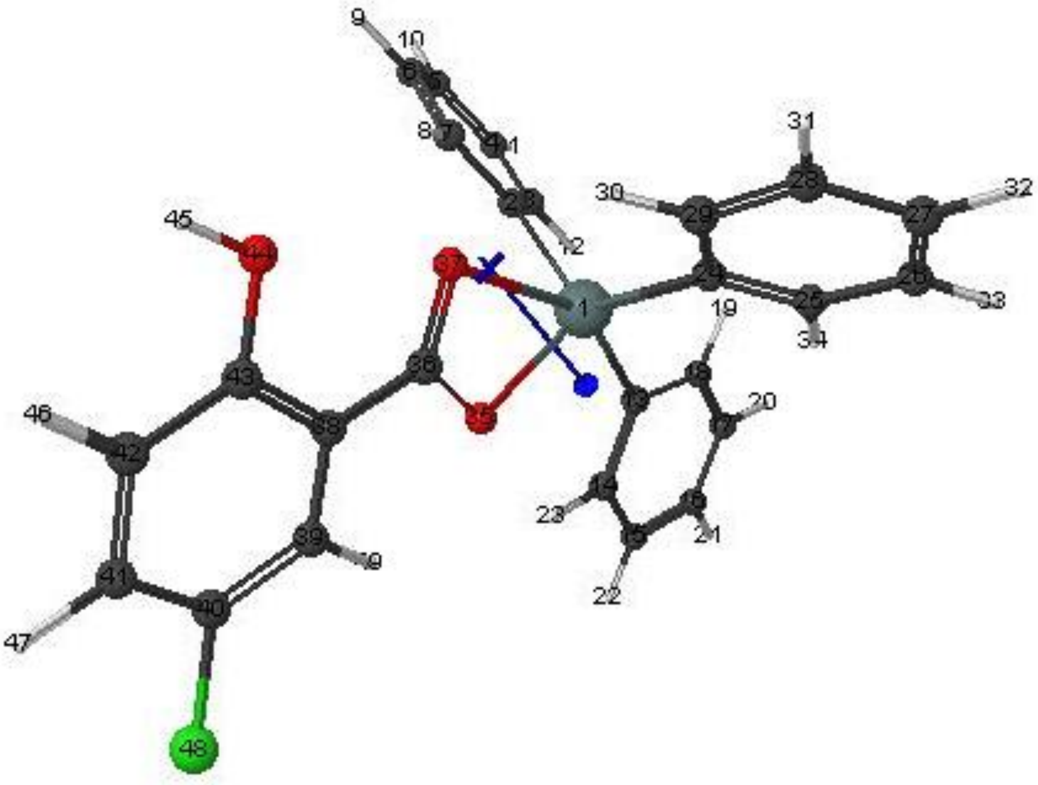


Figure 5. Dipole of complex (3-21G).

Conclusions: DFT calculations of triphenyltin(IV) 5-chlorosalicylate demonstrate that both carboxylic oxygens are linked with the triphenyltin(IV) moiety in a bidentate fashion. A direct relation was found between the values of Sn-O2 bond length and $\Delta_{(Sn\text{-}O2)\text{-}(Sn\text{-}O1)}$; the Sn-O2 bond length was found to increase (1<2<3<4<5<6<7) with the corresponding rise of $\Delta_{(Sn\text{-}O2)\text{-}(Sn\text{-}O1)}$ value. The calculated E_{LUMO} and E_{HOMO} values describe comparative electron accepting and donating abilities of the investigated molecule **1**.

REFERENCES

Abbas, S. M., S. Ali, S. T. Hussain and S. Shahzadi. (2013). structural diversity in organotin (IV) dithiocarboxylates and carboxylates. J. Coord. Chem. 66(13): 2217-2234.

Dias, L., G. de Lima, C. Pinheiro, M. Nascimento and R. Bitzer. (2017). Molecular and supramolecular properties of nitroaromatic thiosemicarbazones: Synthesis, spectroscopy, X-ray structure elucidation and DFT calculations. J. Mol. Struct. 1131: 79-86.

Dubey, R. K., A. P. Singh, N. Jaiswal, D. P. Singh, Meenakshi, A. K. Kushwaha, M. Kumar, and A. Anjum. (2019). Synthesis, spectroscopic characterization, DFT calculations, and antimicrobial activities of N-arylsalicylaldiminate derivatives of diorganotin (IV). J. Coord. Chem. 72(19-21): 3371-3384.

Geerlings, P., R. Vivas-Reyes, F. De Proft, M. Biesemans and R. Willem. (2003). DFT based reactivity descriptors and their application to the study of organotin compounds Metal-Ligand Interactions (pp. 461-495): Springer.

Gielen, M. (2008). Tin chemistry: fundamentals, frontiers, and applications: John Wiley & Sons.

Granovsky, A. A. (2012). www Firefly version 7.1. G. http://classic. chem. msu. su/gran/gamess/index. html.

Hussain, S., S. Ali, S. Shahzadi and C. Rizzoli. (2013). Polymeric three-dimensional crystal structure of a tributyltin (IV) derivative with acetylene dicarboxylic acid. Phosphorus, Sulfur, and Silicon & Rela. Elem. 188(6): 812-818.

Hussain, S., S. Ali, S. Shahzadi, S. K. Sharma, K. Qanungo and I. H. Bukhari. (2012). Homobimetallic complexes containing Sn(IV) with acetylene dicarboxylic acid: Their syntheses and structural interpretation by spectroscopic, semi-empirical, and DFT techniques. J. Coord. Chem. 65(2). doi:10.1080/00958972.2011.648186

Hussain, S., S. Ali, S. Shahzadi, S. K. Sharma, K. Qanungo, M. Shahid, A. Jabbar and I. H. Bukhari. (2015). Organotin(IV) complexes with

5-aminoisophthalic acid: Synthesis, characterization, theoretical study and biological activities. Russ. J. Gen. Chem. 85(10). doi:10.1134/S1070363215100266

Hussain, S., S. Ali, S. Shahzadi, M. N. Tahir and M. Shahid. (2015). Synthesis, characterization, biological activities, crystal structure and DNA binding of organotin (IV) 5-chlorosalicylates. J. Coord. Chem. 68(14): 2369-2387.

Hussain, S., S. Ali, S. Shahzadi, M. N. Tahir, M. Shahid, K. S. Munawar and S. M. Abbas. (2016). Synthesis, spectroscopy, single crystal XRD and biological studies of multinuclear organotin dicarboxylates. Polyhedron. 117: 64-72.

Mariam, S., S. Hussain, S. Ali, S. Shahzadi, S. Ramzan and M. Shahid. (2018). Homobimetallic (Sn, Sn) complexes with [2-Dithiocarboxy (methyl) amino] acetic acid: synthesis, characterization and biological studies. Iran J Sci Technol Trans A Sci. 42(3): 1277-1284.

Nitsch, J., L. P. Wolters, C. Fonseca Guerra, F. M. Bickelhaupt and A. Steffen. (2017). Enhanced π-Back-Donation as a Way to Higher Coordination Numbers in d10 [M (NHC) n] Complexes: A DFT Study. Chem. Eur. J. 23(3): 614-622.

Parr, R. G., R. A. Donnelly, M. Levy and W. E. Palke. (1978). Electronegativity: the density functional viewpoint. J. Chem. Phy. 68(8): 3801-3807.

Parr, R. G. and R. G. Pearson. (1983). Absolute hardness: companion parameter to absolute electronegativity. Journal of the American Chemical Society. 105(26): 7512-7516.

Parr, R. G., L. V. Szentpaly and S. Liu. (1999). Electrophilicity Index. J. Am. Chem. Soc. 121(9): 1922-1924.

Schmidt, M. W., K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen and S. Su. (1993). General atomic and molecular electronic structure system. J. Comput. Chem. 14(11): 1347-1363.

Shahzadi, S., and S. Ali. (2008). Structural chemistry of organotin (IV) complexes. J. Iran. Chem. Soc. 5(1): 16-28.

Shujah, S., S. Ali, N. Khalid, M. J. Alam, S. Ahmad and A. Meetsma. (2018). Synthesis, spectroscopic characterization, X-ray structure, DFT calculations, and antimicrobial studies of diorganotin (IV) complexes of monotopic oxygen nitrogen donor Schiff base. Chemical Zvesti. 72(4): 903-919.

Sirajuddin, M., S. Ali, V. McKee, N. Akhtar, S. Andleeb and A. Wadood. (2019). Spectroscopic characterizations, structural peculiarities, molecular docking study and evaluation of biological potential of newly designed organotin (IV) carboxylates. J. Photochem. Photobiol. B, Biol. 197: 111516.

Sirajuddin, M., S. Ali, V. McKee, S. Zaib and J. Iqbal. (2014). Organotin (IV) carboxylate derivatives as a new addition to anticancer and antileishmanial agents: design, physicochemical characterization and interaction with Salmon sperm DNA. RSC Adv. 4(101): 57505-57521.

Smith, P. J., R. O. Day, V. Chandrasekhar, J. M. Holmes and R. R. Holmes. (1995). Chain structures of trimethyltin esters of salicylic acid and o-anisic acid. Tin-119m Mössbauer study of a series of trimethyltin and triphenyltin carboxylates. Phosphorus, Sulfur, and Silicon & Rela. Elem. 99(1-4): 1-12.

Swisher, R., J. Vollano, V. Chandrasekhar, R. Day and R. Holmes. (1984). Pentacoordinated structures of triphenyltin esters of anthranilic acid, o-(dimethylamino) benzoic acid, and p-aminobenzoic acid formed by intramolecular carboxylate group coordination. Inorg. Chem. 23(20): 3147-3152.

Vollano, J., R. Day, D. Rau, V. T. Chandrasekhar and R. Holmes. (1984). Intramolecularly formed pentacoordinated structures of triphenyltin esters of salicylic acid, o-anisic acid, and p-methylthiobenzoic acid. Inorg. Chem. 23(20): 3153-3160.

Yang, W. and R. G. Parr. (1985). Hardness, softness, and the fukui function in the electronic theory of metals and catalysis. Proceedings of the National Academy of Sciences. 82(20): 6723-6726.