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Chemistry and Applications of Organotin(IV) Complexes: A Review.

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ABSTRACT

Organotin(IV) complexes are known for their outstanding structural diversity and applications. Organotin(IV) cations behave as Lewis acids of different strength depending on the charge, according to the following acidity scale: $RSn^{3+} > R_2Sn^{2+} > R_3Sn^{+}$. For this reason they can react with Lewis bases containing –O, –N, –S donor groups to form complex species of different stability. The synthesis of organotin complexes also involve in this review. The emergence of new experimental techniques (EXAFS, multinuclear ^{1}H, ^{13}C, ^{119}Sn-NMR, ^{119}Sn Mossbauer, etc., spectroscopic techniques) provided useful information about the structure and stabilities of the complexes formed. The interest and application of organotin(IV) carboxylate complexes have also received considerable attention as these complexes display a large array of applications in industries as catalysts, antifouling agents, wood preservatives, crop protection agents, etc.

Keywords: Organotin(IV) , Spectroscopy, Synthesis

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INTRODUCTION

Organotin compounds

Organotins are compounds which have at least one organic substituent linked directly to the tin atom *via* the carbon atom of the organic substituent. Organotin(II) and organotin(IV) compounds are known since tin has two stable oxidation states, that is +II and +IV. However, organotin(II) compounds are not very stable and tends to polymerize rapidly [1]. The organotin(II) compounds are also easily oxidized to organotin(IV) which is more stable. Bis(cyclopentadienyl)tin(II) is the only known stable organotin(II) derivatives. The tin atom of this organotin(II) compound is sp2 hybridized, with two of the hybrid orbitals involved in bonding with cyclopentadienyl ligands and the third containing the unshared pair of electrons as illustrated in Figure 1.

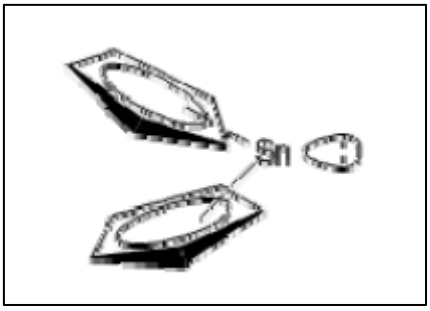

Figure 1 Bis(cyclopentadienyl)tin(II)

Most known tin compounds are derivatives of organotin(IV) due to its stability. In organotin(IV) compounds, sp3 hybridization of the valence orbital give rise to tetrahedral oriented bonds. The four principal classes of organotin(IV) compounds are mono-, di-, tri-, and tetraorganotins, which are represented by RnSnX4-n (n=1-4), where R is any organic group and X is anionic residue . Organotin(IV) compounds with electronegative groups such as organotin halides or pseudohalides are prone to use its empty 5d orbital to expand its coordination number beyond four. Hence, formation of 5-coordinate trigonal bipyramidal sp^3d or six-coordinate octahedral sp^3d^2 coordination geometries are commonly observed in organotin(IV) complexes. In the case tetraorganotin compounds where there is absence of any electronegative groups, evidence for higher coordination in such compounds are also known, especially if the tetraorganotin contained organic groups with donor substituents such as 3-(2-pyridyl)-2-thiophene. These types of higher than four coordination compounds are reported in bis[3-(2-pyridyl)-2-thienyl-C,N]diphenyltin(IV) where the intramolecular coordination of the donor nitrogen atoms to the tin atom resulted in two additional coordination bonds in the tetraorganotin compounds [2].

Polyvinyl chloride, better known by its abbreviation PVC, is one of the most versatile plastics. It is the second largest manufactured resin by volume worldwide currently, its production per annum exceeds 31 million tons. Braun (2004) described the most remarkable milestones in PVC history, their importance in the development of macromolecular chemistry, and some PVC research and industrial applications, with respect to polymerization, stabilization, bulk property modification, and chemical and material recycling of PVC waste (Andrady et al., 1998). The low cost and the good performance of polyvinyl chloride products have increased the utilization of this polymer in building, mainly in exterior applications, such as window profiles, cladding structure and siding[3].

Synthesis

Synthesis of tetraorganotin

Grignard method.

Tetraalkyls, tetraaryls, tetravinyl and tetraethyltin compounds are prepared in coordinating solvents such as diethyl ether (Et_2O) or tetrahydrofuran (THF) [4].

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$$SnCl_4 + 4\ RMgCl \xrightarrow{THF} R_4Sn + 4\ MgCl_2$$
[R = aryl or alkyl]

Wurtz method

The reaction of alkyl halide with alkali metal such as sodium, followed by the addition of stannic chloride also yield the tetraorganotin.

$$SnCl_4 + 4\ RCl \xrightarrow{8Na} R_4Sn + 8\ NaCl$$
[R= alkyl or aryl]

Aluminium alkyl method

Organoaluminium compounds can be reacted with stannic chloride to produce tetraorganotin. The reactions are carried out in the absence of solvents. The addition of a complexing agent such as ether is required for high efficiency [5].

$$3\ SnCl_4 + 4\ R_3Al \xrightarrow{R2O} 3\ R_4Sn + 4\ AlCl_3$$
[R= alkyl or aryl]

Synthesis of tri-, di- and monoorganotins

The first organotin derivative which was isolated some 130 years ago was diethyltin diiodide by Frankland. This organotin compound was synthesized by direct synthesis method. The direct synthesis method was later extended to preparation of other organotin halides which involves the direct alkylation of metallic tin or tin halides by alkyl halides, in the presence of suitable catalyst [6].

$$Sn + 2\ RX \xrightarrow{catalyst} R_2SnX_2$$
[R= alkyl or aryl]

The direct synthesis may be carried out in the absence of a catalyst. The reaction of benzyl chloride with tin powder is one such example, and the toluene or water used as the solvent gave good yield of dibenzyltin chloride [7]. and tribenzyltin chloride[8]. respectively.

$$2\ BzCl + Sn \xrightarrow{PhMe} Bz_2SnCl_2$$

$$3\ BzCl + 2\ Sn \xrightarrow{H2O} Bz_3SnCl + SnCl_2$$

$$3\ Bz_2SnCl_2 + Sn \xrightarrow{H2O} 2\ Bz_3SnCl + 2\ SnCl_2$$

The conventional method of preparing tri-, di- and monoorganotins is by the comproportionation reaction of tetraorganotins using different stoichiometric amounts of stannic chloride.

$$3\ R_4Sn + SnX_4 \longrightarrow 4\ R_3SnX$$
$$R_4Sn + SnX_4 \longrightarrow 2\ R_2SnX_2$$
$$R_4Sn + 3\ SnX_4 \longrightarrow 4\ RSnX_3$$
[R= alkyl or aryl]

The organotin halides particularly triorganotin halides, R3SnX and diorganotin halides, R2SnX2 can be easily converted to organotin hydroxides and oxides by base hydrolysis using sodium hydroxide or ammonium hydroxide.

$$R_3SnX + OH^- \longrightarrow R_3SnOH + X^-$$
$$R_2SnX_2 + OH^- \longrightarrow R_2SnO + 2X^-$$
[R= alkyl or aryl]

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The trialkyltin oxides are distillable liquids or low melting solids which are readily soluble in organic solvents. Diorganotin and monoorganotin oxides are polymeric solids which are insoluble in all solvents except by reaction. Although exact structures for these oxides have not been determined due to their intractability, they are known to consist an extensive network of Sn-O-Sn bonds.

Triorganotin hydroxides in the liquid phase are in equilibrium with the oxides and water. The hydrolysis of the triorganotin halides which involve various intermediate hydrolysis products are shown as below:

$$R_3SnX \longrightarrow R_3SnOH \rightleftharpoons R_3SnOSnR_3 + H_2O$$

On the other hand, triorganotin oxide can be used as starting material to synthesize other organotin with different functional group.

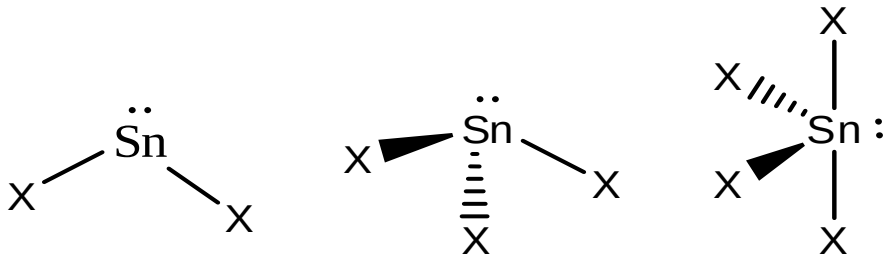
$$R_3SnOSnR_3 + 2HX \longrightarrow 2\ R_3SnX + H_2O$$

[R = alkyl or aryl]

Organotin structures and bonding

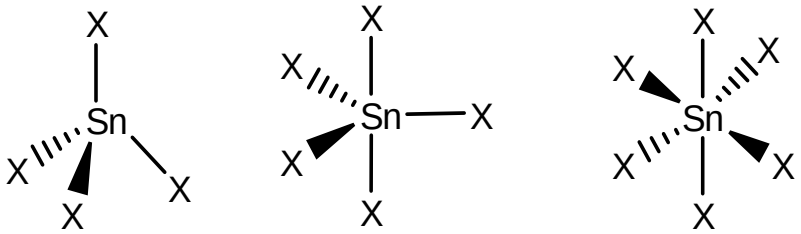
Both the Sn(II) and Sn(IV) state are stable. The Sn(II) state uses mainly the 5p orbitals for bonding leaving the unshared singlet pair in the largely 5s state, with a little p character, and compounds SnX_2 shown in (figure 2) (1, the stannylenes) have an XSnX angle of about 90-100^0. These compound are most stable when there are strongle electron-attracting ligands, which make loss of the remaining electron pair more difficult (e.g. :SnF_2, :$SnCl_2$), or when the ligands X are very bulky, and sterically protect the tin against further ligation (e.g. :$Sn[N(SiMe_3)_2]_2$). Otherwise, oxidation readily occurs to the Sn(IV) state, where the tin is sp^3 hybridized and the SnX_4 (4, stannane) molecule has tetrahedral symmetry.

However, both the stannylenes and the stannanes have vacant 5d orbitals, which can accept one or more further ligands, The stannylenes readily form the trigonal pyramid sp^3 complexes :SnX3 (2), and the seesaw sp^3d complexes :SnX_4 (3), and the stannens form the trigonal bipyramidal sp^3d complexes SnX_5 (5) or octahedral SP^3d^2 complexes SnX_6 (6). All of these may carry charges corresponding to the charge of the new ligands X [9].



1 (sp^2) 2 (sp^3) 3 (sp^3d)

Structures of Sn(II) compounds



(4) Sp^3 (5) Sp^3d (6) sp^3d^2

Structures of Sn(IV) compounds

Figure 2. Proposed structure of organotin(IV) compound.

Physical methods for the study of organotin(IV) derivatives

^{119}Sn-NMR spectroscopy

The most convenient technique used to study organotin(IV) derivatives in solution and in the solid state is ^{119}Sn-NMR spectroscopy[10]. The ^{119}Sn nucleus has a spin of 1/2 and a natural abundance of 8.7%; it is about 25.5 times more sensitive than ^{13}C, taking into account the isotopic abundance. The isotope ^{117}Sn is slightly less sensitive (natural abundance 7.7%) and has not been used much. Both of these nuclei have negative magnetogyric ratios, and consequently the nuclear Overhauser enhancements are negative[11].

^{119}Sn Mossbauer spectroscopy

The effect discovered by R. Mo¨ssbauer in 1957, the 'nuclear resonance fluorescence of gamma radiation', is analogous to the atomic fluorescence of UV–VIS light. The effect is now generally termed the recoil-free emission and resonant absorption of nuclear γ-rays [13]. The characteristic quantities measured are the isomer shift (δ), the quadrupole splitting (*Δ*) and the half-height line-width (*Γ*) in mm s^{-1}. The information extracted from the ^{119}Sn Mo¨ssbauer spectroscopy of Sn compounds is essentially: (1) the valence state in the inorganic derivative; (2) the structure and bonding in the metal environment [(mainly in organotin(IV)s]; and (3) the dynamics of the Sn nuclei, which possibly correlates with the nature of the substrate (mono- or polymeric). Measurements may be made on solids (crystalline or amorphous), gels and solutions (quickly frozen to a glassy state). Mo¨ssbauer spectroscopic measurements give information that is analogous or complementary to data obtained with other spectroscopic techniques, such as NMR spectroscopy, X-ray diffraction, neutron diffraction, EXAFS, etc. As usual, this method has both advantages and disadvantages.

Advantages:

1. The easy experimental procedures.
2. The relative simple and inexpensive instrumentation.
3. The possibility of obtaining information on the metal properties in high molecular weight systems.

Disadvantages:

1. In addition to the high cost of the Sn source, the time required to collect the spectra can also be excessive (about 1 day per spectrum).
2. The sample must contains Sn at the milligram level (about 0.5 mg ^{119}Sn cm^{-2}).
3. The near impossibility of quantitative Sn analysis. This technical limit is shared by other widely employed spectroscopic techniques.

Extended X-ray absorption fine structure (EXAFS) method

The EXAFS method seems to be suitable for determination of the local structure of organotin(IV) complexes formed with biologically active ligands in solution or the solid state. A very high flux of X-rays produced by synchrotron radiation is usually applied the EXAFS method provides structural information relating to the radial distribution of atom pairs in a system: the number of neighbouring atoms around a central atom (the coordination number) in the first, second and sometimes third coordination spheres, the interatomic distances and their root mean square deviations. The XANES spectra should also be analysed, to obtain information on the coordination geometry, possible binding sites and the oxidation number of the metal ion in question. It should be noted, however, that additional, independently obtained information on the metal ion-binding sites and suitable structural models (in most cases) are needed to analyse EXAFS spectra. Advantages of EXAFS as a structural probe:

1. No requirement for crystalline matter: gases, glasses, powders or liquids can be studied.
2. Element-specific for elements suitable for X-ray absorption.
3. For situations with a good contrast of the X-ray absorption edge over the background for the transition metal in a matrix of low atomic number, information can be obtained at a concentration of about one atom in 10^6.
4. Accurate interatomic distances can be obtained (±20 pm) within 350 pm of the primary absorber.

5. Studies as a function of time are also possible.

Disadvantages of EXAFS as a structural probe:

1. No angular information can be obtained.
2. Reliable data are restricted to distances less than 350 pm from the primary absorber.
3. The requirement of sample homogeneity for the element of interest.
4. The possibility of radiation damage.
5. The validity of the interpretation involves the adjustment of several parameters within a theoretical model to reproduce the experimental data [12].

X-ray diffraction method

X-ray crystallographic findings on of compounds containing a ligand and a metal salt in stoichiometric proportions do not constitute evidence of complex formation in solution. The well-defined crystal structure merely indicates that in the solid state the ligands, the metal ion and the anion fill the space in a regular packing, usually held together by coordination and by electrostatic and hydrogen bonding. When the crystals are dissolved in polar solvents (e.g. water), these hydrogen bonds may be broken and water or some other solvent molecule may displace one of the coordinated groups of the ligand from the coordination sphere of the metal ion. On the basis of the crystal structures, it is not possible to predict complex formation in solution. On the other hand, when complex formation is known to occur in solution from independent equilibrium measurements, or there is other spectroscopic evidence, it is very probable that the main binding sites are the same in the crystal and in solution. In the crystal, additional weak binding sites may also be present[12,14].

Application of Organotin Compounds

Nowadays, the synthesis, characterization and structural study of organotin(IV) complexes have been well-known, established and documented since the first organotin(IV) compound was successfully isolated in 1850s. The interest and application of organotin(IV) carboxylate complexes have also received considerable attention as these complexes display a large array of applications in industries as catalysts, antifouling agents, wood preservatives, crop protection agents, etc. [15,16].

Biological Applications

The use of organotin(IV) carboxylates for any specific biological activity is bound to the nature and number of organic groups R directly attached to the tin atom and carboxylate groups attached to the tin atom through Sn-O bonds. These factors decide the effectiveness of organotin(IV) compounds for required purposes. The nature of the R group decides its site of attack for organotin(IV), binding to the different locations in the body, e.g. carbohydrates, nucleic acid derivatives, amino acids [16-17] and to proteins [18]. The presence of hetero atoms such as N, O or S in the ligand play a key role in the geometry and thus effect the biological activity of these complexes [19,20]. Higher biological activity of organotin(IV) compounds encourage their applications in pharmaceutical. Some of the biological applications are discussed below.

Pharmaceutical Applications

Metal ions have a significant role in various physicochemical processes that take place in the living body and they are known for their metallopharmaceutical applications. Organotin(IV) compounds are used as potential biologically agent against various diseases [21,22]. Study of organotin(IV) activity and their mode of effect by interaction 12 with different parts like ATPase and hemoglobin's are a model for studying interactions of drugs with the human body [23,24]. The synthesis of organotin(IV) complexes with new ligands and different coordination geometries are attempts to develop new drugs for different purposes. Potential biological activities of organotin(IV) compounds encouraged their applications in the fields of muoluscicides, veterinary science, antibacterial, antifungal, antitumour, schizonticidal, antimalarial [25] and amoebicidal [26] agents.

Antifouling agents

Organotin(IV) compounds particularly tributyltin (TBT) are used as a part of paint to protect the underwater surface of ships against the attack of microorganism. The ship without this paint causes higher fuel consumption, premature dry docking, and raise the cost of cleaning due to increase weight and roughness of the hull [27].

Wood protection

Insects, fungi and bacteria decompose the cellulose of wood. Tributyltin(IV) complexes show potential biological activities against microorganism (fungi and bacteria) and are used for treatment and preservations of wood. The wood is treated with organotin(IV) compounds in a vacuum. Releasing the vacuum results in a flow of organotin(IV) into the wood and the organotin(IV) compound is attached with terminal OH groups of cellulose preventing the damage of wood by microorganisms [28,29].

Agrochemicals

Triorganotin(IV) compounds are worldwide used in agriculture due to their usefulness in treating pest diseases in crops [30]. They are frequently used against fungi, mites and ticks. Triorganotin(IV) compounds are used to prevents plant pathogenicity and spoilage of natural and synthetic materials. Organotin(IV) compounds have good adhesion to the leaf surface, and rain resistant properties. Triorganotin(IV) compounds attack the plasma membrane and induce the extensive release of K^+ by increasing the permeability of plasma membrane. They also disturb the function of mitochondria by distorting its structure. Triphenyltin hydroxide (TPTH), tricyclohexyltin hydroxide (TCTH), tricyclohexyltin triazole (TCTT), trineophenyltin oxide (TNTO), and triphenyltin acetate (TPTA) are successfully used in the field of agriculture.

Antiviral agents

Organotin(IV) compounds can be applied as metal-based drugs used for the treatment of tumor and some show a higher potential than cis-platin. This encourages scientists to make attempts for designing tin based drugs having good activity and low toxicity for cancer chemotherapy due to their apoptotic inducing character [31], which is linked to the inhibition of mitochondrial oxidative phosphorylation. There are a number of reviews available dealing with anti-tumor potential of organotin(IV) compounds [32-33]. The diorganotin(IV) complexes potential against tumor is geometry based as their coordination to target site depends upon their geometry. The anticancer potential of drugs can be evaluated by their ability of hydrolysis in a suitable medium. Drug molecules produce cis-configuration with at least two water molecules and have both hydrophobic and hydrophilic groups. Both the anticancer complex and its active intermediate species should be polar. The metal should be capable of bonding with DNA. Organotin(IV) compounds fulfilled all the above cited rules and show activity by changing the gene sequence in the DNA.

Non-biological applications

Organotin(IV) compounds have wide ranging industrial and synthetic applications which catch the interest of scientists and demands an increase in production.

As a PVC stabilizer

The main use of organotin(IV) compounds is to stabilize PVC at high temperatures [34]. During its processing at higher temperatures, HCl is eliminated which catalyses further elimination and generated conjugated polyene as an end product. This also causes of change of color and the physical state of the resin. Organotin(IV) stabilizers are good oxidation catalysts and they fulfill all the requirements necessary for an ideal stabilizer. As part of our on-going research on the photostabilization of PVC, the photostabilization of PVC was studied using triorganotin(IV) complexes[35,36].

Catalytic activity

Mono and diorganotin(IV) compounds possess outstanding catalytic activities because of the bonding capability of lone pair electrons on tin [36,37]. They are utilizing in the field of chemical synthesis. In chemical synthesis, the organotin(IV) compounds are used as catalysts for the esterification and transesterification. The tin-based catalysts donot decompose at high temperatures. Organotin(IV) based catalysts are used for the formation of various types of polymers which are used for coating purposes[38].

Glass coating

Organotin(IV) halides are used to form electrically conductive thin films on the surface of glass by using Atmospheric Pressure Chemical Vapor Deposition (AP-CVD) techniques [39-40] due to its economical reason and wide range commercial applications. Tin chloride is used as a precursor for the formation of transparent conductive oxide (TCO) films.

$$SnCl_4 + 2H_2O \rightarrow SnO_2 + 4HCl$$

The coatings of 10 nm thickness provide strength, thermal stability and resistance to oxidation. Coated glass is used in deicing wind shield screens, security glass, or display systems [41] owing to their low electrical resistance and high resistance to chemicals. TCO film also control the loss of heat through glass which is due to the metal oxide film deposition on glass surface. Coating also acts as a p-type or n-type semiconductor or conductor.

Water repellent agents

Due to good water repellent properties of organotin(IV) compounds, particularly mono-n-butyl- and mono-n-octyltin(IV) compounds are used in cotton textiles, paper and wood to impart the water repellent character . Sodium n-butanestannoate, n-butylchlorotin(IV) dihydroxide, n-octylchlorotin(IV) dihydroxide and n-butyltris(triphenyl-silanoxy)tin(IV) compounds are some of the examples used as water repellent in fabric industries [42]. Similarly, n-octyltin(IV) trilaurate has replaced silicone treatment technology, which were used on building materials, bricks, concrete and on cellulose substrates.

CONCLUSION

Organotins compound were synthesized by different type method (Grignard method, Wurtz method and Aluminium alkyl method) or by direct method, The direct synthesis method was later extended to preparation of other organotin halides which involves the direct alkylation of metallic tin or tin halides by alkyl halides, in the presence of suitable catalyst, The use of recently developed sophisticated experimental methods (e.g. EXAFS, mass spectrometry) or developments in the already used and widespread methods (multinuclear ^{1}H-, ^{13}C- and ^{119}Sn-NMR spectroscopy in solution or in the solid state), will greatly accelerate progress. more and more experimental data must to be collected in order to understand the biological (including antitumour) activity of organotin(IV) complexes.

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