Synthesis, Spectral, Structural Characterizations and Study of Mosquitocidal Properties of Trimethyl (Chloro) (4-N, N-Dimethylamino Pyridine) Tin (IV) Complex.

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Abstract: ***The novel organotin (IV) complex such as $Sn(CH_3)_3Cl$ 4-N, N- dimethyl aminopyridine was synthesized and characterized by employing ^1H, ^{13}C, ^{119}Sn NMR and single crystal X-ray analyses. The spectral and structural studies revealed that the complex formation of 4-N, N-dimethylaminopyridine with trimethyltin(IV) chloride at normal reaction conditions. Single crystal X-ray study of the complex has confirmed that the tin atom is in regular trigonal bipyramidal geometry with three methyl groups in the equidirectional position and the 4-N, N-dimethylaminopyridine and chloride are in axial position. Larvicidal and pupicidal activities of synthesized compounds were tested against freshly moulted (0 – 6 hrs) 4th instar larvae of A. aegypti (larvae of dengue mosquito), A. stephensi and C. quinquefasciatus at 25, 50, 75, 100 and 125ppm concentrations. Significant larval and pupal mortality was observed in trimethyl(chloro)(4-N,N-dimethylaminopyridine) tin(IV) complex on tested larvae.***

Keywords: Trimethyltin chloride, 4-N, N-dimethylaminopyridine, ^1H, ^{13}C and ^{119}Sn NMR and X-ray Studies, Larvicidal and Pupicidal activity.

I. INTRODUCTION:

The coordination properties of tin atom cause a stable complex formation of organotin (IV) compounds with heteroatoms, especially, nitrogen atoms [1]. Recently, multiple nitrogen donor ligands are used to prepare new organometallic compounds in different coordination numbers due to its diversity in coordination properties [2]. These compounds have received great attention for further studies because of their ability to produce a fascinating series of ligands [3]. The properties of these compounds can be significantly changed by introducing different organic substituents and thus producing differences in donor properties [4]. Both in inorganic and organometallic complexes, the coordination chemistry of tin is known with numerous geometries and variety of coordination numbers [5]. Various geometries are possible for the complexes formed by the interaction of donor ligands with metal ions with different properties and these complexes are biologically more active [6].

The relationship between the coupling constant of NMR chemical shift values with structural parameters is reported. It established that $|^1J^{119}Sn, ^{13}C|$ coupling constant can be used to calculate the bond angles [Me – Sn – Me] using empirical equations. The calculated bond angles are correlated with bond angles observed by x-ray diffraction in several complexes [7].

Pyridine and substituted ligands such as 4-N, N-dimethylamino pyridine are having importance in making complexes with organotin (IV) compounds. Also, biological studies of these complexes are making an interest in the fields of research [8]. In our current research work, we published the coordination properties of tribenzyl (chloro) (4-N, N-dimethylaminopyridine) tin(IV) by the reaction of 4-N, N-dimethylamino pyridine with tribenzyltin(IV)chloride compound at ambient reaction conditions [9].

In a continuation of our research work, we tried to carry out the reactions of triorganotin (IV) chlorides with 4-N, N-dimethylamino pyridine under the same condition [Scheme 1]. For a lot of viral, bacterial and protozoans diseases mosquitoes act like vector [10]. In the time of virus diffusion and public health, significance mosquitoes are careful as a very essential group of insects. The population of mosquito's increases exponentially that is a major difficulty for many countries as mosquitos increase the different diseases such as filarial, Japanese encephalitis, Lyme disease, Yellow fever, encephalitis, malaria, chikungunya, dengue, and epidemic polyarthritis [11]. Most of the mosquito control programs target the larval stage in their breeding areas with larvicides because the adulticides may only reduce the adult population temporarily [12] [13]. Larvicidal is the use of chemicals to kill mosquito larvae or pupae in the water. It is generally more effective and object-specific than applying chemicals to kill adult mosquitoes. In controlling mosquito's larvae, dichlorodiphenyltrichloroethane (DDT), organophosphate temephos, methoprene, pyrethroids, phytochemicals, and soil bacterium (Bacillus thuringiensis israelensis and Bacillus sphaericus) have been employed [14]. These insecticides have been reported to create serious pressure to the atmosphere in killing non-target species such as larval predators, bioaccumulation, hampering biodiversity, and ecological contamination [15]. Larvicides play a significant role in controlling mosquitoes at their breeding and young stages. Hydrazone derivatives overcome good larvicidal activity in our earlier study [16] [17] [18].

In the present study determination of larvicidal properties synthesized compound against important vector mosquitoes. The most important center of mosquito control in a lot of countries is dropping larval populations and frequently involves the incorporated use of animal territory adjustment and purpose of insecticides. Physical environment change involves digging channels during swamp areas, such as salt marsh, to link isolated pools with the tidal resource. This increases water movement through low amplitude tides and, consequently, larval increase [19] and egg conditioning [20] of mosquitoes is unsuccessful. Even despite the fact that physical habitat alteration has been used broadly, the application of insecticides residue the most common approach in most parts of the world [21] [22].

II. EXPERIMENTAL ASPECTS, MATERIALS AND METHODS

2. 1. Chemicals used

Trimethyltinchloride and 4-N, N-dimethylaminopyridine were purchased from Alfa Aesier. The solvents such as MeOH, $CHCl_3$ and Ethyl Acetate and Petroleum Ether, E- Merck India Limited make, were purchased directly from local dealers.

2.2 Physical Measurements

Melting point was obtained with SIGMA Instruments apparatus. ^{1}H NMR, ^{13}C NMR and ^{119}Sn NMR Spectra were recorded at room temperature in $CDCl_3$ on a Bruker Avance 400 MHz. For ^{1}H NMR, and ^{13}C NMR spectra, tetramethylsilane and for ^{119}Sn NMR tetramethyl tin were used as reference samples respectively.

2.3 X-ray crystallography

Crystals of the complex are obtained as colourless plates in a rectangular shape by slow evaporation of the solution in chloroform. The intensity data were collected at 293 K on a Bruker APEX2 Diffraction System [23] using MoKα graphite monochromated radiation (99.6% complete). Image plate distance 70mm, oscillation scans 0 - 163° with step = 1.3°, exposure time 6 mins, 2θ range 1.11 – 25.00°. The structure was solved by Direct methods using the program SHELXS-97 [24].The refinement and all further calculations were carried out using SHELXL-97[24]. The H- atoms were incorporated in calculated positions also treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, by means of weighted full-matrix least-squares on F2. Empirical absorption corrections were applied using the multi-scan routine in PLATON [25]. Moreover, crystallographic data and refinement details are given in Table 1. The selected experimental and theoretical bond lengths and bond angles are presented in Table 2.

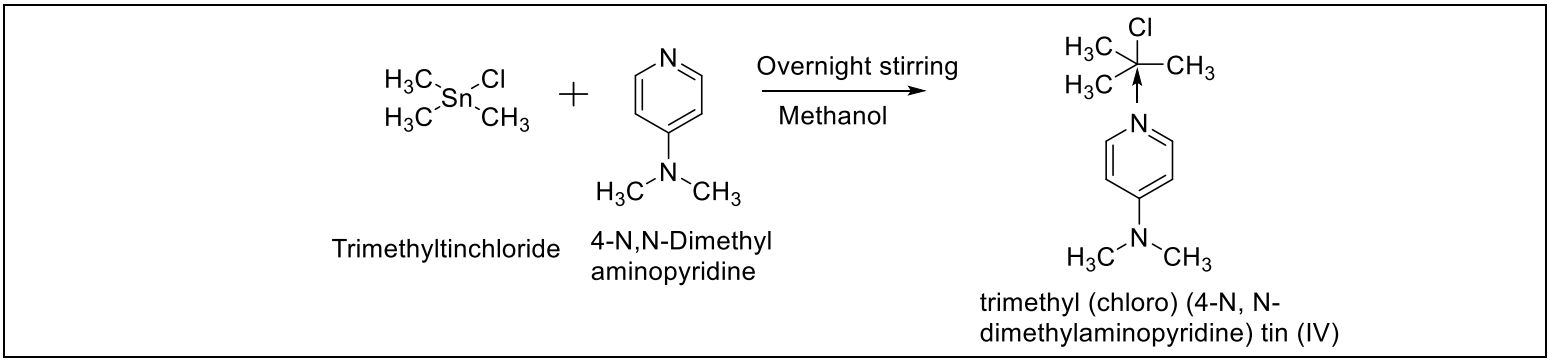
2.4 Synthesis of trimethyl(chloro) (4-N,N-dimethylaminopyridine)tin(IV):

The trimethyl tin chloride 1g (0.005mole) in methanol, 4-N, N-dimethylamino pyridine 0.613 (0.005mole) in methanol was added dropwise using a pressure equalizing funnel. During the addition, the formation of white turbidity is an indication of the formation of the complex. After the completion of the reaction, the solvent was removed completely in a vacuum. A white solid was obtained and crystallized by the vapour diffusion method. The solid was dissolved in chloroform in a vial and was placed in a beaker containing petroleum ether. The reaction between trimethyl tin chloride with 4-N, N-dimethylaminopyridine is shown in scheme I. Crystals were separated after two days. Yield: 1.25 g, 78.12 %.

^{1}HNMR ppm: 0.764, 9H, three CH_3 groups [attached to tin], 3.074, 6H, two CH_3 groups [attached to nitrogen]; $^{2}J^{119}Sn,^{1}H| = 66.4$ Hz, 6.544 and 6.548 d-d, ^{1}H, 6.558 and 6.562 d-d, 1H, 7.964 and 7.960 d-d, 1H, 7.951 and 7.947 d-d, 1H;

^{13}C NMR: 4.828, (CH_3), 38.943 (CH_2), 106.778, 145.945, 154.639 Ar-C.

^{119}Sn NMR: –35.28 Sn – atom.



Synthesis of trimethyl (chloro) (4-N, N-dimethylaminopyridine) tin (IV) complex

2.5 Vector rearing

The larvae of A. aegypti, A. stephensi and C. quinquefasciatus mosquitos were obtained from National Center for disease control, Government of India ministry of health and family welfare, Southern India branch, field station, Mettupalayam, Coimbatore district, Tamilnadu, India. The larvae were preserved in the plastic buckets containing half-filled tap water and fed up with dog biscuit once a day initially and twice during the later stages of development. Water was refreshed by removing a little quantity of water every day and replacing with fresh water in rearing container. This was aimed at preventing scum from forming on the water surface.

2.6 Larvicidal bioassay

The larvicidal activity of trimethyl (chloro) (4-N, N-dimethylaminopyridine) tin (IV) was assessed by using the standard method as prescribed by WHO (2005). Five different test concentrations (25, 50, 75, 100 and 125ppm) were prepared and tested against the freshly moulted (0 – 6 hrs) 4th instar larvae of Ae. Aegypti (larvae of dengue mosquito), An. stephensi and Cx. Quinquefasciatus mosquitos from the stock solution. Twin20 (emulsifier) in water was treated as control. The larvae of these mosquito species (25 larvae) were introduced in 500-ml plastic cups containing 250 ml of aqueous medium (249 ml of dechlorinated water + 1ml of emulsifier) and the necessary amount of trimethyl(chloro) (4-N, N-dimethylaminopyridine)tin(IV). The larval mortality was witnessed and documented after 24 h of post-treatment. Five replicates were sustained at a time, for each experiment. The percentage of mortality was calculated by using Abbott's formula (Abbott, 1925). The LC50, LC90, 95% confidence limit of Lower Confidence Limit (LCL) and Upper Confidence Limit (UCL), chi-square values and the degrees of freedom was calculated by using Probit analysis with Statistical Package for Social Sciences (SPSS) 16.0 Version in MS-Excel, 2007.

2.7 Pupicidal bioassay

The pupicidal activity of trimethyl (chloro) (4-N, N-dimethylaminopyridine) tin(IV)was assessed by using the standard method as prescribed by WHO,(2005). Similar test concentrations as stated in the previous experiments were prepared and tested against the pupae of *An. stephensi*, *Ae. Aegypti* and *Cx.quinquefasciatus*. DMSO (emulsifier) in water treated as control. The pupae of these mosquito species (25 pupae) were presented in 500-ml plastic cups containing 250 ml of aqueous medium (249 ml of dechlorinated water + 1ml of emulsifier) and the required amount of trimethyl (chloro) (4-N, N-dimethylamino pyridine) tin (IV). The pupal mortality was detected and recorded after 24 h of post-treatment. For each experiment, five replicates were maintained at a time. The percentage of mortality was calculated by using Abbott's formula.

3. RESULTS AND DISCUSSION

A new organotin (IV) derivative of 4-N, N-dimethylamino pyridine complex was prepared by the reaction of the 4-N, N-dimethylamino pyridine with trimethyltin (IV) chloride in methanol inappropriate [1:1] mole ratio. The complex was soluble in common organic solvents.

3.1 Spectroscopic data

The complex was characterized by multinuclear (^{1}H, ^{13}C, ^{119}Sn) NMR, Spectroscopy and X-ray analysis in combination with melting points. The spectroscopic data have been mentioned in the synthesis section 2.4.

The ^{1}H NMR spectrum of the complex is shown in Fig.1 In the ^{1}H NMR spectrum, a [27] peak at 0.764 ppm with satellite peaks $|^2J^{119}Sn,^1H|$ = 66.4 Hz is observed due to the protons of the three methyl groups attached to tin in the identical environment and is the indication of bond formation between Sn and carbon atom. The satellite peak shows that a $|^2J^{119}$ Sn, ^{1}H | coupling with 117Sn and 119Sn nuclei is in the range between 45 – 65 Hz. It is the indication of the presence of Sn – N pentacoordinated geometry in the complex $|^2J^{119}Sn, H|$ = 66.4 Hz) which is comparable with reported complexes. The $|^2J^{119}Sn, ^1H|$ value 66.4 Hz is higher than the value of 59 Hz observed for trimethyltin chloride. This may indicate higher s character on tin atom [28]. A sharp singlet peak at 3.074 ppm confirms the presence of two methyl groups attached to the nitrogen in the complex. The doublet value peaks at 6.544 – 6.562(d–d) [J = 5.6 Hz], 7.947 – 7.964 (d–d) [J = 5.3 Hz] and 3.074 (s) reveals the presence of 4-N, N-dimethylaminopyridine protons in the complex and shows upfield shifts with respect to the signals of the free ligand 8.17(d) [J = 6Hz], 6.64 (d) [J = 6Hz] and 2.69 (s) [26].

The ^{13}C NMR spectrum of trimethyl (chloro) (4-N, N-dimethyl amino pyridine) tin (IV) is shown in Fig.2. In ^{13}C NMR a peak at 4.828 ppm is observed with two satellite peaks ($|^1J^{119}Sn, ^{13}C|$ = 482.41 Hz) due to the presence of methyl group carbons attached to Sn atom. The chemical shift value for trimethyl tin chloride is – 0.87 ppm in $CDCl_3$ solvent. This coupling constant, ^{1}J, the value is higher than that of trimethyltin chloride $|^1J^{119}Sn, ^{13}C|$ = 379 Hz.] dueto the increase of s electron density on tin atom over complexation [28] [29]. The $|^1J^{119}Sn, ^{13}C|$ coupling constant value 482.41 Hz for the complex also reveals the pentacoordinated organotin complex and is most comparable with the values of the similar type of complexes [30]. The ^{1}J value is an important parameter to assess the coordination number of the Sn atom in all types of organotin(IV) compounds. The qualitative investigation of an organotin structure has been well-found by the magnitude of the coupling constant, J, value in solution state pertaining to the Sn coordination number [31]. The peak observed at 38.943 ppm is the indication of the presence of methyl group carbons attached to the nitrogen atom. In the aromatic region, the carbon atoms of 4-N, N-dimethyl aminopyridine are confirmed by the peaks at 106.778, 145.945 and 154.639ppm.

The ^{1}J value is an important parameter to assess the coordination number of the Sn atom in all types of organotin (IV) compounds [33]. The interpretation of chemical shift and coupling constants with bond angles [^{1}J and the Me Sn – Me, θ; ^{2}J and θ] around the tin atom is generally based on the following empirical equations. The calculated bond angles obtained from these equations are comparable with bond angles obtained by experimental crystal data structure solution for this complex [34].

$$[^1J] = 11.4\theta - 875. \quad (1)$$

The $|^1J^{119}Sn, ^{13}C|$ coupling constant value for the complex is 482.41 Hz. As per the above equation 482.41 = 11.4θ – 8.75. Hence, θ = 1357.4/11, θ = 123.4. It is quite comparable with the experimental values obtained in our complex as shown below.

Bond	Angle, θ
C8-Sn1-C9	121.4
C8-Sn1-C10	120.2
C9-Sn1-C10	117.8

The ^{119}Sn NMR spectrum of trimethyl(chloro)(4-N, N-dimethylaminopyridine) tin(IV) is shown in Fig.3. The single peak at – 35.28ppm in ^{119}Sn NMR evidences the formation of penta coordinated tin complexes. The ^{119}Sn NMR signal observed at 165.7 ppm for trimethyltin chloride was shifted to – 35.28 ppm in the product. The upfield signal is ascribed to high electron density on tin due to complexation. It is having resemblances of the reported values of similar type complexes. ^{119}Sn NMR shifts in the range of -42 to -53 ppm have been reported for triorganotin tetrazolypyridine complexes [32].

3.2 Crystallographic study

The ORTEP representation including the numbering scheme for the molecular structure of the complex is shown in Fig.4. The crystallographic data, refinement details, the selected bond lengths and angles for the complex of the crystal are listed in Table 1 and 2. There are four independent molecules in the asymmetric unit in the complex and is discussed here. The coordination geometry around the tin atom is trigonal bipyramidal with Sn – N, Sn – Cl, Sn – C, Sn – C and Sn – C bonds. The nitrogen and chlorine atoms of the monodentate ligand are in axial positions and three carbons of methyl groups are in equatorial positions in the complex. These conclusions are confirmed in the packing diagram of the molecular crystal shown in Fig 5.

All the observed bond lengths around a tin atom are close or very close to the mean Sn-Cl, Sn-C, Sn-N distances in the molecule of tribenzyl(chloro)(4-N, N-dimethylamino pyridine)tin(IV) complex reported in our published research work [9]. The Sn-Cl distance is 2.565 (2) Å lies in the range (2.32 Å - 2.58 Å) of Sn-Cl distances found in several reported chloroorganotin (IV) complexes [35] [36]. The Sn-N bond length is 2.450(7) Å in the complex is shorter than the complexes [37] [38]. They are longer than the sum of the covalent radii of tin and nitrogen (2.15Å) and significantly shorter than the sum of their van der Waals radii (3.75 Å) [39]. The longer Sn – N bond lengths in organotin complexes are associated with its higher antitumour activity [40]. Therefore, this complex is also expected to be more active in antitumour activity. The Sn-C distances 2.109(11) Å in the complex are quite close to those found in the similar type of complexes [41] [42] [43] [44]. These results suggest that the monodentate nitrogen donor ligand forms an extensive bonding interaction in axial position with the triorganotin chloride compound in the geometry of trigonal bipyramidal. The deviation from the regular trigonal bipyramidal geometry (N (1)-Sn (1)-Cl (1) 176.58º (18)) in the complex is owing to the presence of the electronegative Cl atom and N atom of the 4-N, N-dimethylaminopyridine ligand in axial positions.

3.3 Mosquitocidal Properties:

Larvicidal effect of Synthesized trimethyl (chloro) (4-N, N-dimethylamino pyridine) tin (IV) was tested against the fourth in star larvae of A. stephensi, A. aegypti and C.quinquefasciatus are shown in Table 3. It was observed that 51.40±2.4, 67.80±2.5, 78.40±3.2, 92.40± 2.4 and 100.00±0.0%; 57.20±2.3, 74.50±3.9, 81.40±2.1, 93.20±3.6 and 100.00±0.0 %; 55.40±3.6, 70.40±2.5, 82.50±2.0, 94.50± 1.1and 100.00±0.0%of larval mortality among the experimental larvae when treated with 25, 50, 75, 100 and 125ppm concentration of the trimethyl(chloro)(4-N,N-dimethylaminopyridine)tin(IV) respectively (Table 3). The LC50 (LCL- UCL), LC95 (LCL- UCL), x2value for the data was 27.1(15.4 - 33.5), 108.4 (97.2 -124.0)4.717; 17.8(2.4-28.1)104.3(93.1-121.6)4.395; 22.3(9.5-31.3), 101.6(91.2-117.1)3.376. Statistical analysis of the data was found significant between the observed larval mortality and the tested concentrations ($p < 0.05$ (ANOVA; LSD -Tukey test; Table 4).

Pupicidal activity of trimethyl (chloro) (4-N, N-dimethylaminopyridine) tin (IV) was tested with 25, 50, 75, 100 and 125ppm concentrations (Table 4). The data pertaining to the above experiment clearly revealed that, the pupal mortality induced by the extract are directly proportional to the concentration of the trimethyl(chloro)(4-N,N- dimethylaminopyridine) tin(IV) and indirect proportion to the adult emergence, i.e., the increase in concentration resulted in increased pupicidal activity with decreased adult emergence. On perusal, the data for trimethyl(chloro)(4-N,N-dimethylaminopyridine) tin(IV) showed 46.5±3.1, 60.4±1.8, 76.5±2.0, 88.5±3.4 and 96.8±2.5 of pupal mortalities with the adult emergence of 53.5±2.8, 39.6±2.5, 23.4±3.1, 11.5±3.2 and 3.2±1.5%; 56.4±3.1, 75.5±3.5, 88.6±2.1, 94.4±1.6 and 100.0±0.0 of pupal mortalities with the adult emergence of 43.6±3.1, 24.4±3.9, 11.4±1.5, 5.6±4.4 and 0.0±0.0%; 52.3±2.4, 71.4±1.9, 82.3±2.2, 91.4±2.8 and 100.0±0.0 of pupal mortalities with the adult emergence of 47.7±3.4, 28.6±2.6, 17.6±1.7, 8.6±2.6 and 0.0±0.0% were observed at 25, 50, 75, 100 and 125 ppm concentrations respectively. The LC_{50} (LCL- UCL), LC95 (LCL- UCL), x2 value for the data 33.0(21.6-41.4), 122.4(109.9-140.8) 0.954; 8. 1(4.3-27.5), 94.8(84.9-109.5)1.838; 23.5(10.6-32.6), 105.9(95.1-122.1)3.645.

It was reported that the synthesized compounds of 1-aryl-4-methyl-3, 6-bis-(5- methylisoxazol-3-yl)-2-thioxo-2, 3, 6,10b-tetrahydro-1H-pyrimido [5, 4-c] quinolin-5- ones showed Mosquito larvicidal activity against fourth instar larvae Culexquinquefasciatus [45]. The compound is evidenced as lethal in the case of mosquito larvae [Some of the compounds are proved to be lethal for mosquito larvae] and tested for mosquito larvicidal activity. The compound exhibited higher mosquito larvicidal activity [46].

4. CONCLUSION

The synthesis of triorganotin (IV) chloride complexes with N-disubstituted pyridine is a typical synthetic method for the generation of trimethyl(chloro)(4-N, N-dimethylaminopyridine)tin(IV) complexes. Both spectral and structural studies reveal that the formation of pentacoordinated tin (IV) complex. These studies indicated that the synthesized compound possessed significant larvicidal and pupicidal activity against mosquitoes. Further studies are currently underway to optimize to enhance the larvicidal activity of these compounds.

5. ACKNOWLEDGMENT

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6. SUPPLEMENTARY DATA:

Crystallographic data (excluding structure factors) for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 990112. Copies of the data can be obtained free of charge on application to CCDS, 12 Union Road, Cambridge CB1 1EZ, UK [Fax: (internet) +44-1223/336-033; E-mail: deposit@ccds.cam.ac.uk].

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Figures

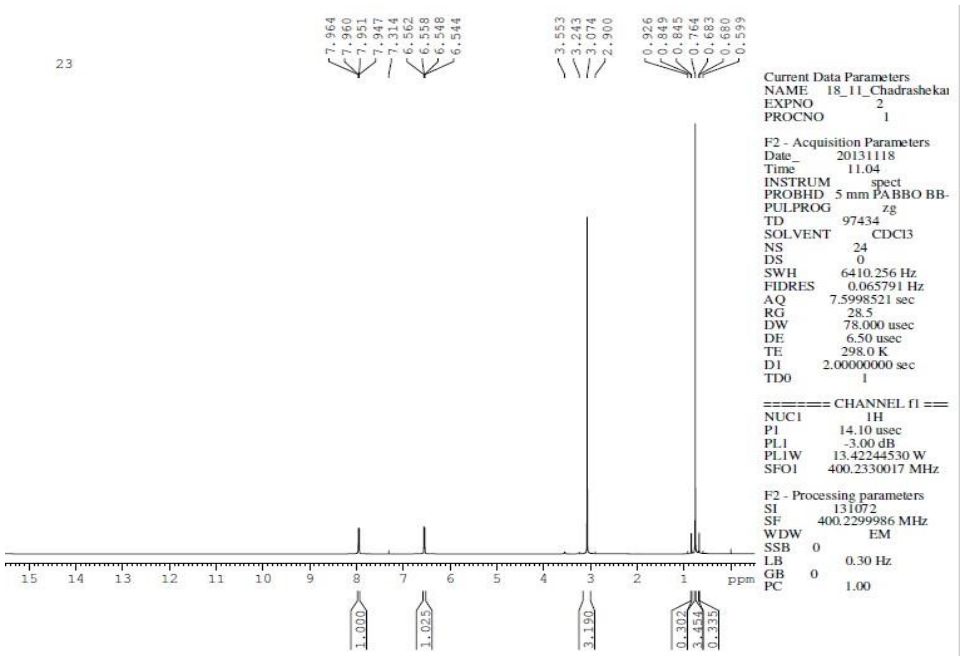

Fig. 1. The ^{1}H NMR spectrum of trimethyl(chloro)(4-N,N- dimethylaminopyridine) tin(IV) Complex

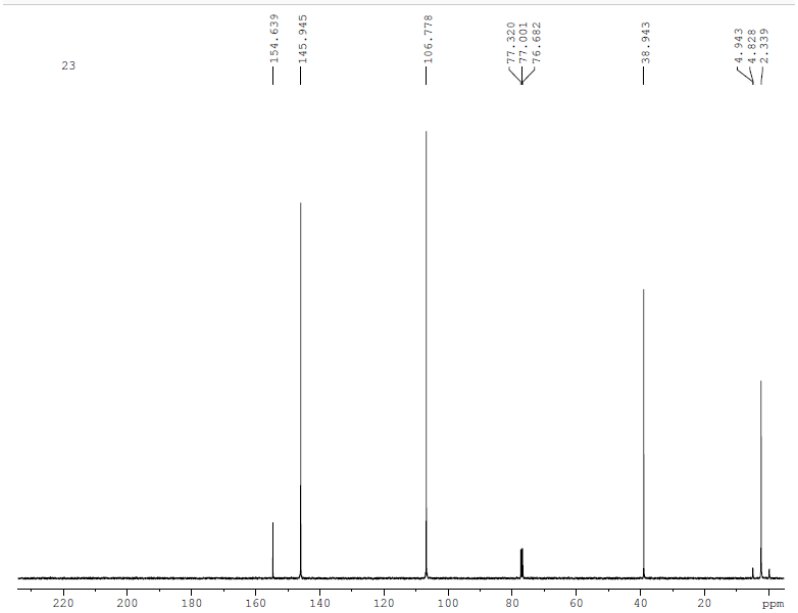

Fig. 2. The ^{13}C NMR spectrum of trimethyl(chloro)(4-N,N- dimethylaminopyridine) tin(IV) Complex

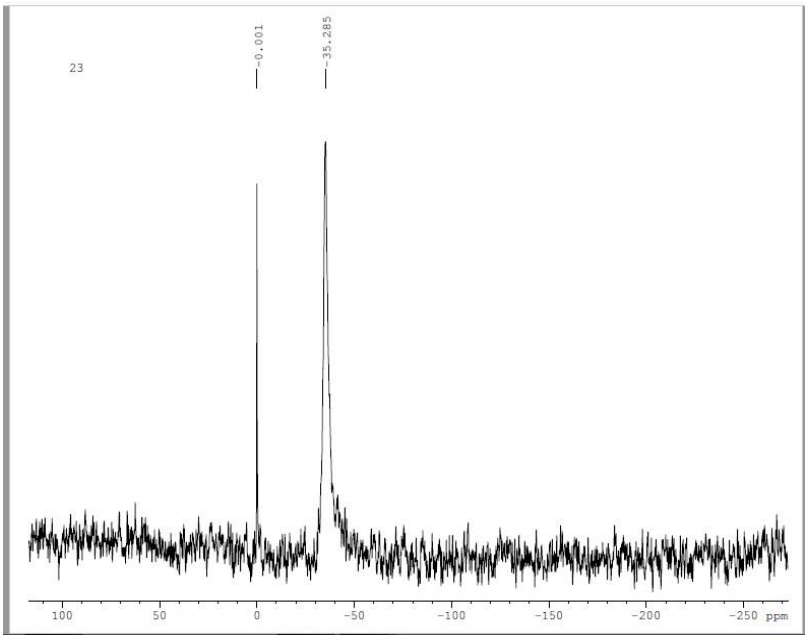

Fig. 3. The ^{119}Sn NMR spectrum of trimethyl(chloro)(4-N,N- dimethylaminopyridine) tin(IV) Complex

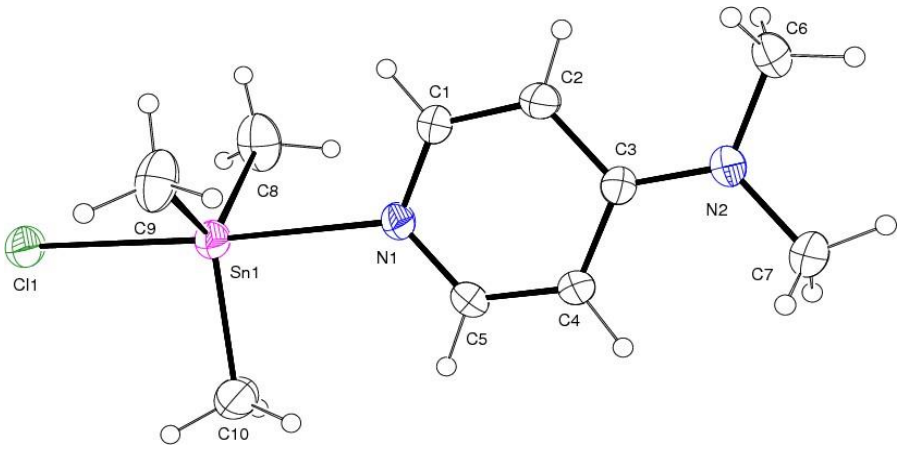

Fig. 4. The ORTEP diagram - The crystal structure of trimethyl (chloro)(4-N,N-dimethylaminopyridine)tin(IV) complex

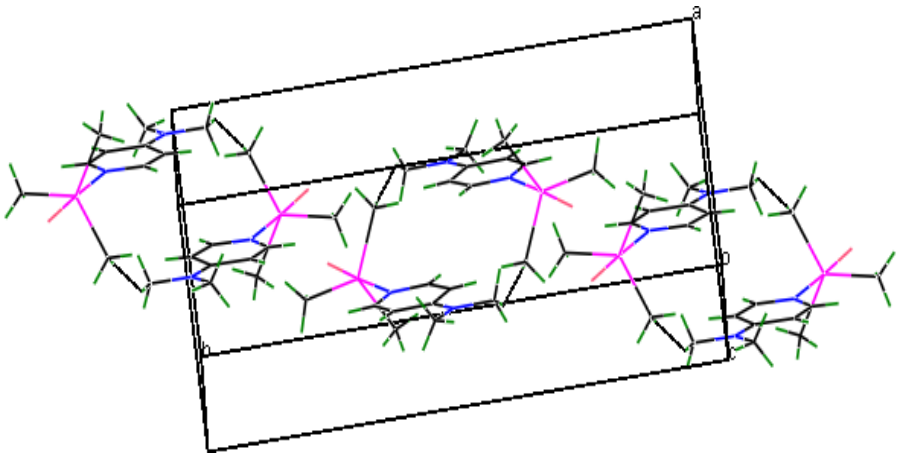

Fig. 5. The packing diagram of trimethyl(chloro)(4-N,N- dimethylaminopyridine) tin(IV) complex