Thiohydrazone Complexes of Organotin (IV): Synthesis, Spectroscopy and Thermal Studies

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ABSTRACT

Organotin (IV) thiohydrazones derived from piperidine were synthesized and characterized. At first the potassium salt of piperidine dithiocarbamate was prepared from dropwise addition of CS_2 to ethanolic mixture of piperidine in basic medium. Then piperidine-N-thiohydrazide was prepared from the reaction of dithiocarbamate with hydrazine hydrate and chloroacetic acid. After that thiohydrazones were prepared from condensation of piperidine-N-thiohydrazide and aldehydes (cinnamaldehyde and salicylaldehyde). Then complexes were prepared from reaction of thiohydrazone with organotin (IV) compounds (diallyltin dibromide, tribenzyltin chloride, tri-p-chlorobenzyltin chloride). The complexes synthesized were characterized through infrared, ultraviolet, H^1NMR spectroscopic methods. Quantitative analyses were carried out using CHNS and tin analysis. Also thermoanalytical techniques (TG, DTA) have been employed to calculate various thermodynamic parameters like order of reaction (n), heat of reaction ΔH, activation energy E_a for solid state decomposition of complexes.

INTRODUCTION

Organotin compounds are known to be biologically active, as they were widely used as wood preservatives, fungicides and marine antifouling agents. In the context of human medicine tin compounds have shown potential towards the treatment of the parasitic diseases and use as antiviral agents. The diorganotins are the largest group of tin compounds studied for antitumor activity. Also, because of technical applications and favourable environmental and toxicological properties /1/ of organotin compounds, the industrial sector was quick to recognize their commercial importance. Organotin compounds with Sn-S bond were used as heat stabilizers. Thiohydrazones have been proved to be biologically active as they have antibacterial, antifungal /2/ and antitumor activity. Thiohydrazones and their complexes have been found to be active against influenza /3/, protozoa /4/, smallpox /5/ and certain kinds of tumors /6/. It is thus anticipated that the new organotin thiohydrazones would exhibit biological importance. So focus has been laid upon synthesis and characterization of some organotin (IV) thiohydrazones. The preparation and characterization of complexes of diallyl tin dibromide, tribenzyl tin chloride, tri-p-chloro benzyl tin chloride with

salicylaldehyde piperidine-N-thiohydrazone and cinnamaldehyde piperidine-N-thiohydrazone are described in this paper.

MATERIALS AND METHODS

The compounds diallyltindibromide, tribenzyltin chloride, tri-p-chlorobenzyl tin chloride were synthesized, while piperidine was supplied by E-Merck, allyl bromide was supplied by Fluka and tin powder was supplied by CDH. All solvents used were purified by accepted methods.

Preparation of diallyl tin dibromide /7/

5.93 g (0.05 mol) of tin powder was taken in 50ml of toluene in a 3-necked round bottom flask. In one neck a separating funnel was fitted, in the second neck a reflux condenser, and the third neck was used for N_2 gas passing. To the tin powder 0.18 g (0.0006mol) of mercuric chloride was added. Then the resulting mixture was heated to reflux up to half an hour with constant stirring. After cooling, 0.08ml (0.0006mol) of triethyl amine was added to the mixture. The mixture was again refluxed and to this 4.23ml (0.05mol) allyl bromide was added dropwise with efficient stirring. The reflux was continued up to 1.5 hour. The unchanged tin with an unidentified amorphous solid was filtered off and the filtrate was evaporated under reduced pressure, yielding diallyl tin dibromide. The whole reaction was carried out in a nitrogen atmosphere.

Preparation of tribenzyl tin chloride /8/

To 1.186g (0.01mol) of tin powder suspended in 10ml boiling water, 1.15ml (0.01mol) of benzyl chloride was added slowly with efficient stirring. The reaction temperature was kept at 100^0C.Reflux with efficient stirring was continued for 1.5 hour. After cooling, the solid mass containing the product and unreacted tin powder was filtered and dried in air. Then the dry solid mass was extracted with acetone for 4 hours in a Soxhlet apparatus. Then the acetone was evaporated at room temperature yielding pale yellow crystals, which were recrystallised from ethyl acetate and dried in vacuum.

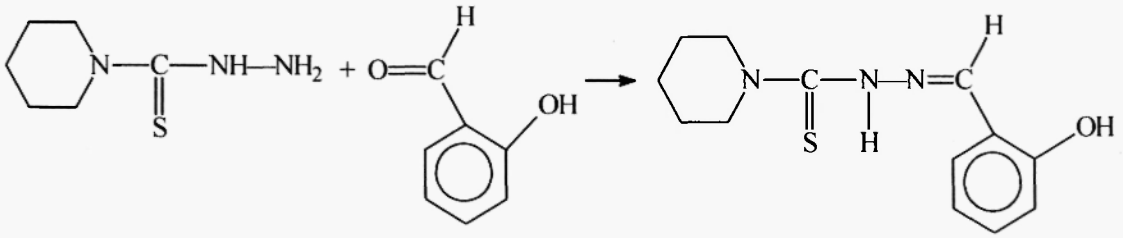
Preparation of tri-p-chlorobenzyl tin chloride /8/

To 3.558 g (0.03mol) of tin powder suspended in 30 ml boiling water, 4.82ml (0.03mol) of p-chlorobenzyl chloride was added slowly with efficient stirring. The reaction temperature was kept at 100^0C.Reflux with efficient stirring was continued for 2.5 hours. After cooling, the solid mass containing the product and unreacted tin powder was filtered and dried in air. Then the dry solid mass was extracted with acetone for 4 hours in a Soxhlet apparatus. Then the acetone was evaporated at room temperature yielding pale yellow crystals, which were recrystallised from ethyl acetate and dried in vacuum.

Preparation of ligands

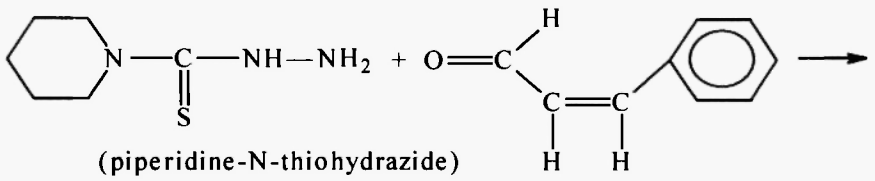
All ligands were synthesized by Gilman and Blat's /9/ method with some modifications. The potassium salt of piperidine dithiocarbamate was prepared by dropwise addition of chilled carbon disulphide(3ml,0.04mol of CS_2 in 4ml of methanol) into the mixed solution of piperidine(0.04mol of piperidine, 3.4g in 10ml of methanol) and potassium hydroxide (0.04mol of KOH, 2.24g in 3ml methanol). The temperature of the reaction was kept below 10^0C. The mixture was stirred for 2-3 hrs. At the end of the reaction, a white crystalline solid of potassium piperidine dithiocarbamate was obtained. Without separating it from methanol, aqueous solution of potassium salt of freshly prepared monochloroacetic acid prepared by dissolving 3.78g of monochloroacetic acid in 2 ml ice cold water and mixing it in 3 ml aqueous methanolic solution of 2.24 g KOH) was added to the reaction mixture. The temperature of the resulting solution was maintained below 40^0C for an hour and the content was allowed to stand overnight at room temperature. After 24 hours 5ml of 99% hydrazine hydrate (in methanol) was added to the reaction mixture. Then the content was evaporated slowly to half of its original volume and then kept in freeze. Then the crude product obtained was recrystallised from hot water and dried to yield piperidine N-thiohydrazide with melting point 76-80°C.

Preparation of salicylaldehyde piperidine-N-thiohydrazone (L^1): 0.16 g (0.001 mol) of piperidine-N-thiohydrazide and equimolar quantities (0.1ml) of salicylaldehyde were refluxed in methanol. Reflux took place for 3 hours. Then the liquid obtained was evaporated at room temperature. The crude product was recrystallised from hot methanol. Then the final product was obtained with 86.66 % yield and melting point 75-80°C. A simple layout for this preparation can be given as,

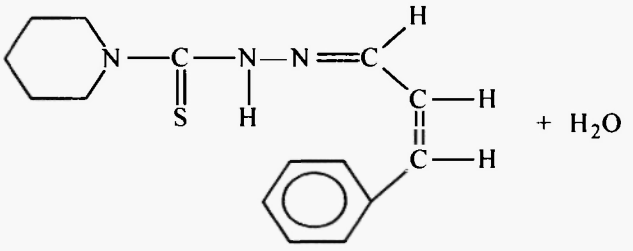


Piperidine-N-thiohydrazide Salicylaldehyde Salicylaldehyde piperidine-N-thiohydrazone

Preparation of cinnamldehyde piperidine-N-thiohydrazone (L^2): 0.16 g (0.001 mol) of piperidine-N-thiohydrazide and equimolar quantities (0.1ml) of cinnamaldehyde were refluxed in methanol. Reflux took place for 3 hours. Then the liquid obtained was evaporated at room temperature. The crude product was recrystallised from hot methanol. Then the final product was obtained with 86.66 % yield and melting point 75-80 ^{0}C. A simple layout for this preparation can be given as:



(piperidine-N-thiohydrazide)



Cinnamaldehyde
piperidine-N-thiohydrazone

Now the complexes were prepared by reacting ligands $L^1$and L^2 with diallyl tin dibromide, tribenzyl tin chloride and tri-p-chlorobenzyl tin chloride in equimolar ratios. Here ligands and organometals are refluxed for 2-3 hours in methanol or acetone as solvent. Then the complexes obtained were recrystallized, dried and finally characterized.

RESULTS AND DISCUSSION

All the yielded products are found to be stable in air. The percentage yields, melting points and elemental analysis data for the isolated products are presented in Table 1. The results obtained from elemental analysis have shown a good agreement with theoretical values.

The assignments of important peaks in the infrared spectra of the products are shown in Table 2

Table 1

Percentage yield, melting point and elemental analysis data.

Found (calculated)

Product %Yield,MP(^{0}C)	%C	%H	%N	%S	%Sn
$(CH_2=CH—CH_2)_2Sn(L^1)Br_2$ 75, 120-125	37.12 (36.57)	5.08 (4.33)	7.24 (6.73)	6.03 (5.14)	18.92 (19.02)
$(CH_2=CH—CH_2)_2Sn(L^2)Br_2$ 70, 98-100	38.43 (39.81)	5.18 (4.58)	5.37 (6.63)	6.36 (5.06)	17.91 (18.73)
$(C_6H_5CH_2)_3Sn(L^1)$ Cl 70, 110	59.87 (60.52)	5.33 (5.63)	4.80 (6.23)	3.66 (4.74)	16.62 (17.59)
$(C_6H_5CH_2)_3Sn(L^2)$ Cl 70, 90	61.18 (61.70)	6.21 (5.71)	7.4 (6.0)	5.20 (4.57)	16.12 (16.94)
$(p\text{-}ClC_6H_4CH_2)_3Sn(L^1)Cl$ 70, 110	50;83 (51.41)	4.11 (4.41)	5.38 (5.29)	3.73 (4.03)	13.68 (14.94)
$(p\text{-}ClC_6H_4CH_2)_3Sn(L^2)Cl$ 75, 90	52.46 (53.75)	4.15 (4.6)	4.67 (5.22)	3.98 (3.68)	14.04 (14.75)

Table 2

Important IR absorption bands (cm^{-1})

Product	ν_{C-N}	$\nu_{C=S}$	$\nu_{C=N}$	ν_{M-S}	ν_{M-Cl}	ν_{M-Cl}
$(CH_2=CH—CH_2)_2Sn(L^1)Br_2$	1030	960	1607	350	-	248, 226
$(CH_2=CH—CH_2)_2Sn(L^2)Br_2$	1140	950	1600	356	-	248, 227
$(C_6H_5CH_2)_3Sn(L^1)$ Cl	1135	965	1610	350	338	-
$(C_6H_5CH_2)_3Sn(L^2)$ Cl	1125	969	1600	353	320	-
$(p\text{-}ClC_6H_4CH_2)_3Sn(L^1)Cl$	1025	960	1605	360	389	-
$(p\text{-}ClC_6H_4CH_2)_3Sn(L^2)Cl$	1130	955	1599	345	320	-

In all complexes a peak at 950-1000cm^{-1} represents the presence of C=S group. Also all complexes show a band at about 1450-1590cm^{-1}, which indicates the presence of thiouride group /10/. A peak at around 1620-1650cm^{-1} is observed in all complexes which represents the imine group (-C=N). A peak at 1020-1200cm^{-1} is observed for C-N. In allyl complexes very strong peaks are observed for C=C at 1625cm^{-1} and peaks at 985cm^{-1}, 905cm^{-1}, which correspond to vinyl group /11/.

All the complexes showed 3 major absorption bands in UV spectra, out of which two can be assigned to $\pi \rightarrow \pi^*$ transition. The third band can be assigned to the transition. $n \rightarrow \pi^*$

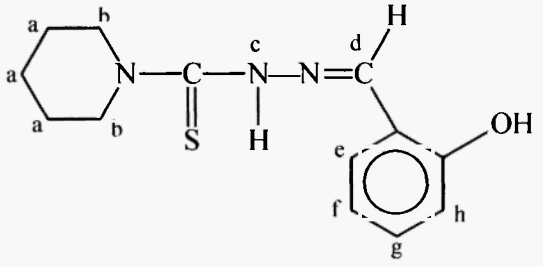
Table 3

Important UV absorption bands (nm).

Product	λ_{max} $n \rightarrow \pi^*$	λ_{max} $\pi \rightarrow \pi^*$	λ_{max} $\pi \rightarrow \pi^*$
$(CH_2=CH—CH_2)_2Sn(L^1)Br_2$	392	334	222
$(CH_2=CH—CH_2)_2Sn(L^2)Br_2$	341	255	213
$(C_6H_5CH_2)_3Sn(L^1)$ Cl	396	333	244
$(C_6H_5CH_2)_3Sn(L^2)$ Cl	380	334	246
$(p\text{-}ClC_6H_4CH_2)_3Sn(L^1)Cl$	393	336	244
$(p\text{-}ClC_6H_4CH_2)_3Sn(L^2)Cl$	406	320	246

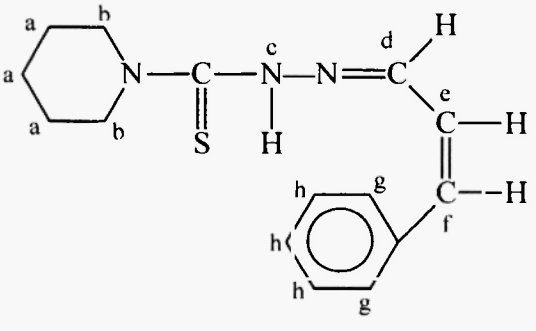
The H^1 NMR spectral data obtained for ligands are shown below. All the quoted values are with reference to tetramethyl silane as standard. On complexation along with these signals additional signals in the region δ (ppm) 6.9- 7.5 (ArH) and δ 2.2-2.5 (CH_2) corresponding to benzyl group moiety appear in H^1NMR spectra of benzyl tin complexes. However in allyl tin complexes additional signals in the region δ (1.5,CH^a_2), δ 5.5 (CH^b), δ 5 (CH^c_2) for allyl group —C^aH_2=C^bH—C^cH_2 in allyl tin.

Salicylaldehyde Piperidine-N-thiohydrazone (L^1):



δ (ppm): 1.7 (t, $6H^a$, CH_2), 3.8(t, $4H^b$, CH_2), 6.85 (br, $1H^c$,NH), 7.9(s,$1H^d$,CH), 7.3 (d,$1H^e$,CH), 7.2 (d,$1H^h$,CH), 6.9 (m,$1H^{f,g}$,CH), 10.38(s, br, OH).

Cinnamaldehyde Piperidine-N-thiohydrazone (L^2):



δ (ppm): 1.7 (t, $6H^a$, CH_2), 3.4(t, $4H^b$, CH_2), 6.8 (br, $1H^c$,NH), 7.4(d,$1H^g$,CH), 7.3 (d,$1H^h$,CH), 8.5(d,$1H^f$,CH), 5.5 (d,$1H^e$,CH), 3.9 (d,$1H^d$,CH),

From Thermogravimetry (TG) and Differential Thermal Analysis (DTA), the activation energy (E_a) and order of reaction(n) have been determined by using the Coats-Redfern /12/ and Horowitz /13/ methods. The order of reaction is found to be one. Also heat of reaction has been determined from the area under the DTA peaks. Here the calibration coefficient used for calculation of heat of reaction has been obtained from Currel equation /14/. The data of thermal analysis have been elaborated in Tables 4 and 5.

Table 4

Mass loss data of complexes.

Complexes	Step No.	Temp. range (K)	% Weight loss Expected (obs.)	Nature of loss
$(CH_2{=}CH{-}CH_2)_2Sn(L^1)Br_2$	1	350-509	13.15(14.00)	Loss of two allyl groups
	2	509-729	38.73(39.50)	Loss of Br_2
	3	729-843	75.84(77.35)	Formation of SnO_2
$(CH_2{=}CH{-}CH_2)_2Sn(L^2)Br_2$	1	373-486	12.94(13.50)	Loss of two allyl groups
	2	486-723	38.17(38.90)	Loss of Br_2
	3	723-850	76.22(77.00)	Formation of SnO_2
$(C_6H_5CH_2)_3Sn(L^1)$ Cl	1	409-583	39.55(38.70)	Loss of three benzyl groups
	2	583-719	44.70(45.30)	Loss of chlorine atom
	3	719-833	78.17(79.00)	Formation of SnO_2
$(C_6H_5CH_2)_3Sn(L^2)$ Cl	1	364-483	38.99(39.50)	Loss of three benzyl groups
	2	483-628	44.06(45.08)	Loss of chlorine atom
	3	628-783	78.48(77.60)	Formation of SnO_2
$(p\text{-}ClC_6H_4CH_2)_3Sn(L^1)Cl$	1	373-498	47.44(46.80)	Loss of three p-chloro benzyl groups
	2	498-609	51.91(51.00)	Loss of chlorine atom
	3	609-830	81.02(81.50)	Formation of SnO_2
$(p\text{-}ClC_6H_4CH_2)_3Sn(L^2)Cl$	1	380-573	46.85(47.00)	Loss of three p-chloro benzyl groups
	2	573-723	51.26(50.90)	Loss of chlorine atom
	3	723-853	81.25(80.80)	Formation of SnO_2

Table 5

Thermal data of complexes

Complexes .	Step No.	Reaction order (n)	TG		DTA		
			Coats-Redfern Ea (KJ/mol)	Horowitz-Metzger Ea (KJ/mol)	Thermal effect	T_{max}	ΔH Cal/g
$(CH_2=CH-CH_2)_2Sn(L^1)Br_2$	1	1	10.594	17.25	Endothermic	403	89.99
	2	1	15.179	27.13	Exothermic	540	360.51
	3	1	60.38	52.82	Exothermic	749	478.3
$(CH_2=CH-CH_2)_2Sn(L^2)Br_2$	1	1	8.842	16.574	Endothermic	419	96.35
	2	1	9.41	19.13	Endothermic	559	162.94
	3	1	36.002	51.056	Exothermic	817	234.63
$(C_6H_5CH_2)_3Sn(L^1)Cl$	1	1	3.055	10.756	Exothermic	422	276.35
	2	1	15.863	22.715	Endothermic	595	411.04
	3	1	27.7	40.755	Exothermic	749	477.68
$(C_6H_5CH_2)_3Sn(L^2)Cl$	1	1	11.135	20.76	Endothermic	388	106.57
	2	1	20.96	31.47	Exothermic	503	422.73
	3	1	15.105	27.09	Endothermic	667	652.92
$(p\text{-}ClC_6H_4CH_2)_3Sn(L^1)Cl$	1	1	5.456	15.179	Endothermic	415	44.02
	2	1	15.216	21.908	Endothermic	513	87.17
	3	1	8.635	18.512	Exothermic	790	221.18
$(p\text{-}ClC_6H_4CH_2)_3Sn(L^2)Cl$	1	1	1.476	9.94	Endothermic	456	22
	2	1	38.22	42.77	Exothermic	645	200.58
	3	1	24.08	38.07	Exothermic	836	223.44

CONCLUSION:

Spectroscopic data indicate that the thiohydrazones form bidentate chelates with the organotin (IV) moieties. Here chelation takes place through the sulphur and nitrogen atoms of thiohydrazone. All the complexes form five-membered rings.

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