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The Organotin Spectroscopic Studies of Hydroxamic as a Ligand: A Systematic Review

Abdualbasit M. Graisa[1], Amani A. Husain[2], Ahmed Al-Ani[3], Dina S. Ahmed[4], Mohammed H. Al-Mashhadani[3] and Emad Yousif[3,*]

[1]Faculty of Civil Aviation, Ministry of Technical and Technical Education, Misurata-Libya
[2]Polymer Research Unit, College of Science, Al-Mustansiriyah University, Baghdad-Iraq
[3]Department of Chemistry, College of Science, Al-Nahrain University, Baghdad-Iraq
[4]Department of Medical Instrumentation Engineering, Al-Mansour University College, Baghdad-Iraq

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Abstract

This review highlighted the analysis techniques of hydroxamic acid (HAs) and Organotin (IV) Hydroxamates. Different isomerism, keto and enol form, as well as, intra and inter hydrogen bonding are confirmed through spectroscopic studies. In addition all organotin (IV) complexes geometries were studied and explained in this review depending on different analysis techniques done by researchers.

Our study is not unique but it gives your attention to be more concern if you will deal with these types of compounds regarding to the functional groups, isomerism, structural information and its geometry.

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*Corresponding author: emad_yousif@hotmail.com

1. Introduction

1.1 Spectroscopic studies of hydroxamic acid:

The structure of hydroxamic acid has considerable controversy [1]. With the evolution of spectroscopic methods, considerable progress has been attained in the last few decades. Many spectroscopic studies have been carried out on simple hydroxamic acids and their *N*-and *m*-substituted derivatives [2] as mentioned before, hydroxamic acid may exist in the keto (I) or enol forms (II) indicating that structure (I) is a correct representation of the hydroxamic acid at least in the solid state and in polar solvents [3,4]. The conclusion made was mainly from the occurrence of the characteristic frequencies of the N–H and C=O group in the infrared spectra of these compounds [5]. X-ray crystallographic studies of acetohydroxamic acid [6] showed the CO bond to be a double bond and thus established the presence of the NHOH grouping. However, the studies based on the infrared frequency in the carbonyl region have provided a proof of structure (I) in the solid state. Infrared studies on the closely related N-substituted amides have revealed that these molecules have a planar peptide linkage due to the fact that the C–N bond acquires a double bond character because of the donating properties of the nitrogen lone pair and the rotation about the C–N bond is found to be restricted [7].

Infrared spectroscopy under high resolution of the closely related secondary amide demonstrates the free N–H stretching hand as a doublet. This twin bands have been allocated to the *Z* and *E* isomers. However, attempts by infrared spectroscopy in order to detect restricted rotation around the C–O bond of unsubstituted hydroxamic acids was not successful due to their partial double bond character [5]. A molecular orbital treatment of formohydroxamic acid by Orville-Thomas & Parsons (1958) resulted in bond lengths of 1.38 A° for the C–O and C–N bonds showing theoretical results which are very similar to those for amides, therefore indicating that the nitrogen's lone pair of electrons is partially delocalized to the carbonyl group [8]. Consequently, isomerism about the partial C–N double bond is expected as shown below in Figure 1.

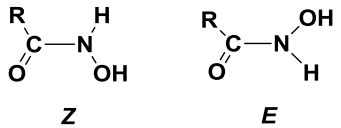


Figure1. *Z* and *E* isomerism of hydroxamic acids.

However, restricted rotation about the C–N bond of both unsubstituted and *N*-and *m*-substituted hydroxamic acids have been confirmed recently by NMR studies [9].

Structures and composition of any naturally occurring or synthetic chemical compounds can be identified by means of a wide range of spectroscopic techniques, which include infrared and nuclear magnetic resonance. Compounds which are exhibiting suitable single crystals can be studied

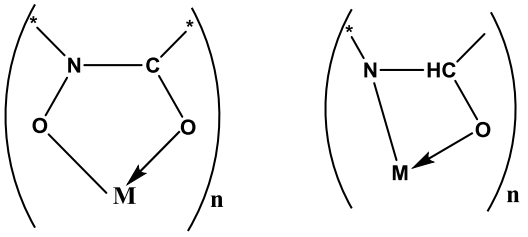
via X-ray crystallography providing perfect proof of structure. A brief discussion of some of the spectral techniques employed is given below.

1.2 Infrared spectra of hydroxamic acids:

The IR spectra of the HAs were verified primarily for their characterization. The IR spectroscopy was able to characterize the bands associated with the functional group of hydroxamic acid (–N(OH)–C=O). The band appeared at 3200 cm^{-1} confirmed the stretching bond of ν(O–H). The intramolecular hydrogen bonding of hydroxyl group confirmed by the lower shift of ν(O–H). The two bands of ν(C=O) and ν(N–O) are assigned at about 920 cm^{-1} and 1620 respectively [10].

The IR spectra of the HAs gives information about the structures of the compounds. The most important characteristic bands which associated with the hydroxamic acid those are because of the ν(N-O), ν(O-H), ν(C=O) and ν(C-N) stretching.

A broad band which assigned to the O-H stretching of the free and hydrogen bonded N-OH groups appeared at 3240-3040 cm^{-1}. The m(C–N) and m(N–O) peaks appear at 1,494–1,436 and 915 cm^{-1} as a sharp peak [11]. In the metal complexes, hydroxamic acids, coordinate by the deprotonation of the OH group and the subsequent (O,O) coordination of carbonyl oxygen and deprotonated OH as confirmed by IR, UV and NMR. It is thus assumed that usually hydroxamic acid metal complexes may have the following structure as shown in **Figure** Error! No text of specified style in document. in which the metal atom coordinate through the oxygen atoms [12].



(a) (b)

Figure Error! No text of specified style in document.**.** Two coordination mode of hydroxamic acid.

Overall, the ν(C=O) stretching of hydroxamic acids shows a sharp absorption peak in the range of 1670-1590 cm^{-1}, however this value is lower than the normal ketonic C=O of 1715 cm^{-1}. This absorption is smaller frequency than the carbonyl of ketones which is due to the resonance influence. The substantial shift of ν(C=O) to smaller region with ν(O–H) broad band could associated with H-bonding [11] as in the crystal structure of glutarodihydroxamic acid dehydrate which is further confirmed on the basis of the solution studies which were conducted in chloroform. In a number of cases the appearance of ν(C=O) is also reported as a double in the solid state. In secondary amine of HAs the ν(C=O) lies lower than primary hydroxamic acids, showing that the N-substitution group has an effect on the infrared spectra as a result of the increased electron donation by substitution group [13]. Hydroxamic acids are liable to both inter- and intra-molecular hydrogen bonding as represented in Figure 3. The intermolecular H-bonding is always dependent onconcentration of the acid whereas the intramolecular H-bonding is not affected by the concentration [11] creating the possibility to distinguish between these two types of bonds using variable concentration studies.

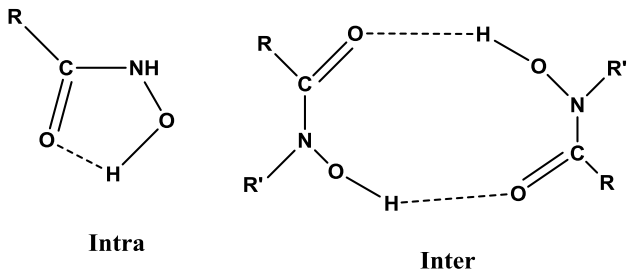


Figure 3. Intra and inter molecular H-bonding.

These modes of bands for ν(N–O) appear as a sharp absorption band in the range 920-873 cm^{-1} and for ν(C–N) mode occur as absorption peaks in the range 1320-1400 cm^{-1}.

1.3 NMR Spectroscopy of hydroxamic acids:

To determine the structure of hydroxamic acids in solution high resolution nuclear magnetic resonance studies have also been conducted, HAs exist in solutions as an equilibrium mixture of tautomers RCONH–OH (I) and ROH=NO–H (II) as presented in, where (I) is the HAs (keto) form and (II) the hydroxylamine or HAs (enolic) form. The clear-cut description of the N–H and O–H protons of the NHOH group of hydroxamic acid was not possible [14]. For instance, the 1H NMR spectra of unsubstituted HAs at room temperature have been showing one broad signal [15] in the region δ 8-11 ppm, or two broad signals [16] in the regions of δ 10-11 and δ 8-9 ppm, which were uncertainly assigned to the OH and NH protons respectively. NMR studies on hydroxamic acids are mainly related to the hindered rotation around the C(O)–N bond with partial double bond character in *N*- and *m*- substituted compounds. It was predicted that in case of the restricted rotation around the carbon-nitrogen the keto of *Z* and *E* isomers should be as shown in Tautomerism could result the enolic hydroxamic acid RCONHOH form.

Widespread NMR studies on monohydroxamic acids and their derivatives which are reported in the literature provide evidence for the existence of a *Z* and *E* isomerism as shown in. However, the *Z* form concentration is reported some higher [14,17], for example, the ^{1}H NMR spectrum of acetohydroxamic acid in dimethyl sulfoxide-d_6 was reported at 20 ^{o}C showing two sets of signals. High intensity signals at δ 10.36 and δ 9.80 were allocated to NH protons and low intensity signals at δ 8.69 and δ 9.13 to the OH protons of the *E* and *Z* isomers, respectively.

The ratio of the *Z*-*E* is solvent dependent which is confirmed by the ^{1}H and ^{13}C NMR studies done on N-substituted HAs [17]. For example, the *Z*-isomer predominates in polar solvents such as dimethyl sulfoxide-d_6 and this because of the stabilization of the *Z*-isomer by the H-bonding with some H_2O present in the solvent. This suggestion is supported by molecular orbital calculations indicating that the isolated *E*-keto forms of formhydroxamic and ectohydroxamic acids possess lowest energy and are non-planar formation. Although H-bonding can occur in the planar *Z*-keto species but it shows less stability as compared to the species formed by solvation of water molecules. Decrease in oxygen-oxygen nteraction and increase in hydrogen bonding may stabilize the keto forms [18]. Naturally, hydroxamic acids are not only liable to proton exchange between protons attached to oxygen and nitrogen atoms, but they also contribute to hydrogen bonding which can also be both inter-or intra molecular.

2. Structure of Organotin (IV) Hydroxamates

As the initial organotin chelates of the type R_2SnCH_2 (CH= bidentate ligand) were produced [19-21], they have been acknowledged and received a lot of attention over the years. The organic substituent R denotes either an alkyl or an aromatic group on the other hand the ligand CH may represent an assorted number of bidentate ligands. The possible participation of tin has made the structure of these molecules a subject of interest among scientists [22].

The geometries of organotin complexes can be verified by the structural investigations of these compounds. It was predicted that nearly all tetra-organotin (IV) complexes are tetrahedral molecules having four coordinated tin atoms according to the decreasing Lewis acidity, and that was because of the enhancing the number of organic groups present at tin. Tin was considered for not being able to extend their coordination number (CN) owing to the low electron accepting ability of the atom. An X-ray diffraction study of monopyridine adducts of trimethyltin chloride revealed the involvement of the five coordinate atoms [23]. Tin, being in possession of 5*d* orbitals has the ability to use these orbitals to increase its CN from four to five, six or seven by the addition of neutral organic donor ligands [24]. Therefore, tin compounds may represent a variety of geometries in their structure. The mainly reported geometries of organotin compounds and their derivatives are trigonal bipyramidal, pentagonal bipyramidal, tetrahedral and pseudo-octahedral, the most common being the penta- and hexa-coordinate environment [25]. As the penta- coordination is concerned, a rare example of the square pyramidal geometry has recently been authenticated [26]. The standard coordination geometries for tetravalent tin are shown in Figure 4.

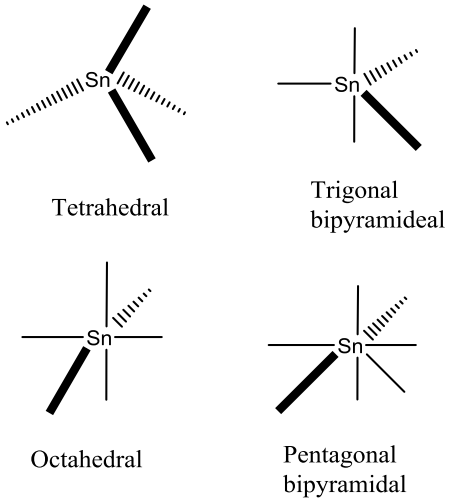


Figure 4. Standard geometries of organotin complexes.

The symmetrical coordination of the carboxylate ligands to the Sn atom may generate distorted octahedral in organotin complexes, which may be defined as a skewed-trapezoidal planar geometry with two extra axial ligands.

During the last few years, even with excellent proven techniques, of ^{1}H NMR and IR spectroscopy have been improved by ^{119}Sn NMR spectroscopy [27-29]. X-ray crystallographic studies of a vast number of organotin compounds show not only five-, six- but even seven-, eight coordinate tin atoms [30]. The numerous information on the structural chemistry of organotin compounds significantly discloses the facts to understand the mode of action in their various applications and explain the variations regarding their toxicity.

Substituted benzoic acids of organotin (IV) carboxylates has shown great interest in recent years by their novel structural variety and wide therapeutic activity. Organotin (IV) carboxylates continues leading to new medical applications. The chemistry and the properties of organotin (IV) compounds directed to studies on their reactions with different bimolecular amino acids, nucleic acid derivatives, carboxylates and peptides.

Alongside the novel synthesis and application studies of organotin hydroxamates a wide range of physical methods were employed for the possible structural studies. Organotin complexes have been shown to undergo structural changes when in solution. However, single crystal X-ray diffraction study demonstrates the most correct data in the crystalline structure [31,32].

Structural characteristics of the organotin (IV) complexes of the hydroxamic acids were determined by using elemental analysis, melting points, infrared, multinuclear (^{1}H, ^{13}C and ^{119}Sn) magnetic resonance spectral investigations to determine the structures of the complexes in solid state and in solution [33,34]. A short discussion of some of spectral techniques employed in the present study is given below:

2.1 Spectroscopic studies of organotin (IV) hydroxamates:

A newly synthesized organotin derivative needs its structure to be investigated by means of a wide range of spectroscopic techniques including NMR (^{1}H, ^{13}C and ^{119}Sn) and IR. The organotin complexes, which yielded a single crystal, may be studied using X-ray crystallography.

2.2 Infrared spectra of organotin (IV) hydroxamates:

Characterization of the IR spectra of the synthesized HAs shown that a band which assigned to –N(OH)–C=O. The band appeared at 3200 cm^{-1} assigned to ν(O-H) stretching band. The lower shift of ν(O–H) was due to the intra-molecular H-bonding of –OH…C=O. The bands at 1620 and 920 cm^{-1} are assigned to ν(C=O) and ν(N=O) respectively.

The IR spectra of the organotin (IV) complexes give an evidence related to the moity's structures in the solid form. The arrangements of the organotin (IV) complexes of the HAs raise many questions: whether the coordination to tin is because of the nitrogen or oxygen atom of the HAs functional group (CONHOH) and the featured coordination geometry of the Sn atom in cases in which the possibility for isomerism occurs. The IR spectra were verified in the range of 4000-250 cm^{-1}. The absorption in the range between 420-490 cm^{-1} and 500-539 cm^{-1} due to the complexation of Sn (IV) with the ligand through Sn-O and Sn-C respectively.

On complexation, the ν(C=O) stretching vibration shifts to lower frequency by 110-40 cm^{-1} [35] suggesting that the coordination of the ν(C=O) group to the metal through the oxygen to give a five membered chelate ring at tin. As a result, the absence of the ν(O–H) modes and the shifting of the ν(C=O) modes towards lower energy support the bidentate nature of hydroxamic acids for diorganotin units. The sharp peak of ν(N–O) occurs at 920-873 cm^{-1} for ligands, and on complexation may shift up field to the range 980-905 cm^{-1} thus signifying that the coordination occurs through the oxygen of the -OH group [36,37].

The stretching vibration band of ν(C–N) of the organotin hydroxamates occurs in the range of 1340-1500 cm^{-1}, which is a higher value compared to the free ligands by 10-50 cm^{-1}. The carbonyl oxygen will tend to serve as a donor centre in the metal chelate. As a result, the increase in the electron density in the ν(C–N) bond occurs because of the electron withdrawal from the carbonyl group. Therefore, a lowering of the carbonyl frequency and an increase in the ν(C–N) frequency can be predicted [3].

Environmentally, all organotin complexes with oxygen donor ligands group have these bands and their assignments different from each other. Generally, the Sn–C and Sn–O stretching take place at low energy along with the lower energy vibration modes of the ligands. The asymmetric and symmetric tin-carbon phenyl modes in phenyl tin compounds have been attributed to occur at 382-261 and 249-225 cm^{-1} respectively [38].

2.3 Nuclear magnetic resonance (NMR) spectroscopy:

NMR is one of the greatest influential physical approach and reliable tool for characterization to study changes and structural information occurring in a chemical reaction or the mode of reaction and for studying intra- and inter-molecules interactions.

With some exceptions all the elements possess in naturally at least isotope with a nuclear magnetic moment (nuclear spin I = 1/2) which is suitable for NMR studies.

The compounds of tin conveniently are studied by more spectra techniques (multinuclear NMR, IR, Mass spectrometry, Mössbauer etc.) than any other elements in nature.

In general, there are three isotopes of tin, ^{115}Sn,^{117}Sn, ^{118}Sn, all of them have number of spins similar to that of hydrogen (I = 1/2). ^{119}Sn chelates with α-chas well as with as directly bonded hydrogen and the other substituents attach themselves via tin received a rapid.

In the last decades, the ^{119}Sn NMR and ^{1}H, ^{13}C parameters have been utilised for the identification of organotin (IV) compounds and their complexes. The NMR may also be utilized for both quantitative and qualitative analysis techniques of organotin moieties. The Sn compounds have the benefit that they can be investigated by techniques stated before.

The nuclear magnetic resonance technique of organotin complexes in solution deals in major cases with ^{1}H, ^{13}C and ^{119}Sn nuclei. In some cases of organotin chemistry, solid-state ^{119}Sn NMR becomes much more important [39].

2.4 ^{1}H NMR Spectroscopy:

The ^{1}HNMR approach may be utilized to get a sense of how the Sn atom in organotin complexes is hybridized [40]. The values of the $^{2}J(^{119}Sn,^{1}H)$ coupling constants are connected to the hybridization of Sn in the organotin, as can be observed. Complexes and determining Sn content in the Sn-C bond (H). The Sn-C bond at the Sn centre tends to proceed via sp, sp^2, and sp^3 hybridization in tetrahedral, octahedral, and trigonal bipyramidal arrangements. Increases in the values of the coupling constants are caused by increasing the s chelator (s electron involvement) in the Sn-C bond. $^{2}J(^{119}Sn,^{1}H)$. $^{2}J(^{119}Sn, ^{1}H)$, the coupling constants, also give information for assessing Sn coordination.

In the ^{1}HNMR study of complexes, the OH resonance of ligands was absent, which indicates the replacement of hydroxide proton by the organotin (IV) moiety. It has been reported that the OH donor group to the Sn atom reduced the electron density which resulted in de shielding of the ligand protons. Singlet and multiples have been observed in the case of methyl and phenyl groups, respectively. At the same time, the ring current effect leads to the signals of the aromatic protons were shifted downfield. The phenyl group gave a multiple due to a complex pattern. The aromatic

proton resonances were allocated in comparison the practical chemical shifts with those measured by the incremental procedure [41].

The NMR spectra were carried out in DMSO and the expected resonance values were assigned on the basis of their intensity and multiplicity pattern in addition to the coupling constants. The number of protons proposed for each component of the molecule was used to determine the peak assimilations of the spectra. The aromatic carbon resonance values were obtained using an incremental technique and comparing experimental chemical shifts to those reported in the literature [42].

2.5 ^{1}H and ^{13}C Nuclear magnetic resonance spectroscopy of organotin (IV) hydroxamates:

The chemical shifts in the ^{1}H and ^{13}C nuclear magnetic resonance spectra are quoted relative to standard tetramethylsilane (TMS). The chemical shift depends upon the magnetic shielding of the nucleus which exists from a number of contributions [43] (i) diamagnetic effects, (ii) paramagnetic effects and (iii) magnetic effects owing to electronic circulation related with other atoms in the molecules as well as on the environment and arrangement of substituent [44-46]. Studies carried out on the electronic effects of the SnR_3 groups on the aryl or hetroaryl indicated the ipso carbon meta to the tin substituent is seen to shift downfield which reflects the degree of inductive electron donation by means of the substituents [47] Similarly, downfield shift in proton chemical shifts of these compounds is also observed [46]

^{13}C NMR spectroscopy has been shown to be a powerful tool for the study of organotin compounds [44] and their derivatives with ligands containing donor atoms such as nitrogen, oxygen or sulphur [48]. The advantage of carbon-13 spectroscopy over proton spectroscopy when studying organotin derivatives may be summed up as follows

(a) The differences in the coupling constant ^{1}J(Sn–C) are much larger than those in ^{2}J(Sn–H).
(b) For the reason that the alpha-carbon of the alkyl and aryl group is directly bonded to tin, the disparity in ^{1}J(Sn–C) further accurately reflects rehybridisation at the tin atom than do those in ^{2}J(Sn-H).
(c) It is probable to measure ^{1}J(Sn–C) accurately for types of alkyl groups (e.g., propyl, isobutyl, butyl and octyl) while ^{2}J(Sn–H) are not measurable under usual circumstances.
(d) For such lengthy chain alkyl groups, the identity of the compound and limits of its purity can be established with no uncertainty. For example, octyltin trichloride. It was named later as the Fermi contact term [49]. It can be described as, when A and B are atoms which are bound by a covalent bond and have nuclei with I = 1/2, the coupling constant *J* (A-B) can be denominated by the contact term.

As the proton NMR spectra of organotin (IV) arylhdroxamates are extremely difficult to be distinguished because of the proton's signal particularly in the aromatic area owing to the presence of more than two phenyl grouping either in the aryl ligands or phenyl tin (IV) moiety. However, the aromatic protons of organotin hydroxamates are shifted up field possibly due to the consequence of the electronic effects because of complexation when compared to the free ligands. The integrated areas in the monoydroxamic acids demonstrate the existence of two protons for NH-OH in the free ligands despite the fact that it is not possible to assign the NH and OH protons which overlap. However, only a single proton can be assigned to the NH which is retained in the NH-OH group/complexes. In several cases, the exchange of active hydrogen took place in a number of compounds and the proton of NH is usually not observed [35] and the proton of OH in the free ligands also disappears as proved by crystallographic studies [50].

2.6 ^{119}Sn Nuclear magnetic resonance spectroscopy:

The ^{119}Sn spectra in all compounds shows harp singlet, confirming the production of a single species. Although the shift ranges are to some part dependent on the composition of the substituents at the Sn atom, the ^{119}Sn chemical shifts generally trend to lower field with increasing coordination number. The ^{119}Sn NMR technique is also useful for determining the coordination numbers (CN) of Sn [51].

Even if the reactions are modest, any rise in Sn's CN causes the 119Sn resonances to move to the lower field. 119Sn NMR investigations of compounds containing Sn-O bonds, such as cage structures and physiologically active species, offer advantages since the Sn atoms can have quite varied CN [52].

^{119}Sn NMR chemical shift of organotin compounds occur in a range of over ±600 ppm, Me_4Sn [24]. An important and valuable information about the structure of organotin complexes in solution can be obtained from ^{119}Sn NMR spectroscopic studies. The chemical shift value depends on the following parameters:

- Coordination number (CN).
- Isotope effects.
- Inter-bond angle at the tin atom.
- Temperature.
- Nature of substituents and multiple substitutions.

By increasing in the CN of Sn atom from four to five, six or seven leads to a large up-field shift of δ (^{119}Sn) [53]. It has been stated that the upgrade the coordination number by one can rise the shift by 60-200 ppm [54]. Organotin compounds $RnSnX_4$-n containing electron withdrawing group have a strong tendency to auto association in the both solid and in solution. The CN of the Sn atom increase on association, which will also increase the $^{1}J[^{119}Sn,^{13}C]$ value. This behaviour of organotin compounds can be studied more easily by ^{119}Sn NMR Spectroscopy.

The normal of ^{117}Sn and ^{119}Sn (7.61% and 8.58%) is sufficient to achieve NMR spectra within a proper time both in solid and in solution. Furthermore, ^{119}Sn is particular for NMR studies because of its higher abundance and magnetic moment. The NMR accessibility of ^{119}Sn is 20 times higher

than that of ^{13}C. Moreover, the repetition and relaxation time of pulses is small, usually less the one second.

Experimental correlations have been projected in order to bind the bond angles C–Sn–C with the magnitude of coupling values $^{1}J(^{119}Sn,^{13}C)$. ^{119}Sn NMR spectroscopy is encouraging because there are no solvent effects unless the solvent coordinates to the Sn atom. A large shift can be deducted even for small differences in electron density around the Sn atom, then ^{119}Sn NMR may detect compounds if they are undetectable by ^{1}H and ^{13}CNMR spectroscopy.

The Sn atom gets steadily more protected as the electron withdrawing groups of the alkyl connected to Sn grow, and the (^{119}Sn) value shifts to a higher field. As previously stated, ^{119}Sn–NMR is a potent method, and the value of (^{119}Sn) is directly related to the central Sn atom's CN.

Organotin compounds have a chemical shift in the region of 600. As the electron releasing power of the alkyl group bound to Sn increases, the Sn atom gets more shielded and the (^{119}Sn) value shifts to a higher field.

The value of (^{119}Sn) is directly connected to the CN of the central Sn atom, according to previous research, and the findings show that all organotin (IV) compounds in solution have a tetrahedral geometry around the Sn atom.

Tin is well known for its versatile chemistry due to its environment, and it's worth noting that the ^{119}Sn nuclear magnetic shielding is found to be very low in Sn(II) compounds with organic substituents and rather high again for tin(II) compounds with 5 bonded cyclopentadienyl ligands, covering a range of about 60 ppm by simple organotin compounds containing tetra-coordinate tin atoms [55].

Even if the interactions are modest, any rise in Sn's CN causes the ^{119}Sn resonances to move to lower fields. Many ^{119}Sn NMR investigations of compounds containing Sn-O bonds, including cage structures and physiologically active species, have shown that the Sn atoms can have quite varied CN values [52]. It has been found that triorganotin (IV) derivatives are more active against fungi than diorganotin (IV) derivatives within the specified series. However, because the ^{119}Sn chemical shift is substantially dependent on the coordination number of the tin atom, Otera recently shown that ^{119}Sn NMR may be used to characterize the tin coordination of organotin (IV) compounds, including dithiocarbamate ligands [53].

In the early 1960s tin NMR was introduced as a breakthrough in tin chemistry and the initial NMR measurements on ^{119}Sn were made in 1960 [56]. Since then, the ^{119}Sn nuclear magnetic resonance has been established as the most expedient technique to determine the structures of organotin (IV) derivatives in solution and in solid state [57,58]. While determining a crystal state structure it formalizes a perfect bridge flanked by X-ray diffraction and also in the case of liquid state NMR for disentangling solution state structure in organotin chemistry. This is particular characteristic of the tin compounds, which are amorphous in the solid state and not suitable for single crystal X-ray diffraction work.

Tin has not less than ten natural isotopes including three possessing non-zero spin, I and others with I = 1/2. ^{115}Sn is the extremely low abundant NMR but favourable isotope. Like twins in NMR, the ^{117}Sn and ^{119}Sn nuclei have pretty similar properties, but ^{119}Sn has slightly higher magnetic moment and its natural abundance has made it more popular to be used in tin chemistry. The sensitivity of ^{119}Sn NMR is 4×10^{-3} times that of ^{1}H and 250 times that of ^{13}C. The sensitivity of ^{119}Sn NMR together with the unfavourable relaxation time of the tin nucleus makes single resonance ^{119}Sn spectroscopy difficult. However, a huge amount of ^{119}Sn data has been collected by straight observation using the Pulse Fourier-Transform method [59].

The chemical shifts in NMR investigation of tin compounds, are frequently measured for ^{119}Sn nuclei because of the greater intensity of their NMR singles and their higher natural abundance as compared to the other isotopes. Generally, the ^{119}Sn chemical shift δ (^{119}Sn) of organotin (IV) derivatives take place over a large range of -400 to +200 ppm and are quoted relative to tetramethyltin with downfield shifts form the reference having a positive signal. Numerous factors, for example the, nature of the organic group (R), ligands, solvent (coordinating or non-coordinating) and concentration are involved on which basis the chemical shift can be evaluated [28]. Presence of electronegative substituents such as halogen, oxygen and sulphur on tin, d-p bonding effects, large atom and diffusion effects, the coordination number and temperature dependence particularly in donor solvents are known to be well recognized factors which may affect the ^{119}Sn chemical shifts values [60]. Electron density on the tin atom as well as interactions with the donor ligands are increased with higher coordination number. This signifies that signal shifts a few hundred ppm to a higher field [28]. It is also evident that the ^{119}Sn values in the compounds linking two oxygen donor atoms are dependent on the size of the chelate ring; increasing the size of chelate ring will increase the value of ^{119}Sn chemical shift. 119Sn resonances lie between –90 and –330 ppm, in the five-coordinate compounds and in case of six-coordinate derivatives it lies between –125 and –515 ppm [53].

It is reported that ^{119}Sn NMR parameters, especially chemical shifts and coupling constants $^{2,3}J(^{119}Sn,^{1}H)$ and $^{1}J(^{119}Sn,^{13}C)$ indicate the nature of the substituents linked to tin as well as its coordination numbers [28] and the structure of organotin complexes [54,61]. The magnitude of the direct one-bond coupling constants $^{1}J(^{119}Sn,^{13}C)$ is extremely sensitive to changes because of the s-character of the Sn–C bond [62]. The ^{119}Sn chemical shifts and both direct one-bond coupling constants ^{1}J ($^{119}Sn,^{13}C$) and two-bond coupling constants ^{1}J ($^{119}Sn,^{1}H$) for dimethyltin hydroxamtes reported in the literature designate these compounds as six-coordinate diorganotin bishydroxamtes [33,34] which confirm the chelate structures of hydroxamates in $CDCl_3$. It is remarkable that the solvents

may influence the ^{119}Sn chemical shifts [60]. Solvents containing donor atoms such as DMSO, DMF and pyridine are found responsible to create substantial changes in the chemical shift of authenticated organotin compounds. Consequently, the solvents used for ^{119}Sn spectroscopy should not be able to interact specifically with the tin compounds. Length or number of R groups increases the activity of the compounds and that's why triorganotin (IV) derivatives show more activity as compared to diorganotin derivatives and butyl derivatives show more activity than methyl derivatives [63].

3. Single Crystal X-Ray Diffraction Studies

Information about the arrangement of atoms in crystalline materials can be obtained by X-ray diffraction method of analysis and X-ray diffraction is helpful to understand the polymeric materials, physical properties of metals, and others. The X-ray diffraction can be used for qualitative identification of crystalline compounds/non crystalline material by measurement of the wavelength of diffracted X-rays, currently this phenomenon is considered as a significance in clarifying the structure of complex compounds.

Crystallography is one of the best techniques available to study the molecules obtainable in the crystalline state. In organometallic and coordination chemistry, a great number of crystal structures have been reported in journals depending on this technique. However, the great disadvantage of X-ray diffraction is that the quality of the single crystal obtained must be of certain orderliness for structure elucidation.

3.1 Crystal structures of hydroxamic acids:

Single crystal X-ray crystallography (SCD) is not a chemical analysis but a technique to study the structure of molecules based on the proposed model which must be in agreement with the treatment and calculation of the X-ray reflections data collected from a single crystal of a compound or reaction product. In other words, there may be a few structural models seemed to be agreeable with the calculation but chemically not logical or acceptable.

The solid-state structures of unsubstituted hydroxamic acids illustrate planar cis conformation [6,7,64-66], while planar *trans* conformation can be seen on N-substituted HAs [67-69]. The intramolecular hydrogen bond N–O–H…O=C favoring the *cis* conformation cannot be detected in the crystal [6] but observed in solution. In the secondary N-substituted hydroxamic acids the planarity of the acid group depends on the nature of the N– or C–substituted groups.

3.2 Crystal Structures of Organotin (IV) Hydroxamates

The distorted geometry in many organotin (IV) complexes are due to steric factors, electronic effects starting from different electronegativities of the ligands, intermolecular interaction and crystal packing [70,71]. Hydroxamic acids form stable complexes with organotin compounds and a few X-ray structure determinations of these complexes are also available. In diorganotin bishydroxamates, the geometry around the tin atom is a distorted octahedral coordination by two organic groups and two monoanionic ligands [33,34]. Whereas in the triorganotin hydroxamtes the tin atoms is in a trigonal bipyramidal environment coordinated by three organic groups and one monoanionic ligands [72,73]; which coordinate to the metal via the oxygen atoms of hydroxyl and the carbonyl groups making one short covalent and one long coordinate tin-to-oxygen bond in the range 2.08-2.10 A° and 2.37-2.42 A° respectively. The shorter distance of Sn–O bond than the sum of the van der Waals radii [74,75] indicate the bidentate nature of hydroxamic acids. The two heterocyclic rings are basically planar. In the case of octahedral geometries, the four donor atoms of the ligands are situated in equatorial positions with $C_2N_2O_4$ grouping deviating from planarity above and below the plane defined by the donor atoms. The value of deviation may differ from one compound to another depending on their composition. In trigonal bipyramidal structures, the two donor atoms of the ligand are located in two equatorial positions with $C_2N_2O_4$ and one axial organic group.

4. Conclusion

This paper reviewed the most important analysis techniques used for the structural study of organotin (IV) and its compounds.

From this study we conclude that the principal functional groups, structural and geometrical studies as well as organotin complexes determination were confirmed and studied using, elemental analysis, Single Crystal X-ray crystallography (SCD) and infrared spectroscopy.

Organotin (IV) and its compounds with hyderoxamic acids were attracted great attention because of its applications in different fields such as biological and industrial fields, therefore advances analysis techniques need to be done after synthesising these compounds to confirm and determine the products.

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Conflicts of Interest

The authors declare that there is no conflict of interest.

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