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Synthesis, Spectroscopic study & Biological Activity Of Some Organotin(Iv) Derivatives Of (2e)-N-Methyl-(2-Oxo 1,2diphenylethylidne)Hydrazinecarbothioamide

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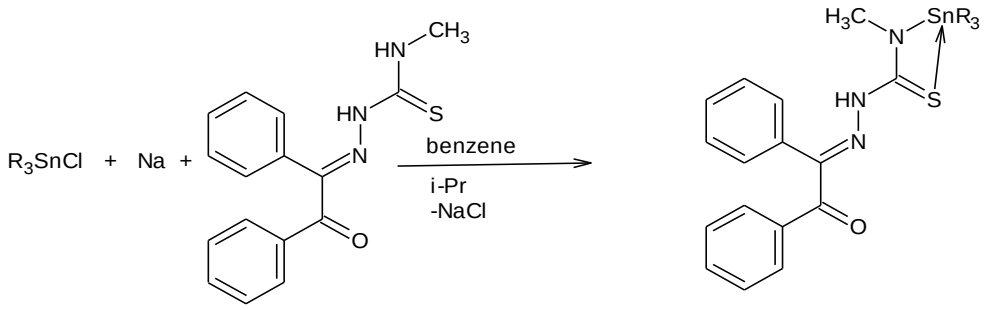
Abstract: *Some di-and triorganotin(IV) derivatives of (2E)-N-methyl-(2 oxo1,2diphenylethylidne)hydrazinecarbothioamide synthesised by the reactions of the corresponding di and triorganotin(IV) chlorides with the sodium salt of (2E)-N-methyl-(2-oxo1,2diphenylethylidne)hydrazinecarbothioamide in different molar ratios. These derivatives have been characterized by elemental analyses ,molecular weights, conductivity measurements and spectral(IR, ^{1}H, ^{13}C and ^{119} Sn NMR) studies.*

I. Introduction

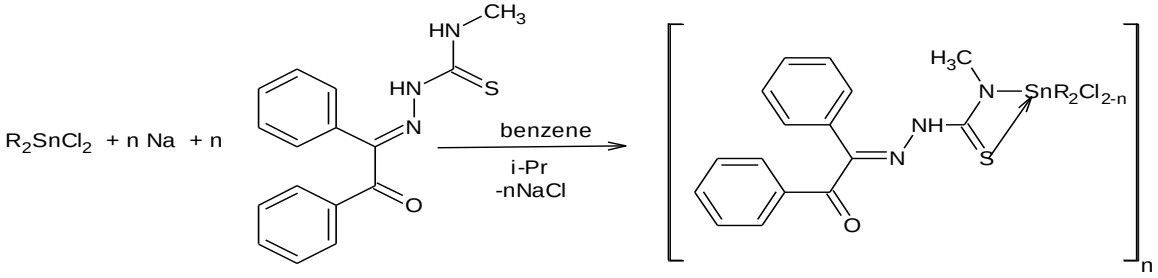
A considerable amount of work has been carried out on organotin(IV) complexes with S, N and O donar ligands[1-3] particularly, derived from salicylaldehyde and various amines,[4-5] from our laboratory. o-hydroxyacetophenone glycine complexes of organotin(IV) have already been reported,[6] exihibiting interesting coordination patterns. A very little attenti- on has been paid to the Schiff base derived from 1,2-diphenylethane-1,2-dione and 2-*N*-methylhydrazinecarbothioamide which is an important metabolite precursor for the synthesis of drugs, known as 1,4-benzodiazepines.[7] In continuation of our studies on organ- otin(IV) derivatives,[8] we report hear the synthesis and characterization of some new com- plexes of organotin(IV) with (2E)-N-methyl-(2-oxo1,2diphenylethylidne) hydrazinecarbothioamide

II. Results And Discussion

Triorganotin(IV) and diorganotin(IV) derivatives of N,N'-o-phenylenebis(salisilidenei mine) have been synthesized by the reaction of corresponding triorganotin(IV) and diorganotin(IV) chlorides with the ligand(prepared in situ by the reaction of sodium isopropoxide with the ligand) in 1:1 and1:2 molar ratios,respectively.



(Where
R=Ph.Compd.**1**; R=n-Bu.Compd.**2**)



(Where R=n-Bu,n=1.Compd.**3**; R=n-Bu,n=2,Compd.**4**;R=Me,n=1,Compd.5;R=Me,n=2,Compd.**6**)

All these newly synthesized compounds are yellow crystalline solids, soluble in common organic and coordinating solvents. Molar conductance values reveal the non-electrolytic nature of the complexes indicating that the ligand is covalently bonded to silicon. Molecular weight determination in $CHCl_3$ solution shows their monomeric nature.

IR Spectral Data :

The infrared spectra of these organotin(IV)complexes have been recorded in the form of KBr pellets in the range 4000-400 cm^{-1}.Tentative assignments have been made on the basis of earlier publications.[4,5]

The spectrum of the ligand shows bands in the regions 1750 - 1680, 1620 cm^{-1}, two stretch 3280&3400, 1488,which have been assigned to υ(C=O), υ(C=N),(NH),(C=S) respectively.[9] The disappearance of3280cm^{-1} indicates the deprotonation of one of the N-H and consequent coordination of Nitrogen atom to tin metal, which is further substantiated by the appearance of bands in the region 570-440 cm^{-1}, that may be due to Sn-C and Sn-N streaching vibrations.[10-11] The band at 3400 cm^{-1} is uneffected indicates non involvement of the second NH bond in the coordination. The band present at 1615 cm^{-1} due to υ C=S in the ligand is found to be shifted for about 20-25 cm^{-1} to lower wave number in the complexes suggesting coordination of the sulphur of C=S to the central metal atom.[13]

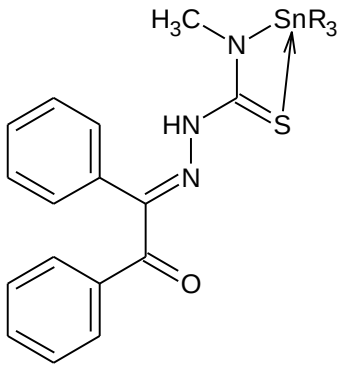
NMR Spectral Data :

The PMR spectra of ligand is characterised by appearance of a siginal at 8.64ppm for two –NH groups ,2.5ppm for N-CH_3 group and a multiplet at 6.84-7.86 ppm attributable to protons of phenyl moiety. The resonance at 8.64ppm is present in the spectra of the complexes, integration of protons along with appearance of Sn-O streaching band in IR and Sn NMR suggesting the selective deprotonation of one of the –NH and its subsequent involvement in coordination. The resonance due to the phenyl moiety remains uneffectd. The PMR spectra of complexes exhibit phenylene proton resonances are overlapping with the phenylene proton resonances of the ligand to give a complex pattern at 6.76-8.25 ppm. The resonances due to the butyl protons are observed in the region 0.60-1.86 ppm, with a well defined triplet at 0.85 ppm (J=8Hz) wich is due to methyl protons of butyl group.

The methyl protons of the dimethyltin(IV)derivatives appear as a sharp singlet at 0.44 ppm. A particular advantage of methyl tin derivatives is the ease with wich proton spin – spin coupling constant can be determined. The coupling constant provides valuable information about hybridisation state of tin.[15,16] For the four coordinate dimethyl tin (IV) compounds have been found to be 72 Hz wich is in the range of values observed for six coordinate dimethyltin (IV) compounds, indicating that the ligand behaving as bidendate moiety.

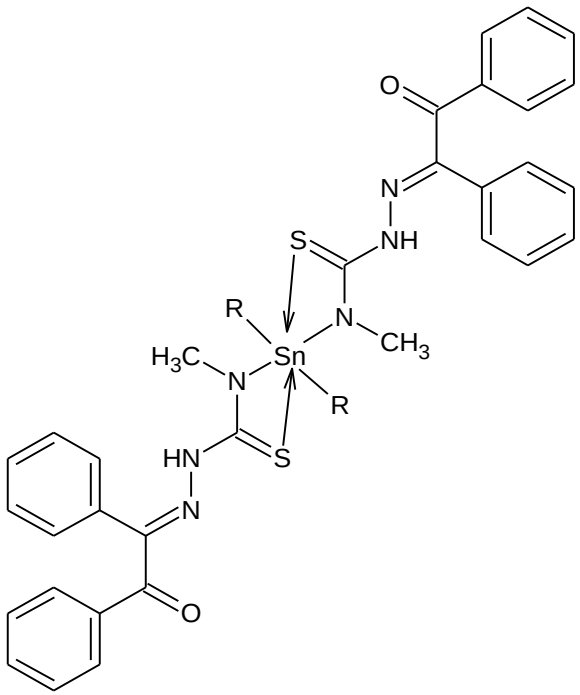
The ^{119}Sn chemical shiftes of all the derivatives have been observed in the range at -86.85 to -433.27 ppm. These ^{119}Sn NMR chemical shifts of triphenyltin (IV) and mixed chlorodimethyltin (IV)derivatives contain six coordinate tin

Thus based on above spectral studies, five-coordinate (a) and sixcoordinate (b) structures may be tentatively proposed for triorganotin(IV) and diorganotin(IV) derivatives of the ligand, respectively.



(a)

(R=Ph,Bu)



(R=Me,Bu) (b)

EXPERIMENTAL

Due to the highly hygroscopic nature of the metal alkoxides stringent precautions were taken to exclude moisture throughout the experiments, using glasswares with the interchangeable joints. All the reactions were carried out under strictly anhydrous conditions and analytical grade chemicals were used for all experiments. The Schiff base have been synthesized by the condensation of salicyldehyde and o-phenylenediamine in 2:1 molar ratio in benzene as reaction medium. Thus solution was refluxed for 3-4 h and then allowed to cool to room temperature. The products so obtained were recrystallised from pet.ether-benzene mixture.

Tin was determined as tinoxide gravimetrically and nitrogen was determined by Kjeldahl's method. Infrared spectra were recorded on a perkin-Elmer model 377 spectrophotometer in the range 4000-400 cm^{-1}. The ^{1}H NMR spctra were recorded on a jeol FX -90 using tetramethylsilane as an external standard.

Reactin between triphenyltin(IV)chloride and sodium salt of (2E)-N-methyl-(2-oxo1,2diphenylethylidne)hydrazinecarbothioamide in a 1:1 molar ratio:

0.07g of sodium metal and 15 ml of isopropanol were taken in a round bottom flask (fitted with a dried and a cooled water condenser and guard tube) and refluxed for about half an hour till a clear solution of sodium isopropoxide was obtained. After cooling.91(3mmole)of(2E)-N-methyl-(2-oxo1,2diphenylethylidne)hydrazinecarbothioamide was added and the mixture was for two hours again. 1.17 g (3mmole) of triphenyltin choride was added and mixture was further refluxed for two hours to ensure the completion of the reaction. The desired product (80%) was isolated by evaporation of the solvent under reduced pressure, after filtering of the precipitated sodium chloride. The product was further purified by crystallization using a benzene-petrolium ether (40^{o}-60^{o}) mixture.

All other organotin (IV) derivatives of (2E)-N-methyl-(2-oxo1,2diphenylethylidne)hydrazinecarbothioamide were synthesized analogously. The pertinent data for this compound and other derivatives are listed bellow.

Compound 1.$C_{34}H_{29}N_3OSn$

Yield 79%; Mol.Wt.[F(C)]: 646.38(511.16);yellow solid;M.P.103-105^{o}c.

Analysis[%F(C)]:Sn,18.37(23.22),H,3.20(3.39);N.6.50 (5.48);O,2.48(6.26),S,4.96

IR(cm^{-1}):υC= O,1680; υ C= N,1605; υ Sn-O, 485.

PMR(ppm): 2.65(s,3H, N-CH_3),7.46-7.65(m,12H,Ar). ^{119}Sn NMR(ppm): -115.62

^{13}CNMR(ppm):166.23,160.65,154.34,142.46,133.42,132.48,127.63,119.42,119.12,118.86,116.43; MS (El, 70Ev): m/z 342 (M^{+},26),314,298,282,208,192,77.

Compound 2 $C_{28}H_{41}N_3OSSn$

Yield 89%; Mol.Wt.[F(C)]: 585 (491.17);yellow solid;M.P.104-106^{o}c.

Analysis[%F(C)]: Sn(20.17%)
(24.17),H, H(7.00 (4.93); N(7.17%) (5.70);O, O(2.73 (6.51) ,S(5.47%)
IR(cm^{-1}):υC= O,1685; υ C= N,1600; υ Sn-O, 480.
PMR(ppm): 2.70(s, 3H, N-CH_3),7.50-7.69(m,12H,Ar). ^{119}Sn NMR(ppm): -84.82
^{13}CNMR(ppm):166.35,161.00,154.45,142.50,133.50,133.00,127.70,119.50,119.17,117.90,116.52; MS (El, 70Ev): m/z 342 (M^+,26),316,297,284,209,193,79.

Compound 4 $C_{31}H_{27}N_6O_2S_2Sn$
Yield 89%; Mol.Wt.[F(C)]: 698.4 (562.08);yellow solid;M.P.104-106^{o}c.
Analysis[%F(C)]:Sn,22.12(21.12),H,9.16( )(4.30);N12.02(4.98);O, 4.58 (5.69), C53.26(51.28). S(9.16)
IR(cm^{-1}):υC= O,1685; υ C= N,1600; υ Sn-O, 480.
PMR(ppm): 2.70(s, 3H, N-CH_3),7.50-7.69(m,12H,Ar).,^{119}Sn NMR(ppm): -118.6
^{13}CNMR(ppm):166.35,161.00,154.45,142.50,133.50,133.00,127.70,119.50,119.17,115.90,116.52; MS (El, 70Ev): m/z 342 (M^+,26),316,297,284,209,193,79.

Compound 3 $C_{24}H_{32}ClN_3OSSn$
Yield 89%; Mol.Wt.[F(C)]: 564.75838 (967.86);yellow solid;M.P.109-110^{o}c.
Analysis[%F(C)]: C(51.04%) H(5.71%) Cl(6.28%) N(7.44%) O(2.83%) S(5.68%) Sn(21.02%).
IR(cm^{-1}):υC= O,1687; υ C= N,1608; υ Sn-O, 480.
PMR(ppm): 2.70(s, 3H, N-CH_3),7.50-7.69(m,12H,Ar). ^{119}Sn NMR(ppm): -420.20
^{13}CNMR(ppm):166.35,161.00,154.45,142.50,133.50,133.00,127.70,119.50,119.17,114.90,116.52; MS (El, 70Ev): m/z 342 (M^+,26),314,298,284,209,193,79.

Compound 5 $C_{18}H_{20}ClN_3OSSn$
Yield 89%; Mol.Wt.[F(C)]: 480.59 (484.54);yellow solid;M.P.110-114^{o}c.
Analysis[%F(C)]: C(44.98%) H(4.19%) Cl(7.38%) N(8.74%) O(3.33%) S(6.67%) Sn(24.70%)
IR(cm^{-1}):υC= O,1685; υ C= N,1600; υ Sn-O, 480.
PMR(ppm): 2.70(s, 3H, N-CH_3),7.50-7.69(m,12H,Ar). ^{119}Sn NMR(ppm): -126.52
^{13}CNMR(ppm):166.35,161.00,154.45,142.50,133.50,133.00,127.70,119.50,119.17,113.90,116.52; MS (El, 70Ev): m/z 342 (M^+,26),315,299,284,209,191,79.

Compound 6 $C_{34}H_{34}N_6O_2S_2Sn$
Yield 89%; Mol.Wt.[F(C)]: 740 (870.68);yellow solid;M.P.104-106^{o}c.
Analysis[%F(C)]: C(55.13) H(4.59) N(11.35) O(8.64) S(8.64) Sn(15.94)
IR(cm^{-1}):υC= O,1685; υ C= N,1600; υ Sn-O, 480.
PMR(ppm): 2.70(s, 3H, N-CH_3),7.50-7.69(m,12H,Ar). ^{119}Sn NMR(ppm): -420.32
^{13}CNMR(ppm):166.35,161.00,154.45,142.50,133.50,133.00,127.70,119.50,119.17,115.90,116.52; MS (El, 70Ev): m/z 342 (M^+,26),316,299,281,209,192,79.

Biological Properties

Antibacterial Activity

The newly synthesized ligands and their complexes were tested for their in vitro antibacterial activity against Staphylococcus aureus and Bacillus subtilis by using the agar disc diffusion method [25]. Among the tested compounds, three complexes 1–3 showed considerable activity almost equal to the activity of ciprofloxacin. The other compounds were found to be moderate or least effective. The compounds have no effect on Gram-negative bacteria whereas they are moderately active for Gram-positive strains. Representative figure of antibacterial activity against Staphylococcus aureus (ligands) and Bacillus subtilis (metal complexes) is given in Figure.

Figure

(ligands) and Bacillus subtilis (metal complexes).

Antifungal Activity

The newly synthesized ligands and their complexes were also screened for their antifungal activity against Aspergillus niger and Alternaria alternate by agar disc diffusion method . The results of the preliminary antifungal testing of the prepared compounds were compared with the typical broad spectrum of the potent antifungal drug amphotericin B. The antifungal activity data (Table) reveal that compounds 2–4 showed good activity for both the fungal strains whereas L_1 showed excellent activity against Alternaria alternate, which is nearly equal to the standard amphotericin B.

Table : Antibacterial and antifungal activities of the compounds.

Compound	Staphylococcus aureus	Bacillus subtilis	Aspergillus niger	Alternaria alternate
L 1	—	+	+	++
1	+	++	—	+
L 2	—	+	—	—
2	—	++	+	+
L 3	—	+	—	+
3	—	+++	—	+
L 4	—	+	—	+
4		+	+	+
DMSO	—	—	—	—

+++ is the activity of zone of clearance radius of 2.5 cm when it is compared to control. ++ is the activity of zone of clearance radius of 1.5 cm when it is compared to control. + is the activity of zone of clearance radius of 1.0 and ≤0.6 cm when it is compared to control. The concentration was 1 mg/mL and prepared in DMSO, and the results are compared with solvent activity also, and each well was loaded with 100 µL, that is, 100 µg was loaded.

III. Conclusions

In summary, four binuclear complexes have been prepared and characterized. The metal ion was coordinated through the thioketonic sulphur and the nitrogen of the azomethine group. The bonding of ligand to metal ions was confirmed by the analytical data, as well as spectral and magnetic studies. The complexes had higher antibacterial and antifungal activities than the ligand. In this study, we have attempted to unravel the DNA interactions of these complexes. The observed trends in binding constants of the complexes may be due to the presence of a phenyl ring in the ligands that facilitate pi-stacking interaction.

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