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EVIDENCE FOR *cis*-BIS(2,4-PENTANEDIONATO)DIMETHYLTIN(IV) IN SOLUTION: A SPECTROSCOPIC STUDY

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Summary

Infrared spectra of bis(2,4-pentanedionato)dimethyltin(IV), bis(tropolonato)dimethyltin(IV), bis(8-quinolinolato)dimethyltin(IV) and their deuteriomethyl analogs have been obtained in carbon disulfide solution. As expected for a *cis* structure the oxinate shows two peaks at 517 and 529 cm^{-1} assignable to the symmetrical and antisymmetrical $(CH_3)_2Sn$ skeletal stretching vibrations, which shift about 50 cm^{-1} to lower energies for the deuteriomethyl derivative. Solutions of the corresponding tropolonates and acetylacetonates have been shown to possess corresponding peaks which shift in similar fashion. This indicates very strongly that a substantial amount of *cis*-bis(2,4-pentanedionato)dimethyltin(IV) is present in carbon disulfide solutions. However, the dimethyltin acetylacetonate spectra in contrast with the other spectra include a third stronger peak at 578 cm^{-1} which also shifts 50 cm^{-1} upon deuteration. Since the peak is best assignable to the antisymmetrical stretching vibration of a linear $(CH_3)_2Sn$ moiety it is concluded that the dimethyltin acetylacetonate solutions are mixtures of *cis* and *trans* isomers.

Introduction

The structures of six-coordinate organotin chelate compounds of the type R_2SnCh_2 (Ch = chelate) have remained of considerable interest since they were first prepared. If the bidentate ligand, Ch$^-$, has C_{2v} symmetry there will be only two likely structural possibilities, one, *trans* with a linear R_2Sn moiety (Fig. 1) and the other, *cis*, with the R_2Sn group substantially bent (Fig. 2). If the ligand is of lower symmetry, two *trans*- and three *cis*-type isomers are possible.

For some time it has been apparent that bis(8-quinolinolato)dimethyltin(IV), $(CH_3)_2Sn(Ox)_2$, possesses a *cis*-type structure [1]. Likewise bis(2,4-pentanedio-

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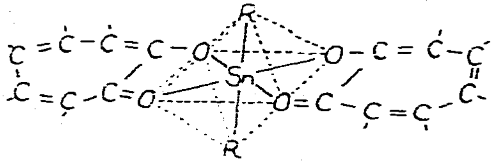

Fig. 1. The *trans* structure.

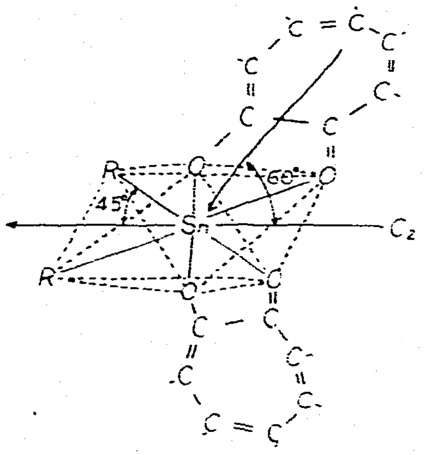

Fig. 2. The C_2 *cis* structure.

nato)dichlorotin(IV), $Cl_2Sn(acac)_2$, and bis(2,4-pentanedionato)diphenyltin(IV), $Ph_2Sn(acac)_2$, adopt the *cis* configuration [2—5]. Evidence [6] for *cis*-bis(tropolonato)dimethyltin(IV), $(CH_3)_2Sn(trop)_2$, is also quite strong.

In contrast $(CH_3)_2Sn(acac)_2$ in the solid state in undoubtedly *trans*. X-ray crystal studies [7], Mössbauer [8], infrared and Raman [9,10] results all are consistent with that assignment.

Yet, the solution structure of $(CH_3)_2Sn(acac)_2$ has remained controversial. Elaborate Raman studies [11,12] strongly favor a *trans* assignment in solution as do NMR coupling constant results [9]. However, an observed dipole moment [3] of 2.95 Debye in benzene is good evidence for the presence, if not predominance, of a *cis*-type structure. Supportive dielectric loss studies [13] definitely show that a substantial portion of the dipole moment is due to orientation polarization.

In brief, there is good evidence for the presence of both *cis*- and *trans*-$(CH_3)_2$-$Sn(acac)_2$ structures in solution. It might be expected that a problem of this type should be resolvable by variable temperature NMR techniques. There has been little success by such means to date though because of the very rapid rates of ligand exchange [14] or rearrangement exhibited in solution. It appears that only techniques capable of measuring phenomena with very short relaxation times will be of any use in solving this structural problem.

In this study infrared solution spectra have been recorded for a number of complexes. The observation of the $(CH_3)_2Sn$ symmetrical stretching vibration, properly verified, must conclusively demonstrate the presence of the *cis* structure. Likewise, as observed for the solid state, absence of the symmetrical stretch in the infrared combined with its presence in the Raman spectra will strongly indicate the presence of a *trans*-type structure.

Because of the presence of several ligand bands in the region of interest, 400—600 cm^{-1}, which in some instances partially or completely overlap $(CH_3)_2$-Sn bands, it was believed necessary to prepare $(CD_3)_2Sn(acac)_2$, $(CD_3)_2Sn(trop)_2$ and $(CD_3)_2Sn(Ox)_2$ and determine their infrared spectra also in order to make assignments with confidence. This paper reports the synthesis of these compounds as well as their infrared spectra. Appropriate structural assignments have been made.

Experimental

Reagents. All solvents obtained for synthesis were of reagent grade and have been used without further purification. Deuteriomethyl iodide was obtained from K & K Fine Chemicals and used directly. Tin metal was 30 mesh and of analytical grade from Mallinckrodt Chemical Works. A.R. grade acetylacetone was obtained from the same source. Spectrophotometric grade carbon disulfide used unmodified for infrared spectra and tropolone used for synthesis were purchased from Aldrich Chemical Company. The tropolone was recrystallized once from ethanol before use. The other ligands, 1,3-diphenylpropanedione and 8-quinolinol were obtained from Eastman Chemical Company and were used without modification. The melting points or boiling points of all reagents were routinely checked against literature values and materials were used without further purification only if values were found to be in close agreement.

Infrared spectra. All solution spectra were obtained at 25°C using a Perkin—Elmer Model 457A spectrometer. Carbon disulfide solutions were approximately 0.01 *M*.

Synthesis of complexes. The four deuteriomethyl complexes were synthesised in similar fashion. Stoichiometric amounts (1 : 2) of $(CD_3)_2SnO$ and ligand were placed in 125 ml of benzene and refluxed for 10 hours. Typically, about 1 gram of 85% pure $(CD_3)_2SnO$ and corresponding amounts of ligand were refluxed. Water formed was collected azeotropically in a Barrett distilling receiver. Crystals were collected after flash evaporation and purified by dissolving them in a minimum amount of hot benzene followed by addition of cyclohexane until turbidity appeared. After standing overnight at 0°C the pure crystals were collected on a glass filter and dried at room temperature for 12 hours under vacuum. Yields ranged between 50 and 70 percent. Melting points listed in Table 1 are very close to those reported earlier [3,6] for normal methyl derivatives.

Synthesis of $(CD_3)_2SnO$. Tin metal (4.07 g, 0.0342 mol) and deuteriomethyl

TABLE 1

RESULTS OF CHEMICAL ANALYSIS

Compound	Analysis found (calcd.) (%)			
	H + D	C	N	M.p. (°C)
$(CD_3)_2Sn(acac)_2$	7.56	40.96		178—180
	(7.40)	(40.83)		
$(CD_3)_2Sn(dbzm)_2$	5.77	63.80		186—188
	(5.68)	(63.92)		
$(CD_3)_2Sn(Ox)_2$	5.28	54.40	6.39	232—235
	(5.45)	(54.22)	(6.32)	
$(CD_3)_2Sn(trop)_2$	5.39	49.78		179—181
	(5.57)	(48.41)		

iodide (10.0 g, 0.0685 mol) were placed in a 15 cm long × 1.2 cm o.d. glass tube. The tube and contents were placed in an ice bath and the neck of the tube was sealed with an oxygen torch. The sealed tube was then immersed in an oil bath and heated to 150°C for 30 hours. The cooled contents were then removed and dissolved in 20 ml of water. After filtration to remove unreacted tin, the the solution was made 6 *M* in NH_3. The white fluffy precipitate which came down immediately was filtered after standing for 30 minutes, and was washed with ethanol and dried at 100°C. Yield was 3.76 g of impure products, judged from carbon, hydrogen analysis to contain 85% $(CD_3)_2SnO$. Because of small quantities available no attempt was made to purify this material. IR spectra could be interpreted as resulting from a $(CD_3)_2SnO$, SnO_2 mixture. Presence of SnO_2 did not interfere with the synthesis of the complexes.

Results

Carbon disulfide solution spectra of $(CH_3)_2Sn(acac)_2$, $(CH_3)_2Sn(Ox)_2$, $(CH_3)_2$-$Sn(trop)_2$ and their deuteriomethyl analogs are shown in Fig. 3. Only the region between 400—600 cm^{-1} has been included since it is well-established by measurement and calculation that the skeletal $(CH_3)_2Sn$ vibrations lie within that range.

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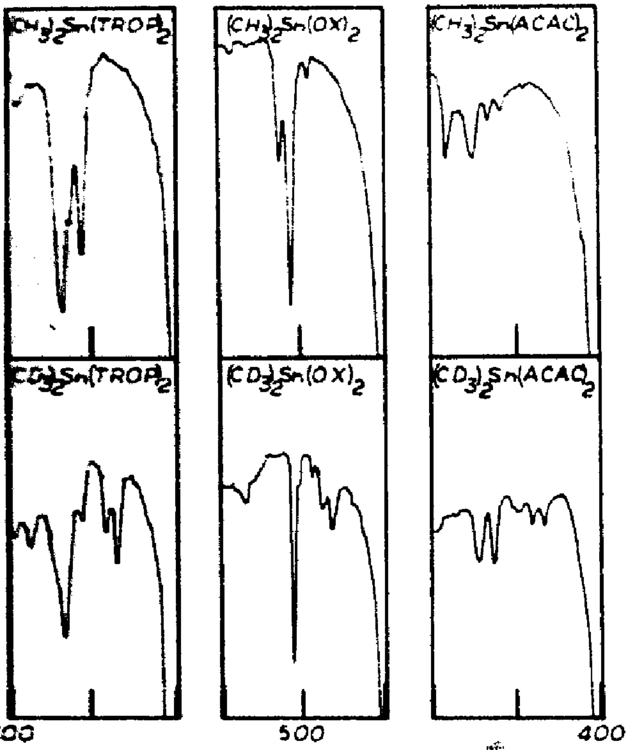

Fig. 3. Infrared spectra of CS_2 solutions in the region 400—600 cm^{-1}

Fig. 4. Infrared CS_2 solution spectra of C, $(CH_3)_2SnCl_2$, and D, $(CH_3)_2Sn(acac)_2$.

TABLE 2

RAMAN SPECTRA IN THE REGION 500–600 cm^{-1}

Compound	State	Bands (cm^{-1})[a]				
$(CH_3)_2SnCl_2$	$CHCl_3$ solution	526s	564w			
$(CH_3)_2Sn(Ox)_2$	$CHCl_3$ solution	516s				
$(CH_3)_2Sn(trop)_2$	$CHCl_3$ solution	518s	530m	548s	592m	
$(CH_3)_2Sn(Ox)_2$	C_6H_6 solution	517s				
$(CH_3)_2Sn(trop)_2$	C_6H_6 solution	517s	529m	548s	592m	
$(CH_3)_2Sn(acac)_2$ [9]	solid	514s		565w		
$(CH_3)_2SnCl_2$	solid	517s	568w			
$(CH_3)_2Sn(Ox)_2$	solid	516s	567vw			
$(CH_3)_2Sn(trop)_2$	solid	515s	531m	553s	585w	595
$Cl_2Sn(trop)_2$	solid			589s		
$(C_6H_5)_2Sn(trop)_2$	solid			558m	597m	

[a] Assignment $\nu_s(Sn-C_2)$, $\nu_{as}(Sn-C_2)$.

TABLE 3

INFRARED SPECTRA OF CS_2 SOLUTIONS IN THE REGION 500–600 cm^{-1}

Compound	Bands (cm^{-1})[a]					
$(CH_3)_2Sn(trop)_2$	517s	529ms	540s	572w	592m	
$(CH_3)_2Sn(Ox)_2$	518s	530ms		570w	590w	
$(CH_3)_2Sn(acac)_2$	517m	529ms	547s	578s		
$(CD_3)_2Sn(acac)_2$	470w	482w	500vw	529m	547m	
$(CD_3)_2Sn(Ox)_2$	468m	479m	492w	516s	572w	592w
$(CD_3)_2Sn(trop)_2$	470m	482m	511m	531s	575m	592w

[a] Assignment $\nu_s(Sn-C_2)$, $\nu_{as}(Sn-C_2)$.

Solution spectra of $(CH_3)_2SnCl_2$ and $(CH_3)_2Sn(acac)_2$ between 500–600 cm^{-1} shown in Fig. 4 allow the detailed comparison of peaks due to symmetrical and antisymmetrical stretching vibrations of those molecules.

Tables 2 and 3 allow easy comparison to be made of infrared and Raman data.

Discussion

X-ray studies have shown that $(CH_3)_2Sn(acac)_2$ and $(CH_3)_2Sn(Ox)_2$, respectively, possess *trans* [7] and *cis* [1] structures in the solid state. Since some solid state spectral assignments [9,15,16] have been made for both the $(CH_3)_2Sn$ symmetrical and antisymmetrical vibrations of each molecule, and because it seems likely that solution and solid-state spectra will closely resemble one another if structural change does not occur upon placing molecules in solution, it should be possible to use the solid state spectra of the above molecules for making solution spectral and structural assignments.

The energy of the symmetrical $(CH_3)_2Sn$ stretching vibration is not nearly as sensitive to structural change as is that of the antisymmetrical vibration. A difference of only 2 cm^{-1} is observed in the former while the antisymmetrical stretch is reduced from 578 cm^{-1} for *trans*-$(CH_3)_2Sn(acac)_2$ to 529 cm^{-1} for *cis*-$(CH_3)_2Sn(Ox)_2$.

Since the symmetrical $(CH_3)_2Sn$ stretching vibration is not observed in the infrared for a *trans*-type structure, but is observed for the *cis*, and since both structures exhibit antisymmetrical vibrations which are infrared active, it is believed that infrared solution spectra should be the best means of determining solution structures for compounds of the type $(CH_3)_2SnCh_2$. Specifically, presence of a band in the range 514—518 cm^{-1} accompanied by another near 530 cm^{-1} should be evidence for a *cis* isomer while a band at 578 cm^{-1} appearing in the absence of a band at 514—518 cm^{-1} should indicate the presence of a *trans* isomer, exclusively.

Thus, it is most significant that $(CH_3)_2Sn(acac)_2$ and $(CH_3)_2Sn(trop)_2$ in CS_2 solution possess distinct bands at 517 and 529 cm^{-1}. Certainly, this alone is good evidence for the presence of *cis*-type structures since such bands have not been assigned previously to the ligands themselves nor have they been observed for solid $(CH_3)_2Sn(acac)_2$. However, there are strong ligand bands nearby, and it was decided that assignment would be much more convincing if it could be shown that the bands in question shifted to lower energy upon deuteration of the methyl groups. This is especially true regarding the band at 529 cm^{-1}, the assignment of which is somewhat less certain on the basis of previous work [16].

Comparison of the solution spectra of $(CH_3)_2Sn(trop)_2$ and $(CD_3)_2Sn(trop)_2$ shows quite clearly that the *cis* assignment is correct. Pronounced bands at 517 and 529 cm^{-1} are shifted to 470 and 482 cm^{-1} as one would expect for the symmetrical and antisymmetrical $(CH_3)_2Sn$ stretching vibrations. Absence of any band at 578 cm^{-1} further supports the assignment. The *trans* isomer if present must be overwhelmingly outnumbered by the *cis*. $(CH_3)_2Sn(acac)_2$ bands at 517 and 529 cm^{-1} appear at 470 and 482 cm^{-1} in $(CD_3)_2Sn(acac)_2$. This observation taken with the similar behavior of oxinate and tropolonate derivatives provides definitive evidence for *cis*-$(CH_3)_2Sn(acac)_2$ in solution. At the same time it must be emphasized that $(CH_3)_2Sn(acac)_2$, unlike the other two, has quite a pronounced infrared absorption at 578 cm^{-1} which is shifted to 529 cm^{-1} for $(CD_3)_2Sn(acac)_2$. Such an observation is consistent with the presence of the *trans* isomer. Relative intensities of the peaks associated with antisymmetrical stretching vibrations suggest, but do not prove, that the *trans* isomer exists in greater concentration than the *cis*. Other methods currently are being pursued to determine the equilibrium isomer ratios.

This paper presents the first conclusive evidence for the coexistence of *cis* and *trans* isomers of $(CH_3)_2Sn(acac)_2$ in solution. Previously, optical properties [3] have been studied carefully as a function of concentration and temperature in other solvents and reported data is consistent with that expected for a solution possessing only one solute species.

It is interesting that the dimethyltin symmetrical stretching vibration gives rise to a very sharp peak in its Raman spectra which shows no signs of splitting at all, as might be expected for a mixture of *cis* and *trans* isomers. Likewise, even though $(CH_3)_2Sn(acac)_2$ and related compounds possess substantial amounts of atom polarization, trends in observed dipole moments for a homologous series of dichloro, diphenyl and dimethyl derivatives are consistent only with the assumption of a dominant *cis*-type structure in solution or *cis*—*trans* equilibrium mixtures of almost constant isomer ratio [13].

Rather extensive earlier studies of the infrared spectra of $(CH_3)_2Sn(acac)_2$ in the solid state [9] and careful Raman studies of the solid state and benzene and carbon tetrachloride solutions [11,12] have shown no trace of the *cis* isomer. No evidence of the *cis* isomer is expected for the solid state since the X-ray study [7] has shown the structure to be *trans*. If the *cis* isomer is present in solution, however, it is not clear why evidence for the Raman-active antisymmetrical stretching vibration has not been observed. This is best attributable to the observation that benzene is not an ideal solvent for either infrared or Raman studies due to its considerable interference in the region of interest, 400—600 cm^{-1}. That is, the antisymmetrical $(CH_3)_2Sn$ stretching vibration which has a very low Raman intensity should be difficult to detect against the large background signal characteristic of benzene itself. Low solubilities of complexes in carbon tetrachloride make sensitivity a serious problem in that solvent. Given the probable coexistence of the *trans* isomer, the spectra of the *cis* would be even harder to detect than otherwise expected.

Because energies of Raman-active symmetrical $(CH_3)_2Sn$ stretching vibrations are so very similar for *cis* and *trans* isomers, analysis of infrared spectra for the antisymmetrical stretching vibration appears to be the best practical spectroscopic method for detecting the *cis—trans* equilibrium. It is perhaps somewhat more surprising that splitting of the $Sn—CH_3$ resonance has not been observed in proton NMR. It appears that rapid solution exchange rates [14] for $(CH_3)_2$-$Sn(acac)_2$ have nearly completely frustrated NMR structural studies of this system. Perhaps the use of a higher resolution instrument would lead to success.

There is no doubt that the structure of $(CH_3)_2Sn(acac)_2$ like $(CH_3)_2SnF_2$, in the solid state is exclusively *trans* [17]. It appears that past uncertainties concerning the structure of $(CH_3)_2Sn(acac)_2$ in solution have stemmed from the probability that the molecule exists in a very rapid *cis—trans* equilibrium.

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