SYNTHETIC AND SPECTROSCOPIC STUDIES OF SOME ORGANOTIN PSEUDOHALIDE 4-PICOLINE COMPLEXES

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ABSTRACT

Trimethyltincyanate and thiocyanate complexes of 4-picoline, the first such stable complexes of 4-picoline reported, have been synthesized and their spectra studied. The products have been obtained through reaction of trimethyltin chloride, 4-picoline and silver pseudohalides. The attempt to substitute the silver pseudohalide salts with alkali metal pseudohalides could not yield the desired 4 - picoline complexes but the corresponding methyltin isocyanate and isothiocyanate salts respectively.

INTRODUCTION

The Chemistry of organotin halides has been extensively studied and severally reported[1-5]. Their substitution reactions with pseudohalogens and carboxylates have also been variously reported[6-9].

The di- and mono-substituted organotin halides and the lower trialkyltin halides have been known to complex with suitable Lewis bases to give adducts[10,11] Generally, di- and mono-organotin halides form 1:2 (Lewis acid: Lewis base) adducts whereas the lower trialkyltin halides form 1:1 adducts. However, it appears that the ability of organotin-pseudohalides to complex with common Lewis bases such as the pyridines has been little reported. The ability of organotin halides to complex with Lewis bases may not be unconnected with the halogen substituent on tin which, being more electronegative than tin, would attract electrons away from the tin centre rendering it slightly positive and therefore easily susceptible to binding with electron donors. Thus, it can be suggested that the ability of the tin centre to bind with a Lewis base is much decided by the ability of the substituent on tin to decongest the tin centre of electrons. How much the pseudohalogens would be able to do this does not appear much known or reported.

Steric factors around the tin centre is another important parameter that could also influence the ablity of tin centre to form an adduct.

The scope of the present work is to study the ability of the trimethyltin-cyanate and -thiocyanate to form isolable adducts with 4-picoline in non-aqueous media.

EXPERIMENTAL

Materials
All reagents were of high purity grade and were used without further purification. The Me_3 SnCl and 4-picoline were obtained from Aldrich.

The solvents were purified according to conventional procedures[12]. Dry acetone was prepared by refluxing the analytical grade acetone with p-toluene sulphonyl chloride (2g/l) for 45 minutes and distilled into a protected stoppered bottle.

Preparation of silver cyanate (and thiocyanate)
Silver nitrate (3.4g, 0.02 mole) was dissolved in 100ml distilled water in a 250ml conical flask. This was added to 100ml aqueous potassium-cyanate (-thiocyanate) (0.019 mole) in a 500ml conical flask covered with aluminium foil and

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mixed. The precipitate was filtered in the dark and dried in an oven at 25°C for 5 hours. The product was stored in vacuo for 24 hours in the dark and about 70 - 75% yield was obtained.

Preparation of trimethyltin cyanate and thiocyanate
Trimethyltin chloride (2.59g, 0.013 mole) dissolved in dichloromethane (50ml) and silver pseudohalide (cyanate and -thiocyanate) (0.014 mole) suspended in dichloromethane were mixed in a 250ml reaction flask. The mixture was stirred magnetically for 24 hours and filtered. The filtrate was evaporated at low pressure to almost total dryness. The concentrated filtrate was stoppered and allowed to stand at room temperature for 48 hours. The resulting mass of solid was recrystallized from acetone for trimethyltincyanate and 50:50 toluene/petroleum spirit (60 - 80°C) for trimethyltin thiocyanate and stored in vacuo for 24 hours. The mass of solid products obtained was 1.81g for the cyanate and 1.78g for the thiocyanate compounds respectively.

Reaction of trimethyltin chloride, 4-picoline and silver cyanate (-thiocyanate)
Trimethyltin chloride (2.59g, 0.013mole) in dichloromethane (50ml) and silver pseudohalide (cyanate or thiocyanate) (0.015 mole) suspension in dichloromethane (25ml) were mixed in a 250ml conical flask. 4-picoline (1.21g, 0.013 mole) in dichloromethane (25ml) was then added. This was stoppered and stirred magnetically for 24 hours. The mixture was filtered and solvent in the filtrate removed at low pressure to almost total dryness. This was stoppered and allowed to stand at 5°C for 48 hours. Yellowish crystals of the cyanate adduct were filtered, washed several times with petroleum spirit (40-60°C) to rmeove the yellowish impurities and dried in vacuo for 24 hours to give a 65% (3.0g) yield. A 72% yield was obtained for the thiocyanate adduct.

Attempts to prepare $Me_3SnOCN.4\text{-}Pic$ and $Me_3SnSCN.4\text{-}Pic$ from NaCN, KOCN and KSCN using dry acetone as solvent was made and isolable products were obtained.

Physical measurement
Melting temperatures are reported uncorrected. I.r. spectra (in Nujol) were run on a Perkin-Elmer RB 3100 i.r. spectrometer and calibrated with polystyrene. The ^1H n.m.r. spectra were run on EM 360L Varian spectrometer with TMS as internal standard.

All i.r. and n.m.r. spectra were run at the Departments of Chemistry, University of Sussex, England and Abubakar Tafawa Belewa University, Bauchi, Nigeria respectively. Microanalyses (C.H.N.) of the complexes were performed at the micro-analytical laboratories of Medac Ltd, Uxbridge and University of Sussex, all in the United Kingdom (U.K.). The Sn content was determined at the analytical laboratories of the Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria.

RESULTS AND DISCUSSION

General properties
The isolated complexes and their parent compounds are white solids, stable under ordinary conditions as shown in Table 1. The melting temperatures are reported uncorrected. Although a variation is observed, there is no clear trend in the relationship between the metling points of the trimethyltin pseudohalides and their 4-picoline complexes. Trimethyltin cyanate-4-picoline complex melts at a lower temperature than the parent trimethyltin cyanate but trimethyltinthiocyanate-4-picoline complex melts at a temperature slightly higher than the parent trimethyltinthiocyanate.

Elemental analysis data agreed sufficiently with the calculated values to suggest the successful formation of the two complexes.

Infrared spectra
The infra red spectra of the complexes hav been studied and characteristic absorption frequencies are summarized in Table 2. The Sn-Me stretch is noted at about 770-790cm^{-1} while the pseudohalides give stretching bands at 2240-2180cm^{-1} for -C≡N, 2250cm^{-1} for -O-C≡N, 2120 cm^{-1} for -S-C≡N and 1360 - 1180cm^{-1} for $-N_3$[13].

Table 1: Physical properties of synthesized compounds

Compound/ Adduct	Physical appearance	Melting point (°C)	Elemental Composition calc. (obs.) C	H	Sn	N
Me_3SnOCN	White	99	-	-	-	-
$Me_3SnOCN.4pic$	White	54	36.16 (36.21)	4.72 (4.78)	39.70 (39.81)	9.31 (9.42)
Me_3SnSCN	White	33				
$Me_3SnOCN.4pic$	Off-white	50	36.32 (36.30)	4.48 (4.52)	37.68 (38.10)	8.89 (8.95)

In addition, where the 4-picoline complex is formed, an aromatic stretch at about 1600cm^{-1} assignable to -C=C- of the pyridine ring is noted. Indeed, the spectra of $Me_3SnOCN.4Pic$ and $Me_3SnSCN.4Pic$ appreciably agreed with the above. The Sn-Me stretch is observed at 780cm^{-1} for both complexes. The -O-C≡N band appeared at 2215cm^{-1} and -S-C≡N band at 2070cm^{-1}. Both complexes have shown strong bands at about 1605cm^{-1} assignable to the pyridyl ring C=C stretch. Although the first Sn-N dative bond could not be observed as it comes well below 300cm^{-1}, the second band at about 1010-1030cm^{-1} conspicuously showed in the spectra of all the complexes formed. In addition, the fact that the pyridyl C=C band was observed at about 1605cm^{-1} as opposed to about 1580cm^{-1} in the free ligand[14] is an evidence for the binding of the nitrogen of pyridine to Sn.

The spectrum of the product of the reaction of NaCN, Me_3SnCl and 4-picoline did not indicate any characteristic band assignable to picoline. The absence of picoline was later confirmed through n.m.r. analysis. The -C≡N band expected at about 2200-2210cm^{-1} appeared at 2060cm^{-1} assignable to isocyanide. This agrees with the general opinion that alkali metal cyanide, cyanate and thiocyanate yield the isopseudohalides when used in reactions like these[2].

If trimethyltin isocyanide was produced, then there would be a negative charge on the carbon to bind, albeit datively, to the tin of another molecule. A five-coordinate tin centre in each molecule results thereby making it rather impossible for the tin to bind to a Lewis base like picoline. The product would be polymeric[6] and rather have high melting point as characterized by our product (1) which melts at 138-140°C with decomposition.

The same argument goes for the product of the reaction of Me_3SnCl, NaN_3 and 4-picoline which also indicated absence of picoline in the complex formed. The band shift from the expected 2160 - 2095cm^{-1} to 2070cm^{-1} strongly suggests the coordination of the terminal nitrogen of the azide to make the central Sn pentacoordinate and, therefore, unable to bind with the picoline.

The failure to obtain the desired product from the reaction of Me_3SnCl, KOCN and 4-picoline and also Me_3SnCl, KSCN and 4-picoline is not easily explainable. For if the "isocyanate" and "isothiocyanate" rather than the 'cyanate' and 'thiocyanate' methyltins are formed, the terminal O and S atoms of the pseudohalogen groups would also datively bind to Sn of another molecule thereby making it rather difficult for the N of the picoline to bind with the Sn centre, if only on the basis of steric factors. The considerable shift noted on the i.r. spectral bands of the "cyanate" and "thiocyanate" from 2200cm^{-1} and 2140cm^{-1} to 2215cm^{-1} and

Table 2: Some characteristic frequencies (cm^{-1}) of the products of trimethyltinpseudohalides-4-picoline

Compound	Sn-Me	C=C (py)	N≡C-O U_{as}	$-N_3$ U_{as}	-C≡N U_{as}	-S-C≡N U_{sym}	-O-C≡N U_{sym}	N≡C-S U_{as}
MeSnCN.4Pic	775s,b	-	-	-	2050vs	-	-	-
$Me_3SnOCN.4Pic$	780s,b	1605m	-	-	-	-	2215s,b	-
$Me_3SnSCN.4Pic$	780s,b	1607s	-	-	-	2070s	-	-
$Me_3SnNCN.4Pic$	780s,b	-	2050w	-	-	-	-	-
$Me_3SnNCS.4Pic$	780s,b	-	-	-	-	-	-	2070s,b
$Me_3SnN_3.4Pic$	770s,b	-	-	2050	-	-	-	-

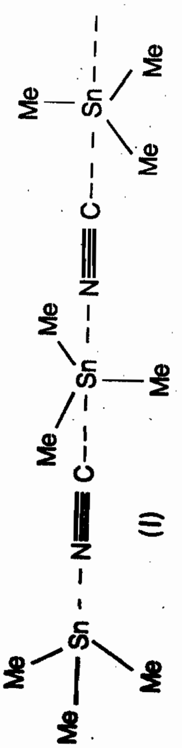

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Table 3: Some characteristic nmr bands (δ in ppm) for trimethyltinpseudohalides and their 4-picoline adducts.

Characteristic protons	Me_3SnCN. 4Pic (in DMSO)	Me_3SnCN (in d-acetone)	Me_3SnCN. 4pic (in $CDCl_3$)	Me_3SnSCN (in $CDCl_3$)	Me_3SnOCN 4pic (in DMSO)	Me_3SnOCN (in d-Acetone)	Me_3SnN_3 4pic (in DMSO)	Me_3SnN_3 (in d-Acetone)	Me_3SnNCO.4pic (in DMSO)	$N(C_5H_4)CH_3$
$Sn\text{-}CH_3$	0.53Svs	0.4Mm	0.58Svs	0.63Svs	0.42Svs	0.50Ss	0.52Ss	0.53Ss	0.56S	-
$\text{-}CH_3$	-	-	2.37Ss	-	2.35Ss	-	-	-	2.46Sw	2.0Ss
Pyridyl-m-H	-	-	7.23Dm	-	7.10Dm	-	-	-	-	6.7 - 6.9Dvs
Pyridyl-o-H	-	-	8.23Dm	-	8.20Dm	-	-	-	-	8.3 - 8.5Dvs

Ss = Singlet, strong; Sm = Singlet, medium; Sw = Singlet, weak; Svs = Singlet, very strong; D = Duplet; T = Triplet; q = quartet; Sh = Shoulder; Mm = multiplet, medium.

2070cm^{-1} respectively rather strongly suggests the formation of the isocyanate and isothiocyanate compounds.

Nuclear magnetic resonance spectra

The $Sn\text{-}CH_3$ protons are reported[14, 15] to appear within 0.0 - 1.0ppm; the CH_3- group of picoline molecule at about 2.40ppm, and the pyridyl-ortho-hydrogens at about 8.50ppm. The $Sn\text{-}CH_3$ protons appear as singlet, the CH_3 protons of picoline as singlet while the ortho and meta hydrogens appear as quadruplets. All these signals have been observed in the spectra of Me_3SnOCN.4-Pic and Me_3SnSCN.4 Pic complexes (Table 3). However, the products of the reaction of M_3SnCl with NaCN and 4-picoline did not show any signals assignable to 4-picoline, the reasons having been suggested earlier.

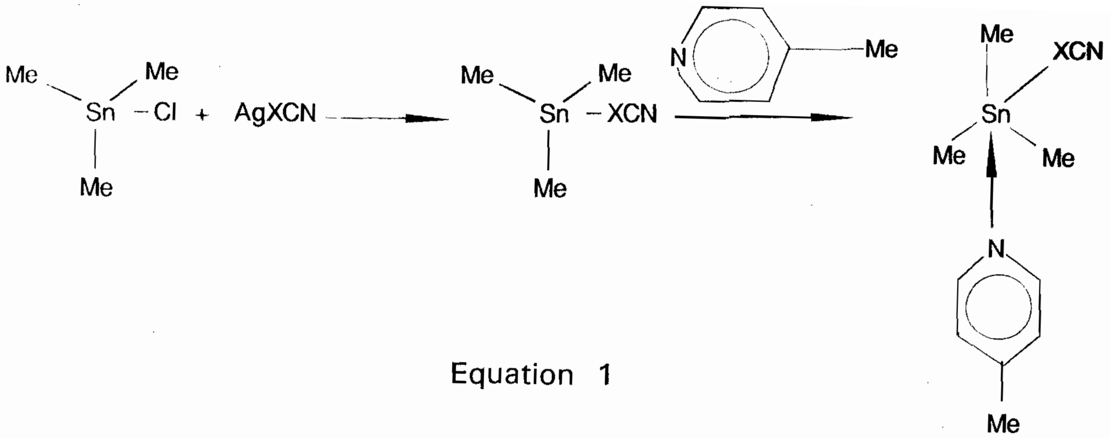
Deductions from the elemental, spectral and other analyses

The various analytical methods used in this work have indeed shown that trimethyltin pseudohalides do form adducts with the pyridines, the process being through a simple substitution reaction as shown in equation 1, where X = O or S.

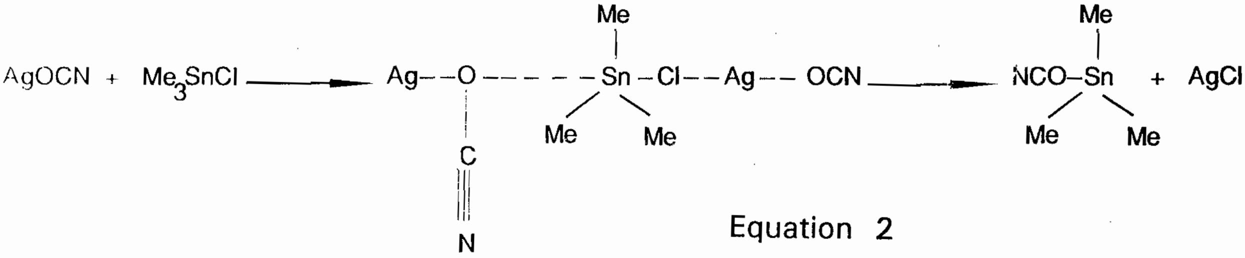
The alkali metal or silver assists in the removal of the chloride on the tin and replacing it with the rather less nucleophilic pseudohalide radical. For instance, the K-OCN bond is more polar and, therefore, ionizes more easily than Ag-OCN which requires the Cl to pull the Ag for easier ionization, as shown in equation 2. For alkali metal pseudohalides, equation 3 is suggested.

CONCLUSION

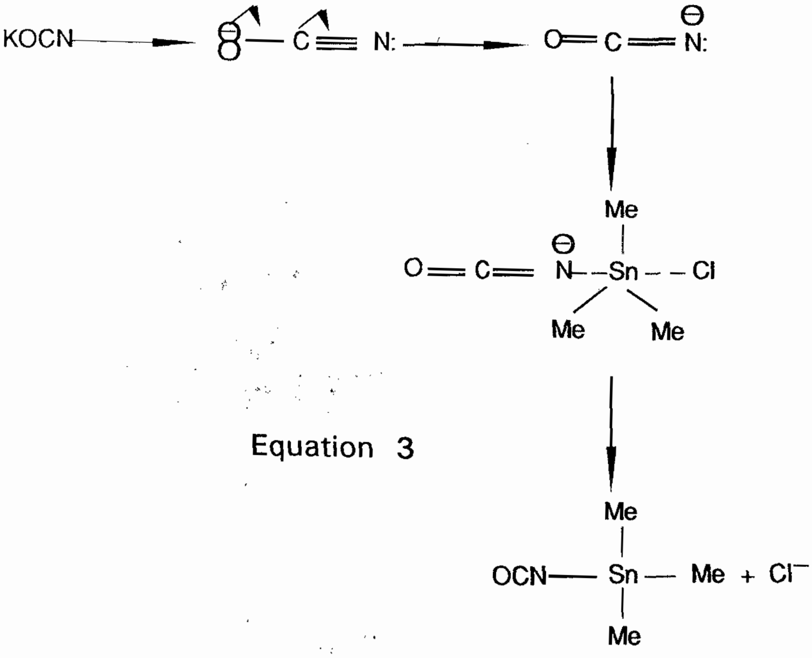
This work has revealed that when silver pseudohalides, or at least silver-cyanate and -thiocyanate, are used, the required organotin pseudohalide-4-picoline complexes are obtained. However, where alkali metal pseudohalides are used, the organotin pseudohalide pyridine complexes are not obtained.



Equation 1



Equation 2



Equation 3

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