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EVIDENCE FOR THE FORMATION OF APPARENT FIVE-COORDINATED TIN(IV) β-DIKETONATE COMPLEXES: THE SYNTHESIS AND CHARACTERISATION OF THE PYRIDINE ADDUCT OF n-BUTYLDICHLORO-(2,4-PENTANEDIONATO)TIN(IV)

DAVID W. THOMPSON*
Department of Chemistry, College of William and Mary, Williamsburg, Virginia 23185 (*U.S.A.*)
and JOHN F. LEFELHOCZ
Department of Chemistry, Virginia Commonwealth University, Richmond, Virginia 23220 (*U.S.A.*)
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SUMMARY

Reaction of n-butyltrichlorostannane with 2,4-pentanedione in the presence of pyridine leads to the isolation of a complex which can be described as the pyridine adduct of n-butyldichloro(2,4-pentanedionato)tin(IV).

INTRODUCTION

Recently, we have reported on the reaction of the tin tetrahalides with 2,4-pentanedione in the presence of pyridine[1]. The goal of that research was to prepare mono-substituted 2,4-pentanedionate–tin(IV) complexes whose stoichiometry would be consistent with five-coordination, *e.g.* trichloro(2,4-pentanedionato)tin(IV), although the complexes might well be dimeric (*i.e.* six-coordinate) with either halogen or oxygen bridges.

Prior to initiating the above study no firm evidence for the existence of trihalo-(β-diketonato)tin(IV) complexes had been reported. In fact to the contrary it has been reported that even when tin tetrachloride and 2,4-pentanedione were allowed to react at reflux in molar ratios up to 5/1, respectively, in carbon tetrachloride, only the well-characterized *cis*-dichlorobis(2,4-pentanedionato)tin(IV) was isolated[2,3]. Additionally, allowing tin tetrachloride and 2,4-pentanedione to react in a 5/1 molar ratio at room temperature or reflux in methylene chloride led only to the Lewis acid–base adduct formed between tin tetrachloride and the keto tautomer of 2,4-pentanedione[3].

In a further attempt to effect the formation of trichloro(2,4-pentanedionato)-tin(IV), we thought it worthwhile to add pyridine to the tin tetrachloride-2,4-pentanedione adduct in order to remove only one equivalent of hydrogen chloride as pyridinium chloride. Indeed, with the inclusion of pyridine, a mono-substituted 2,4-pentanedionato–tin(IV) complex was isolated; however, the complex did not contain apparent or real five-coordinated tin but hexa-coordinated tin as pyridinium tetra-

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* Address correspondence to this author.

chloro(2,4-pentanedionato)stannate(IV), $[C_5H_5NH][Cl_4Sn(C_5H_7O_2)]$. Coordination of the keto tautomer with the acidic (Lewis) tin tetrachloride enhances the acidity of the enolizable proton such that it can be transferred to pyridine which in the absence of a perturbing Lewis acid is a weaker base than the 2,4-pentanedionate anion. Apparently, the overall thermodynamics in methylene chloride of coordination of a chloride ion to trichloro(2,4-pentanedionato)tin(IV) and the formation of the insoluble salt-like $[C_5H_5NH][Cl_4Sn(C_5H_7O_2)]$ is more favorable than the formation of pyridinium chloride and a tin(IV) complex with the $Cl_3Sn(C_5H_7O_2)$ stoichiometry. However, it seems reasonable to think of the chloride ion as having stabilized as an adduct the apparent five-coordinated tin(IV) complex. (Tin tetrabromide and tin tetraiodide behave similarly.)

It is reasonable to postulate that a trihalo(2,4-pentanedionato)tin(IV) species is formed as an intermediate product en route to the well-known and well-characterized dihalobis(2,4-pentanedionato)tin(IV) complexes which are formed from reaction of a tin tetrahalide and 2,4-pentanedione at reflux in carbon tetrachloride, benzene, and other similar solvents. The disubstituted product can be formed then in one of two (or both) ways from the trihalo intermediate. First, the trihalo species may react directly with a second molecule of 2,4-pentanedione with subsequent loss of hydrogen halide and formation of the disubstituted product. Second, the trihalo-(2,4-pentanedionato)tin(IV) species may react with a second trihalo complex (or in a dimer, may react within itself, *i.e.* disproportionate) to give the disubstituted derivative

$$(X_3SnL)_2 \text{ or } 2\,X_3SnL \rightleftarrows X_2SnL_2 + SnX_4 \qquad (1)$$

plus tin tetrahalide [eqn. (1)]. The regenerated tin tetrahalide may then react with another molecule of 2,4-pentanedione to give another monosubstituted species which can sustain the product-forming reaction.

The reasonableness of a trihalo(monosubstituted) intermediate in the tin tetrahalide/β-diketone systems is substantiated by work in the analogous titanium tetrachloride/2,4-pentanedione system. Here a crystalline well-defined complex of stoichiometry $Cl_3Ti(C_5H_7O_2)$ can be isolated by reaction of the two components in a 1/1 molar ratio, respectively[4]; a 1/2 molar ratio yields the disubstituted product[5]. Trichloro(2,4-pentanedionato)titanium(IV) has been shown from X-ray analysis to be dimeric in the solid state[6]. It has also been shown[7] that complexes of the type X_3TiL (X = halogen and L = β-diketonate anion) do disproportionate in solution according to eqn. (2):

$$(X_3TiL)_2 \text{ or } 2X_3TiL \rightleftarrows X_2TiL_2 + TiX_4 \qquad (2)$$

This latter observation especially lends plausibility to the suggestion that the dihalo-(2,4-pentanedionato)tin(IV) complexes are formed from the inter- or intramolecular reaction of the monosubstituted complexes.

Having completed a study of the tin tetrahalide/2,4-pentanedione/pyridine systems, it was decided to examine in the behavior of the n-butyltrichlorostannane/2,4-pentanedione/pyridine system. Herein we report the results of this investigation which led to the unexpected trapping of another apparent five-coordinate monosubstituted tin(IV)-β-diketonate complex.

EXPERIMENTAL

Preparation of n-butyldichloro(2,4-pentanedionato)pyridinetin(IV)

n-Butyltrichlorostannane (3.0 ml, 1.8×10^{-2} mol) was dissolved in 25 ml of methylene chloride in a 100 ml round bottom flask equipped with a dropping funnel and nitrogen inlet. 2,4-Pentanedione (2.0 ml, 2.0×10^{-2} mol) and pyridine (1.6 ml, 2.0×10^{-2} mol or 3.2 ml, 4.0×10^{-2} mol) were dissolved together in 15 ml of methylene chloride, and the resulting solution was added dropwise at room temperature. A white precipitate formed. Hexane (25 ml) was added to the reaction mixture and the solid (I) filtered. Solvent was removed from the filtrate under reduced pressure at room temperature and an oil remained which solidified on standing overnight. After triturating the solid in hexane, a white product (II) was isolated. Product (II) is readily recrystallized to give large colorless crystals from a methylene chloride/hexane mixture. All synthetic manipulations were performed under nitrogen in Schlenk-type glassware. All solvents were purified and dried by distillation from suitable dehydrating agents. The title complex is not sensitive to atmospheric moisture.

Product (I). M.p. ca. 140° (Found: Cl, 31.8. C_5H_6NCl calcd.: Cl, 30.8%.) The infrared spectrum is similar to that reported for pyridinium chloride[8].

Product (II) (title compound). M.p. 143–146°. [Found: C, 39.48; H, 5.11; Cl, 16.5. $(C_4H_9)Cl_2(C_5H_5N)Sn(C_5H_7O_2)$ calcd.: C, 39.57; H, 4.98; Cl, 16.8%.] Molar conductivity, Λ_M: 0.13 $cm^2 \cdot ohm^{-1} \cdot mol^{-1}$ at 2.6×10^{-2} M in nitrobenzene.

Conductance measurements

An Industrial Instruments Model RC-18 conductivity bridge operating at 1000 Hz was used for all measurements which were made in nitrobenzene at room temperature using a Freas-type cell (cell constant 0.17 cm^{-1}) with bright platinum electrodes.

Melting points

Melting points were measured in sealed capillaries with a Thomas–Hoover apparatus and are uncorrected.

Spectral data

Proton NMR spectra were run on a Perkin–Elmer R-20B spectrometer. Infrared spectra were taken with a Perkin–Elmer 457 spectrophotometer. Mössbauer spectra were obtained with a constant acceleration velocity drive system similar to that developed at the National Bureau of Standards (U.S.)[9]. Velocity calibration of the instrument was accomplished with an iron source of Co^{57} diffused into a chromium matrix and absorbers of iron foil and sodium nitroprusside. A $BaSnO_3/^{119m}Sn$ source at room temperature with a palladium filter was used to obtain spectra of the samples which were held at the liquid nitrogen temperature. The tin isomer shifts were reported with respect to the centroid of the $BaSnO_3$ spectrum.

RESULTS AND DISCUSSION

n-Butyldichloro(2,4-pentanedionato)tin(IV) can be isolated in good yield as the pyridine adduct from the reaction of n-butyltrichlorostannane, 2,4-pentanedione, and pyridine in methylene chloride at room temperature in molar ratios of 1/1/1 or 1/1/2, respectively. The hydrogen chloride evolved in the substitution process is separated from n-butyldichloro(2,4-pentanedionato)pyridinetin(IV) as pyridinium chloride. This synthetic result was contrary to expectations. Having isolated the series of pyridinium tetrahalo(2,4-pentanedionato)stannate(IV) salts from the tin tetrahalide/2,4-pentanedione/pyridine systems[1], it was anticipated that n-butyltrichlorostannane in combination with 2,4-pentanedione and pyridine would yield the analogous pyridinium n-butyltrichloro(2,4-pentanedionato)stannate(IV) salt.

The IR spectrum of n-butyldichloro(2,4-pentanedionato)pyridinetin(IV) shows two strong bands at ca. 1525 and 1570 cm^{-1}. These bands are consistent with the presence of an oxygen-chelated 2,4-pentanedionate ligand. Several additional bands are readily identifiable with a chelated β-diketonate ligand*. Comparatively, dimethylbis(2,4-pentanedionato)tin(IV) exhibits two strong bands in the 1500–1600 cm^{-1} region at ca. 1515 and 1565 cm^{-1}[11].

The absence of several prominent bands in the 3000–3300 cm^{-1} region eliminates the possibility of the product containing pyridinium ion. However, the strong sharp band at ca. 1600 cm^{-1} is assignable to a ring vibration of neutral pyridine molecules coordinated to a metal center. Pyridine itself has a strong band near 1590 cm^{-1}[8].

The NMR spectrum of n-butyldichloro(2,4-pentanedionato)pyridinetin(IV) in chloroform-*d* at 34° displays peaks at -2.02 and -5.56 ppm relative to TMS with an intensity ratio ca. 6/1. These observed resonances are consistent with a coordinated 2,4-pentanedionate anion. Additionally, complex patterns observed at low and high fields (ca. $\tau \approx 3$ and $\tau \approx 8$–9.5 ppm) are consistent with the presence of coordinated pyridine and an n-butyl group. The IR spectrum of the complex in chloroform is similar to the solid state (mull) spectrum indicating that the complex remains essentially intact in solution; no evidence of free 2,4-pentanedione or pyridine was observed. Di-n-butyl- and dichlorobis(2,4-pentanedionato)tin(IV) have 2,4-pentanedionate methyl and vinyl resonance peaks at -1.97 and -5.30 and -2.15 (average) and -5.69 ppm (relative to TMS), respectively[12,13]. Since the resonance positions of the 2,4-pentanedionato ligands can be interpreted to a significant extent in terms of inductive effects of the ligands[14–16], it is expected that replacement of ligands with chlorine, nitrogen or oxygen donor atoms with an alkyl group would shift the resonances to higher fields. Indeed, as just cited this is what is observed with the dibutyl- and dichlorobis(2,4-pentanedionato)tin(IV) complexes. This effect can also be seen in the series of dimethyl-[11,12], chloromethyl-[17] and dichlorobis(2,4-pentanedionato)-tin(IV)[13] complexes which exhibit ring proton shifts (relative to TMS) of -5.30, ca. -5.5, and -5.69 ppm. If the inductive differences among chlorine, nitrogen, and oxygen donors of the types involved in the title complex are small with respect to the difference between any of these donors and an alkyl group, then substitution of an n-butyl group in the pseudo-octahedral coordination sphere should place the 2,4-pentanedionate methyl and ring proton resonances between the corresponding positions in di-n-butyl- and dichlorobis(2,4-pentanedionato)tin(IV). It is evident that this is the case.

The Mössbauer spectrum of n-butyldichloro(2,4-pentanedionato)pyridinetin-

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* The IR spectrum of the title compound is available on request, see ref. 10.

(IV) displays an isomer shift of 0.92 $\text{mm} \cdot \text{sec}^{-1}$ and exhibits quadrupole splitting (1.76 $\text{mm} \cdot \text{sec}^{-1}$). The observation of substantial quadrupole splitting is firm evidence for the presence of a tin–alkyl linkage. Noncubic arrangements of nitrogen, oxygen, and chlorine donor ligands do not give resolvable quadrupole splittings*,[18]. Apparently, the electronic difference among these elements is not substantial enough to provide a field-gradient sufficient to give splitting. However, replacement of electronegative donor atoms with alkyl groups does result in measurable splitting. The magnitude of the quadrupole splitting for n-butyldichloro(2,4-pentanedionato)pyridinetin(IV) compares closely with that reported for other hexa-coordinated n-butyltin complexes. For example, for the series of complexes of the type n-$C_4H_9SnCl_3L$, L = 2-pyridine, *o*-phenanthroline, and bipyridyl, the quadrupole splittings are 1.86, 1.60, and 1.62 $\text{mm} \cdot \text{sec}^{-1}$, respectively[19]. The quadrupole splittings for the hexa-coordinated complexes $[(\text{n-}C_4H_9)SnCl_2 \cdot \text{Terpy}]ClO_4$, $[(C_2H_5)_4N]_2[(\text{n-}C_4H_9)SnCl_5]$, $[(C_2H_5)_4N]_2[\text{n-}C_4H_9SnCl_3Br_2]$, and $[C_5H_6N]_2[C_6H_5SnCl_5]$ are 1.74, 1.86, 1.85, and 1.92 $\text{mm} \cdot \text{sec}^{-1}$, respectively[19]. The relatively narrow range of quadrupole splitting values for pseudo-octahedrally coordinated tin containing a single n-butyl group and varying combinations of halogen and nitrogen donors supports the view that the organic group is the dominant factor in controlling the magnitude of the splitting.

A plausible reaction pathway to the title compound is illustrated in the first portion of Fig. 1. Initially n-butyltrichlorostannane interacts with 2,4-pentanedione to inductively enhance the acidity of the enolizable proton such that it can transfer to pyridine with formation of intermediate (I). As mentioned previously, this type of intermediate has been isolated in the tin tetrachloride/2,4-pentanedione/pyridine system. The n-butyltrichloro(2,4-pentanedionato)stannate(IV) ion then reacts with pyridine most probably by a dissociative mechanism (*i.e.* expulsion of chloride ion) which is enhanced by the formation of insoluble pyridinium chloride. The apparent five-coordinated n-butyldichloro(2,4-pentanedionato)tin(IV) then reacts with pyridine to form the six-coordinated adduct. The fact that a similar reaction does not occur with the isolable pyridinium tetrachloro(2,4-pentanedionato)stannate(IV) may be ex-

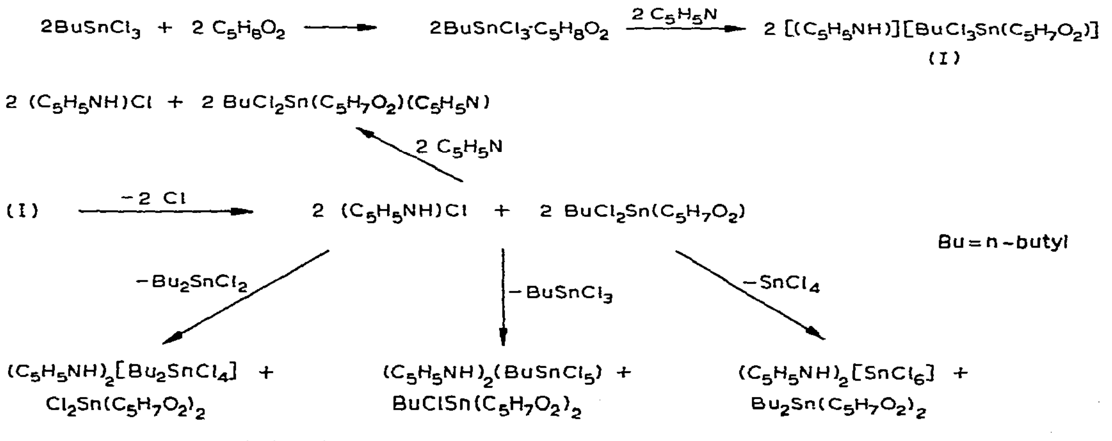

Fig. 1. Reaction possibilities in the n-butyltrichlorostannane/2,4-pentanedione/pyridine system.

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* A copy of the Mössbauer spectrum is available from the authors on request.

plained in part by the greater electron withdrawing ability of the chloride ion relative to an n-butyl group. This makes it much more difficult for a chloride ion to dissociate to form the apparent five-coordinated intermediate. The equilibrium (3) lies to the left

$$(C_5H_5N_4)[Cl_4Sn(C_5H_7O_2)] \rightleftarrows C_5H_5NHCl + Cl_3Sn(C_5H_7O_2) \qquad (3)$$

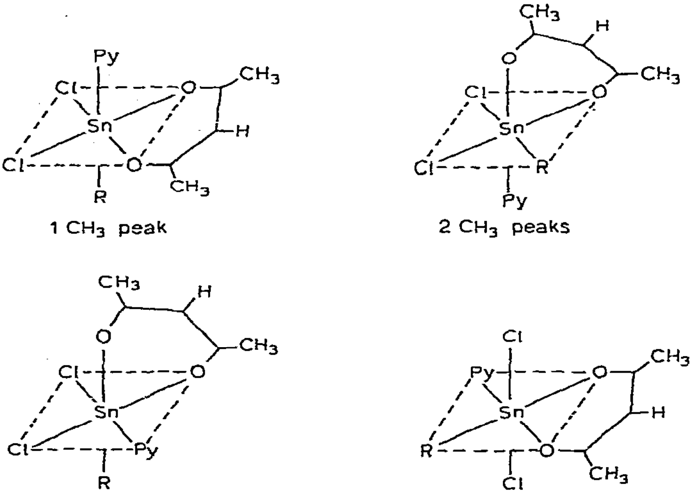
to such an extent that the equilibrium concentration of $(C_5H_5NH)[Cl_4Sn(C_5H_7O_2)]$ exceeds its solubility; hence, only the salt-like product is isolated.

It is of interest to note that no disubstituted products such as $Bu_2Sn(C_5H_7O_2)_2$, $BuClSn(C_5H_7O_2)_2$, or $Cl_2Sn(C_5H_7O_2)_2$ are isolated. These disubstituted complexes may be formed from a disproportionation of the apparent five-coordinated n-butyldichloro(2,4-pentanedionato)tin(IV) intermediate as illustrated in Fig. 1. Indeed, disproportionation reactions of the type suggested have been established in titanium(IV)/β-diketonate systems[7].

n-Butyldichloro(2,4-pentanedionato)pyridinetin(IV) may exist as one or more of four possible geometric isomeric structures. Three have the chlorine atoms *cis* to one another; the fourth has the chlorine atoms *trans* with respect to each other. These isomeric possibilities are illustrated in Fig. 2.

Assuming no accidental degeneracy and that exchange between non-equivalent groups is slow relative to the time scale of the NMR experiment, seven 2,4-pentanedionate methyl resonance peaks and four ring proton peaks are expected if all isomers are present.

At 34° a single 2,4-pentanedionate methyl resonance peak and one prominent ring proton peak* are observed. However, as the temperature is lowered both the me-



1 CH_3 peak

2 CH_3 peaks

2 CH_3 peaks

2 CH_3 peaks

Fig. 2. Possible geometric isomers for n-butyldichloro(2,4-pentanedionato)pyridinetin(IV) and methyl proton resonances expected at slow exchange.

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* A small peak is observed on the high-field side of the main =CH– resonance at 34°. This peak persists at low temperatures. The chemical shift agrees with that for free 2,4-pentanedione (enol), however, none of the peaks visible in the methyl region coincide with free 2,4-pentanedione as determined from a 1/1 mixture of the title complex and 2,4-pentanedione in chloroform down to –40°. Furthermore, as mentioned, the IR spectrum in chloroform gives no indication of free 2,4-pentanedione.

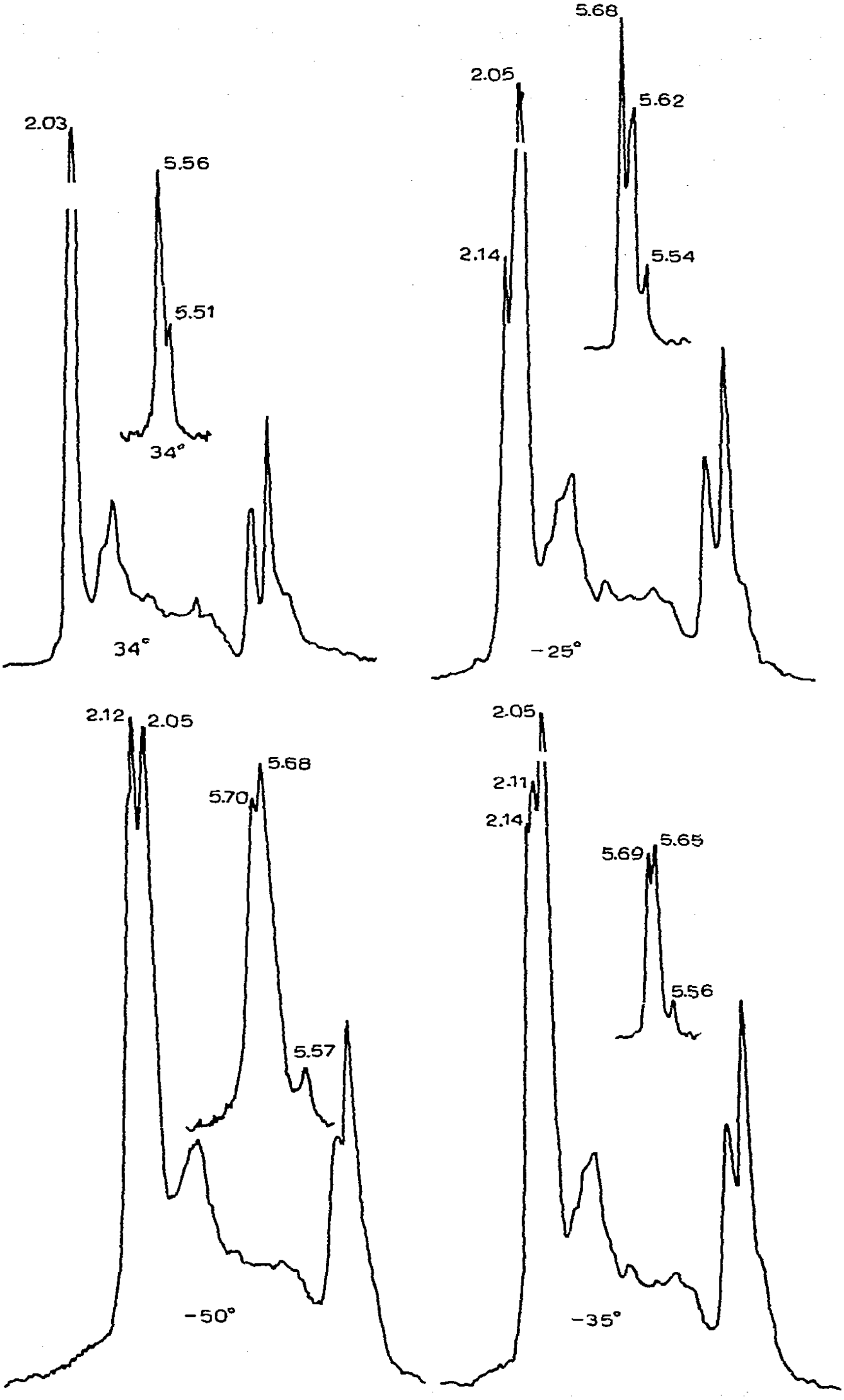

Fig. 3. Variable temperature proton spectra for n-butyldichloro(2,4-pentanedionato)pyridinetin(IV). Lower traces display a region ca. 0.5–2.5 ppm downfield from TMS; upper traces display the =CH–region ca. 5.5 ppm downfield from TMS. Solvent is chloroform.

thyl and ring peaks broaden and finally exhibit splittings as illustrated in Fig. 3. One can identify with confidence at least three 2,4-pentanedionate methyl peaks and two ring peaks. Other peaks may be present but not observable due to lack of resolution and/or accidental chemical shift degeneracies. The pyridine region of the spectrum also shows a pronounced temperature dependence. At 34° several broad resonance peaks are observed; at low temperature (−50°) several resonance peaks are observed relative to free pyridine which appears consistent with the presence of at least two pyridine environments (see Fig. 4). Chemical shift measurements exclude the possibility that any of the low temperature peaks are due to uncoordinated pyridine.

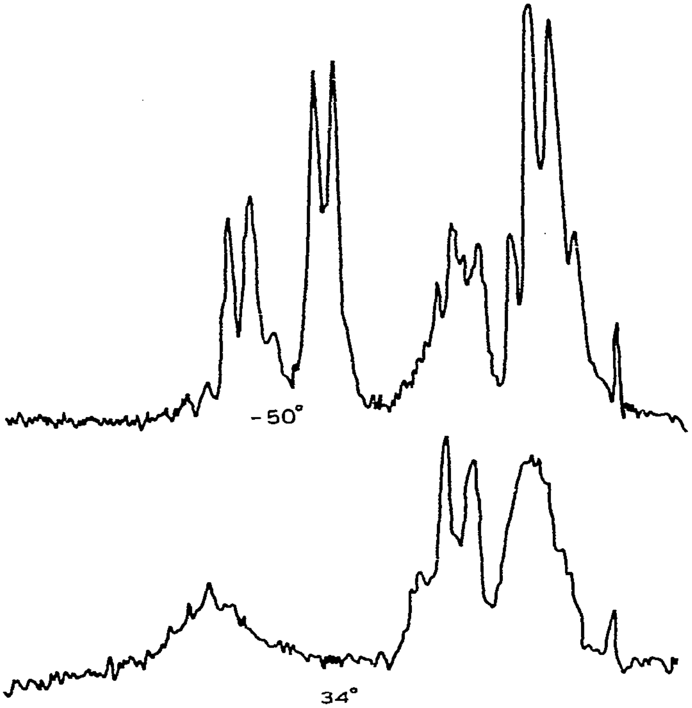

Fig. 4. Variable temperature proton NMR spectra for the pyridine region in n-butylchloro(2,4-pentanedionato)pyridinetin(IV). Solvent is chloroform.

Since it has been observed that $Cl_3Ti(Bzac)$ (Bzac = 1-phenyl-1,3-butanedionate anion) disproportionates to a disubstituted product[7], it is conceivable that the title complex in solution might react in one of the following ways:

$$2\,BuCl_2(Py)Sn(C_5H_7O_2) \rightleftarrows Bu_2Sn(C_5H_7O_2)_2 + SnCl_4\cdot 2Py \quad (4)$$

$$2\,BuCl_2(Py)Sn(C_5H_7O_2) \rightleftarrows Cl_2Sn(C_5H_7O_2)_2 + Bu_2Cl_2Sn\cdot 2Py \quad (5)$$

$$2\,BuCl_2(Py)Sn(C_5H_7O_2) \rightleftarrows BuClSn(C_5H_7O_2)_2 + BuCl_3Sn\cdot 2Py \quad (6)$$

Chemical shift data eliminate the possibility for any significant concentration of dichloro- or di-n-butylbis(2,4-pentanedionato)tin(IV) (see previous discussion of NMR spectra). Although observed chemical shifts are in the region expected for $BuClSn(C_5$-

$H_7O_2)_2$, the presence of this complex can be excluded on other grounds. First, since phenyl- and methylchlorobis(2,4-pentanedionato)tin(IV) and methyl- and ethylbromobis(2,4-pentanedionato)tin(IV)[17,20] adopt the *cis* configuration in solution, it seems probable that $BuClSn(C_5H_7O_2)_2$ would have the *cis* configuration. If this were the case, one would expect four 2,4-pentanedionate methyl peaks of equal intensity and two ring proton resonance peaks of equal intensity at slow exchange. Indeed, these patterns have been observed for the phenyl- and methylchloro complexes. [A similar pattern has also been observed for phenylchlorobis(2,4-pentanedionato)-germanium(IV)[21].] The intensity patterns for the title compound do not resemble those observed for the above *cis* complexes in either the methyl or ring proton region. Second, the title complex can be recovered in pure from (identical m.p.) as large crystals by slow evaporation of solvent from the NMR tube. Lastly, as mentioned previously the IR spectrum in chloroform is very similar to the solid state (mull) spectrum in all regions of comparison.

In summary, all the data presented are consistent with the tin-containing product from the reaction of n-butyltrichlorostannane, 2,4-pentanedione, and pyridine being the monomeric and non-ionic n-butyldichloro(2,4-pentanedionato)pyridine-tin(IV) which in solution exists as a mixture of at least two geometric isomers.

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