

Synthesis and Characterisation of Addition Compounds of Pyridine Carboxylic Acid Hydrazides with Tin (IV) Halides, Organotin (IV) Halides and Thiocyanates*

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Abstract. Addition compounds of the compositions $SnX_4 \cdot xL$ and $R_nSnX_{4-n} \cdot xL$ where $X = Cl^-, Br^-, I^-$, or $(NCS)^-$, $R =$ phenyl or n -butyl, $L =$ picolinic acid hydrazide (PH), nicotinic acid hydrazide (NH) or isonicotinic acid hydrazide (INH), $x = 1$ or 2 and $n = 1, 2$ or 3 have been prepared and characterised with the help of elemental analysis, molar conductance, UV and IR spectral studies. All the adducts are nonionic as evidenced from their low molar conductances in DMF. UV and IR spectral studies show that NH and INH coordinate through carbonyl oxygen and terminal nitrogen; and (PH) through carbonyl oxygen and ring nitrogen in monoadducts. All the three isomeric pyridine carboxylic acid hydrazides are coordinated through pyridine nitrogen alone in the di-adducts. Octahedral geometry has been proposed for mono- as well as di-adducts.

1. Introduction

There has been continuing interest associated with the metal complexes of pyridine carboxylic acid hydrazides, owing to their biological importance¹, analytical applications^{2,3}, and varied bonding and stereochemical possibilities offered by these⁴⁻⁷. In the previous communications⁴⁻⁷ from this laboratory, the synthesis and structural studies of the complexes of these hydrazides with titanium and zirconium tetrahalides and with some first row transition metal ions were reported. In view of lack of previous work on tin (IV) halide, organotin (IV) halide and pseudohalide complexes of isomeric pyridine carboxylic acid hydrazides and their potential applications as biocides and in marine antifouling paints, the work on the title complexes was undertaken and the results of these investigations are reported in this paper.

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2. Symposium on Metal-Organic & Organometallic Compounds and their Uses in Chemical Synthesis held at University of Rajasthan, Jaipur, October 3-6, 1978.

2. Experimental Procedure

INH procured from Sigma was used as such. *PH* and *NH* were prepared as described earlier^{5,6}. All the solvents were dehydrated before use.

Preparation and Analysis of Tin (IV) Adducts — Addition compounds of *PH* were obtained by mixing the $CHCl_3$ solutions of the hydrazide and tin (IV) compounds in 1 : 1 and 1 : 2 molar ratios. The adducts which precipitated immediately or within a few minutes of stirring were suction filtered through a specially designed filtering unit, washed several times with $CHCl_3$ and dried in a vacuum desiccator.

NH and *INH* adducts were prepared by mixing the CH_3CN solution of the hydrazide and $CHCl_3$ solution of the tin compound in 1 : 1 and 1 : 2 molar ratios and stirring the reaction mixture for ~ 2 hr. The addition compounds were either precipitated during the course of stirring or their precipitation was affected by the addition of a mixture of $CHCl_3$ and petroleum ether (40° - $60^\circ C$) after concentrating the reaction mixture in vacuo.

Tin, halides and sulphur were estimated gravimetrically as SnO_2 , silver halides and $BaSO_4$ respectively⁸ in their addition compounds after fusing these with fusion mixture and subsequent necessary manipulations. Hydrazine was estimated by titrating against standard KIO_3 , after subjecting the addition compounds to acid hydrolysis for ~ 3 hr⁸. Nitrogen was determined microanalytically. Satisfactory analytical data were obtained for tin, halides, sulphur, hydrazine and nitrogen in all the addition compounds.

Physico-Chemical Studies — Molar conductances of the adducts were measured on a WTW conductivity meter in DMF. UV and IR spectra of the adducts were recorded on Cary-14 and Perkin-Elmer-621 spectrophotometers respectively. Important IR and far IR spectral bands and their assignments are listed in Tables 1 and 2 respectively.

3. Discussion

The analytical data suggest the formation of mono- as well as di-adducts. All the addition compounds are insoluble in common organic solvents such as CCl_4 , $CHCl_3$, C_6H_6 and CH_3CN , sparingly soluble in THF and freely soluble in DMF and DMSO. The molar conductances of the adducts lying in the range 6.60-14.40 mhos cm^2 mole⁻¹ indicate their nonelectrolytic nature¹¹.

Infrared Spectra — Conclusions regarding the modes of bounding of hydrazides in the addition compounds have been reached by a careful peak by peak comparison of the mull spectra of the adducts with the acetonitrile solution spectra of the corresponding ligand.

1 : 1 *Adducts* — A negative shift in amide I ($10\text{-}44\text{ cm}^{-1}$) and amide II ($10\text{-}20\text{ cm}^{-1}$) and a positive shift in amide III ($8\text{-}24\text{ cm}^{-1}$) frequencies in the spectra of all the adducts indicate the coordination of carbonyl oxygen to the metal¹². A positive shift in $\nu(N-N)$ band ($12\text{-}30\text{ cm}^{-1}$) in the spectra of all the addition compounds of *NH* and *INH* and negative shift in NH_2 rocking ($10\text{-}25\text{ cm}^{-1}$) and wagging ($5\text{-}17\text{ cm}^{-1}$) vibrations indicate the coordination of terminal nitrogen in these addition compounds¹³ but all these three

modes of free *PH* remain practically unchanged in the spectra of its adducts signifying the noninvolvement of its terminal nitrogen in coordination. The in-plane and out-of-plane ring deformation modes of *NH* and *INH* are undisturbed in the spectra of their adducts, but undergo a marked positive shift of 7-52 and 10-25 cm^{-1} respectively in the spectra of the addition compounds of *PH* suggesting that ring nitrogen is free in the former adducts and coordinated in the latter¹⁴.

Table 1. Important IR spectral bands (cm^{-1}) and their assignments in pyridine carboxylic acid hydrazide adducts.

	Amide I	Amide II	Amide III	NH_2 rocking	$\nu(\text{N}-\text{N})$	NH_2 wagging	In-plane ring deforma- tion	Out-of- plane ring deforma- tion
<i>PH</i>	1674s	1518s	1340m	1120m		980	633m	405m
$\text{SnCl}_4 \cdot \text{PH}$	1630s	1505m	1355m	1125		988	685m	430m
$\text{SnCl}_4 \cdot 2\text{PH}$	1675s	1518m	1340m				658m	416m
$\text{SnBr}_4 \cdot \text{PH}$	1630s	1508m	1350w	1120		986	680m	422m
$\text{SnBr}_4 \cdot 2\text{PH}$	1675s	1518m	1340m				652m	436m
$\text{SnI}_4 \cdot \text{PH}$	1648m	1504m	1354m	1120		984	664m	420m
$\text{SnI}_4 \cdot 2\text{PH}$	1674s	1520s	1340m				665m	416m
$\text{PhSnCl}_3 \cdot \text{PH}$	1632s	1505m	1355m	1119		988	642m	420m
$\text{BuSnCl}_3 \cdot \text{PH}$	1648m	1502m	1348m	1124		982	643m	420m
$\text{Ph}_2\text{SnCl}_2 \cdot \text{PH}$	1635vs	1503m	1350m	1122		990	642m	419w
$\text{Bu}_2\text{SnCl}_2 \cdot \text{PH}$	1655s	1504m	1352w	1120		990	641m	420m
$\text{Ph}_2\text{Sn}(\text{NCS})_2 \cdot \text{PH}$	1648m	1508m	1352w				640m	420m
$\text{Ph}_3\text{Sn}(\text{NCS}) \cdot \text{PH}$	1660m	1508m	1350w				645m	415m
<i>NH</i>	1680s	1555s	1310m	1130m	1020s	965m	670m	390m
$\text{SnCl}_4 \cdot \text{NH}$	1640s	1535s	1330m	1105w	1035m	955w	670m	392m
$\text{SnCl}_4 \cdot 2\text{NH}$	1680s	1555s	1305m	1020m	1020m		685m	398m
$\text{SnBr}_4 \cdot \text{NH}$	1660s	1545s	1320m	1100m	1050m	948m	670m	390m
$\text{SnBr}_4 \cdot 2\text{NH}$	1685s	1555m	1308w		1020m		695m	420m
$\text{SnI}_4 \cdot 2\text{NH}$	1680s	1556m	1310m	1130m	1020s	966m	700m	404m
$\text{PhSnCl}_3 \cdot \text{NH}$	1664vs	1540m	1328m	1110m	1035m	955m	670m	390m
$\text{BuSnCl}_3 \cdot \text{NH}$	1652vs	1544m	1334m	1108w	1030m	956w	670m	390m
$\text{Ph}_2\text{SnCl}_2 \cdot \text{NH}$	1665s	1530s	1328m	1115w	1045m	955w	670m	392m
$\text{Bu}_2\text{SnCl}_2 \cdot \text{NH}$	1668s	1535s	1325s	1120m	1045m	956w	672m	388m
$\text{Ph}_3\text{SnNCS} \cdot \text{NH}$	1668m	1544m	1326m		1036m		668m	389m
<i>INH</i>	1670s	1560s	1328m	1140	982s	890	658m	400m
$\text{SnCl}_4 \cdot \text{INH}$	1640s	1550m	1340m	1120w	1000m	822w	660m	400m
$\text{SnCl}_4 \cdot 2\text{INH}$	1680s	1560m	1328m	1140m	980w	888w	688w	416m
$\text{SnBr}_4 \cdot \text{INH}$	1655m	1546s	1340m	1120w	1000m	884w	658m	400m
$\text{SnBr}_4 \cdot 2\text{INH}$	1675s	1560m	1326m		980m		674m	425m
$\text{SnI}_4 \cdot 2\text{INH}$	1680s	1562m	1324w		980m		680w	408m
$\text{PhSnCl}_3 \cdot \text{INH}$	1655s	1540m	1345m	1130m	990m	878w	658m	400m
$\text{BuSnCl}_3 \cdot \text{INH}$	1656s	1552m	1348s	1124w	1000m	885w	658m	398m
$\text{Ph}_2\text{SnCl}_2 \cdot 2\text{INH}$	1670s	1560m	1325m		980m		670m	420m
$\text{Bu}_2\text{SnCl}_2 \cdot 2\text{INH}$	1670s	1560m	1325m		982m		680m	412m
$\text{Ph}_3\text{SnNCS} \cdot \text{INH}$	1660m	1548w	1336w		992m		656m	395m

s = strong, *m* = medium, *w* = weak

Table 2. Important far IR bands and force constants, log K, I. P. values of the addition compounds.

	$\nu(\text{M—O})$ (dynes/Å)	$\nu(\text{M—O})$ (Cm ⁻¹)	$\nu(\text{M—X})$ (Cm ⁻¹)	$\nu(\text{M—N})$ (Cm ⁻¹)	$f(\text{C=O})$ (dynes/Å)	Log K	I.P. (e.V.)	F ^{o*} (k. Cal./mole)
<i>SnCl₄ . PH</i>	1.463	420	322 295s br	278	10.63	5.2605	7.5684	7.0517
<i>SnCl₄ . 2PH</i>			308s br	252				
<i>SnBr₄ . PH</i>	1.429	415	—	255	10.03	5.2605	7.5684	7.0517
<i>SnBr₄ . 2PH</i>				251				
<i>SnI₄ . PH</i>	1.408	412		252	10.815	6.0310	8.1849	8.0854
<i>SnI₄ . 2PH</i>				252				
<i>PhSnCl₃ . PH</i>	1.443	417	320—300 290s br	268	10.655	5.3461	7.6369	7.1680
<i>BuSnCl₃ . PH</i>	1.422	414	296—280	256	10.815	6.0310	8.1849	8.0854
<i>Ph₂SnCl₂ . PH</i>	1.443	417	305—295	255	10.693	5.4745	7.7397	7.3383
<i>Bu₂SnCl₂ . PH</i>	1.394	410	320—295	250	10.9555	6.3305	8.4246	8.4859
<i>Ph₂Sn(NCS)₂ . PH</i>	1.429	415			11.0755	6.0310	8.4256	8.4898
<i>Ph₃Sn(NCS) . PH</i>	1.435	416			11.1155	6.5490	8.5993	8.7802
<i>SnCl₄ . NH</i>	1.360	405	320—290s br	268	10.63	5.6885	7.9109	7.6315
<i>SnCl₄ . 2NH</i>				262				
<i>SnBr₄ . NH</i>	1.314	398		255	11.02	6.5490	8.5993	8.7802
<i>SnBr₄ . 2NH</i>				272				
<i>SnI₄ . 2NH</i>				250				
<i>PhSnCl₃ . NH</i>	1.249	388	325vs br	260	10.8955	6.7275	8.7429	9.0940
<i>BuSnCl₃ . NH</i>	1.223	384	300—292s br	262	10.915	6.2025	8.3217	7.9253
<i>Ph₂SnCl₃ . NH</i>		406	295s	265	10.955	6.7585	8.7671	9.0594
<i>Bu₂SnCl₂ . NH</i>	1.223	384	335	265	11.128	6.8896	8.8716	9.2363
<i>Ph₃SnNCS . NH</i>	1.360	405		206	11.128	6.8865	8.8695	9.2321
<i>SnCl₄ . INH</i>	1.327	400 br	320—290s br	265	10.9655	5.6885	7.9109	7.6315
<i>SnCl₄ . 2 INH</i>			324—310s br	277				
<i>SnBr₄ . INH</i>	1.295	395		270	10.90	6.3305	8.4246	8.4859
<i>SnBr₄ . 2 INH</i>				268				
<i>SnI₄ . 2 INH</i>				250				
<i>PhSnCl₃ . INH</i>	1.211	382	315—305s br	265	10.90	6.3305	8.4246	8.4859
<i>BuSnCl₃ . INH</i>	1.223	384	310—300s	264	10.90	6.3757	8.4606	8.5468
<i>Ph₂SnCl₂ . 2 INH</i>			280	255				
<i>Bu₂SnCl₂ . 2 INH</i>			345 325s	255				
<i>Ph₃SnNCS . INH</i>	1.275	392		260	11.02	6.5490	8.5993	8.7802

* Calculated at 23°C

s = strong, br = broad

1 : 2 Adducts -- In the spectra of all the di-adducts, amide I, amide II, amide III, $\nu(\text{N—N})$, $\beta(\text{NH}_2)$ wagging and rocking vibrations remain practically unaltered, but the in-plane and out-of-plane ring deformations modes of the hydrazides shift to higher frequencies (12-32 and 8-31 cm⁻¹ respectively) suggesting that the ring nitrogen alone is coordinated in the above adducts^{12,14}.

The $\nu(\text{CN})$, $\nu(\text{CS})$ and $\delta(\text{NCS})$ modes of the thiocyanate ion, which are diagnostic of the mode of its bonding are observed in the 2040-2050, 774-797 and 470-492 cm⁻¹ regions respectively in the spectra of all our adducts containing thiocyanate ion, indicating its N-bonded nature¹⁵. A distinct negative shift in $\nu(\text{CN})$ in the adducts compared

to its position in the parent organotin (IV) thiocyanate suggests an increase in the coordination number of tin atom^{16,17}.

The non-ligand bands appearing in the spectra of addition compounds in the 420-382, 335-280 and 270-248 cm^{-1} regions are tentatively assigned to $\nu(\text{Sn} \leftarrow \text{O})$, $\nu(\text{Sn}-\text{Cl})$ and $\nu(\text{Sn} \leftarrow \text{N})$ modes¹⁸⁻²¹ respectively. The occurrence of a broad $\nu(\text{Sn}-\text{Cl})$ band in the above region suggests *cis* octahedral geometry for all the adducts of tin (IV) chloride and organotin (IV) chlorides^{19,20}.

UV Spectra — The vapour phase spectrum of pyridine shows ¹La and ¹Lb transition bands at 192 and 250 nm respectively^{22,23}. The transitions are considerably red shifted in the spectra of substituted pyridines due to the inductive and/or conjugative effects of the substituents²³. The two intense bands observed in the 218-228 and 267 nm regions in the spectra of all the three hydrazides are therefore assigned to ¹La and ¹Lb transitions of pyridine ring in conjugation with the hydrazide group.

On coordination of carbonyl oxygen, its conjugative effect on the pyridine ring diminishes and a blue shift (i.e. towards the position of these bands in unsubstituted pyridine) is expected. In the spectra of monoadducts of *NH* and *INH* these two transitions are considerably blue shifted and are obtained in the 217-225 and 247-264 nm regions confirming the coordination of carbonyl oxygen. A red shift in these transitions occurring in 222-225 and 270-287 nm regions in the spectra of monoadducts of *PH* and in the 222-237 and 270-285 nm regions in the spectra of all the di-adducts of pyridine carboxylic acid hydrazides indicate the coordination of ring nitrogen²⁴. The IR spectra of the monoadducts of *PH* discussed earlier show that besides ring nitrogen, carbonyl oxygen is involved in coordination. The observed red shift in the UV transition bands of these adducts is, therefore, probably due to the more predominant coordination of ring nitrogen compared to carbonyl oxygen. An additional band observed in 320-435 nm region in the spectra of almost all mono as well as di-adducts may be attributed to charge-transfer band.

The values of force constant of ($\text{C} = \text{O}$) and ($\text{M} - \text{O}$) bonds, ionization potential (I. P.) of the ligands, stability constant ($\log K$), free energy change ($-\Delta F^\circ$), have been calculated for the monoadducts (Table 3) using the following equations^{9,10}

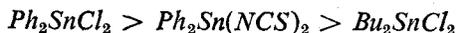
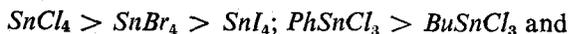
$$\frac{1}{\nu} = \frac{1}{e} \sqrt{\frac{f}{4\pi^2\mu}} \quad \text{where } \mu = \text{reduced mass } \frac{m_A m_B}{m_A + m_B} \quad (1)$$

$$\nu(\text{C} = \text{O}) = 29.20 (\text{I. P.}) + 1409 \quad (2)$$

$$\log K = 1.25 (\text{I. P.}) - 4.2 \quad (3)$$

and $-\Delta F^\circ = RT \ln k \quad (4)$

The values of force constant for *M-O* bond in our monoadducts suggest the following relative acceptor strength of the Lewis acids :



These sequences of relative Lewis acidity of tin (IV) compounds are consistent with the magnitudes of negative shift in $\nu(\text{C} = \text{O})$ in the above adducts and are also in good agreement with those reported in the literature^{25,26}. The I.P., $\log K$ and $-\Delta F^\circ$ values which are reported²⁷ to be inversely proportional to $\nu(\text{C} = \text{O})$ also support the above relative order of acceptor strengths.

As the hydrazide carbonyl group is in direct conjugation with the pyridine ring, the relative donor strength of the three isomeric hydrazides should be in $NH > PH > INH$ order in their monoadducts, based on the σ values at *ortho*, *meta* and *para* positions²⁸ with respect to pyridine nitrogen. However, from the magnitudes of negative shift in $\nu(C=O)$ of the $Sn(IV)$ chloride adducts, we observe the sequence $PH > NH > INH$. In case of monoadducts of NH and INH ring nitrogen is free and hence the observed relative donor strength for them is as expected from the σ values at *meta* and *para* positions. The σ values become identical at the *ortho*, *meta* and *para* positions of pyridine ring when the ring nitrogen gets involved in bonding as in our mono-adducts of PH . This is probably the reason for difference in the observed and expected sequences for the relative donor strength of pyridine carboxylic acid hydrazides.

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