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MijSSBAUER AND RELATED STUDIES OF SOME DIVINYLTIN(IV) COMPLEXES*

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Summary

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Mdssbauer parameters are reported for twenty-five divinyltin(IV) compounds. EIectric moments of some of these compounds indicate greater overall electron withdrawal from tin by vinyl than by phenyl groups. A comparison of isomer shifts of octahedral divinyl- and diphenyl-tin compounds suggests some $C_6H_S=Sn^$ double bond **character. Quadrupole** splittings of these pairs of compounds **reveal similar configurations except for (bis) picolinates and dialkyldithiocarbamates, in which the phenyl** groups are *cis* and the vinyl **groups** *trans.* **Infrared absorption in the C-Sn stretching region reveals different patterns for cis and** *trans* compounds.

Introduction

Mossbauer studies of divinyltin(IV) compounds are of interest in comparing the inductive effects of phenyl and vinyl groups and the relative C=Sn double bond character in these two sets of compounds, and in determining the arrangement of carbon-tin bonds, *cis* **or** *trans, in* octahedral **complexes. A previous study has indicated** *bans* alkyl and vinyl **and** *cis* **phenyl groups ir. R,Sn(picolinate)z** complexes [11. Complexes investigated in the present study include chlorides, isothiocyanates, and those with bidentate anionic ligands. Electric dipole moments of some of these compounds in benzene solution have also been determined.

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experimental design and the contract of the co

Divinyltin chloride was donated by M & T Chemicals, Inc. Anhydrous $\text{tin}(IV)$ chloride, pyridine and potassium thiocyanate were Baker analyzed reagents. Tetramethylammonium chloride and bromide were obtained from Matheson, Coleman and Bell. Pyridine N-oside, tropolone, sodium dimethyldi- I thiocarbarnate and the sodium salt of 2-pyridinethiol-N-oxide were Aldrich Chemical Co. products. Dimethyl sulfoxide and sodium diethyldithiocarbamate were obtained from Fisher Scientific Co. Chloranilic acid and heramethylphosphoric triamide were supplied by Eastman Organic Chemicals. The sources of other reagents have been mdicated previously [2].

Sodium salts of tropolone and chloranilic acid were prepared by mixing methanol solutions of each **ligand and sodium methylate in a** l/l mole ratio and **evaporating to dryness. Divinylbis(tropolonato)tin(IV) was prepared by adding** a methanol solution of the dichloride to a boiling methanol solution of sodium tropolonate in a l/2 ratio. The product separated as yellow crystals on stirring, concentrating and cooling in ice. It was crystallized from hot methanol. Divinyl- (chi) (chloranilato)tin(IV) was prepared by adding $1/1$ a methanol solution of divinyltin dichloride to a suspension of the sodium salt of chloranilic acid in hot methanol. After stirring for 2 h the product precipitated as a blue-black powder. Divinylbis(dialkyldithiocarbamato)tin(IV) and divinylbis(2-thiopyridine -N-oside)tin(iV) were prepared by reacting divmyltin dichloride with the sodium salt of the respective ligands in ethanol in a $1/2$ ratio. The white precipitates were recrystallized from the same solvent.

Dinvinyldisothiocyanatotin(IV) was prepared by the method of Seyferth and Stone [3 1, using a 3/l mixture of benzene and acetone as a solvent for recrystallization. The compleses of this compound with monodentate ligands were obtained by mixing ethanol solutions in a $1/2$ ratio. The white precipitates were recrystalhzed from ethanol. Complexes of divinyltin dichloride with these ligands were obtained in **a similar manner; anhydrous ether was used as a solvent in the preparation of the complex with dimethylsulfoxide. Only the** l/l complex of the dichloride with tetramethylthiourea was obtained, even when escess of the latter compound was used. Complexes of the dichloride and diisothiocyanate with 2.2'-dipyridyl and 1.10-phenanthroline were prepared by the method of Tanaka et al. [4], and the compleses with 2,2',2"-terpyridyl were obtained as indicated previously $[2]$. Divinyldichlorobis(aquo)tin(IV) was obtained by spreading divinyltin dichloride in a thin layer on a flat petridish open to moist air. White crystals began to form in fifteen min. This complex reverts to the anhydrous compound in dry air. $[(C_2H_3)_4N]_2[(C_2H_3)_2SnCl_4]$ precipitated immediately on mixing ethanol solutions of divinyltin dichloride and tetramethylammonium chloride in a 1/2 ratio. $[(C_2H_5)_4N]_2[R_2Sn(NCS)_4]$, where $R = n$ -butyl, phenyl and vinyl, were obtained immediately as white precipitates when ethanol solutions of $R_2Sn(NCS)$, and $[(C_2H_3)_3N/(NCS)]$ were mixed in a l/2 ratio. [**(C,H,),N](NCS) was** prepared by mising ethanol solutions of tetraethylammonium bromide and potassium thiocyanate in a 1/1 ratio. Divinyltin(IV oxide was prepared by the method of Rosenberg and Gibbons [5].

Fig. 1. Mossbauer spectrum of Vin₂SnCI₂ - tetramethylthiourea.

infrared and hlossbauer spectra

These were obtained as indicated previously [2]. Mossbauer measurements were made with the barium stannate source at room temperature and the absorbers ; at 80 K. **The spectrometer was calibrated with** iron foil obtained from the National Bureau of Standards. The isomer shifts relative to barium stannate are considered to be accurate to \pm 0.03 mm s⁻¹ with a relative precision of \pm 0.02 mm s-'. The **Mossbauer spectrum of divinyltin** dichloride - tetramethylthiourea is illustrated **in Fig. 1.**

Dielectric constants of benzene solutions

These were obtained with a \V.T.W. Dipolmeter, hlodel **Dhl 01.** obtained from Kahl Scientific Instruments Corp. The cell used was a pipette type Kahlisco Model DFL/2D. The dipole moments were evaluated from the Higasi equation [6, 7], μ = 0.8481 ($\Delta \epsilon / x$)^{1/2}. The latter ratio, the change in dielectric constant with solute mole fraction, was a constant for each set of solutions studied.

Results and discussion

The value, 4.37 Debyes, of the electnc dipole moment of di-n-butyltin dichloride (Table 1) is the same as that obtained previously with a different instrument in this laboratory [8]. The smaller moment, 4.06 D, for the diphenyl compound reveals very little, if any, $C_6H_5=Sn^-$ double bond character, and the value 3.83 D for the divinyl compound indicates the greatest electron withdrawal by the vinyl group in these tetrahedral compounds. These moments are somewhat samller than those reported by Huang, Hui and Chui [9], but are in the same order.

A comparison of the relative electron withdrawal by viny1 and phenyl **groups in octahedral** compounds is afforded by the moments of the complexes of (C_2H_3) , Sn(NCS)₂ and (C_6H_5) , Sn(NCS)₂ with o-phenanthroline and α , α -di-

TABLE 1

ELECTRIC DIPOLE MOMENTS (µ) IN DEBYE UNITS IN BENZENE SOLUTIONS AT 25°C

	10^4x	$\Delta \epsilon / x$	μ = 0.05
n-Bu ₂ SnCl ₂	$3.8 - 21.7$	26.7	4.37
Ph ₂ SnCl ₂	$28 - 17.8$	22.9	4.06
VinoSnClo	$8.0 - 26.1$	20 ₄	3.83
$Ph_2Sn(NCS)$ ² o phen			$6:0.5^a$
$Vin_2Sn(NCS)_2 \cdot o\text{-phen}$	$0.9 - 4.5$	90.7	8.08
$Ph\text{-}Sn(NCS)$, dipy	$1.5 - 3.8$	68.5	704
V in ₂ Sn(NCS) ₂ - dipy	$1.7 - 4.5$	93.8	8.22

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pyridyl. Mössbauer data indicate (see below) $\text{cis } C - \text{Sn} - C$ bonds in these four compounds. **The magnitude of the dipole moments of these compleses in** benzene solution indicates *trans* NCS groups $[10]$. The resultants of the Sn-C dipoles **in these complexes are approslmately in line with the overall moments**

N 1, YC sn e .The larger moments obtained for the divinyl complexes (Table 1) 7 1, I N C

suggest **a greater** electron withdrawal by vinyl than by phenyl groups in octahedral tin(IV) complexes.

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Isomer shifts of octahedral diorganotin compounds are expected to increase with increasing tin share of the electrons of the $C-Sn-C$ bonds and with increasing tin s-character **for these bonds, and to decrease with increasing** C=Sn double bond character involving the 5d orbitals of tin, because of increased shielding. As the tin s-character depends on the C-Sn-C bond angle, comparison **of isomer shifts of dlphenyl and divinyl compounds in terms of relative electron** withdrawa! (or release) are meaningful only if the $C-Sn-C$ bond angles in the two sets of compounds are approximately **equal.** This equality is expected for trans $R_2S_nX_4^2$ anions, with a $C-Sn-C$ bond angle close to 180^o. Both the **isomer shifts and quadrupole splittings for these anions are expected** to increase with increasing tin share of the C-Sn σ -bonding electrons. The isomer shift for $[Et₄N]₂[Vir₂Sn(NCS)₄]$ (compound V, Table 2) is about equal to that of the corresponding diphenyl compound VI, and the quadrupole splitting is slightly larger, 3.94 compared to 3.82 mm s⁻¹. The majority of the octahedral divinyl compounds listed in Table 2 which have quadrupole splittings simikr to the **corresponding diphenyl compounds (suggesting** similar configurations) have slightly larger isomer shifts than the diphenyl compounds and the great majority **of pairs have differences in isomer shifts less than** \pm **0.06 mm s⁻¹. This similar tin s-electron density, despite the evidence** from dipole moments of greater overall electron withdrawal by the vinyl groups, suggests some $C_6H_5=Sn^$ double bond character in the octahedral diphenyltin compounds*.

^l**A referee has suggested Lhat the difference III isomer shifts may be assoclaled wth a difierence** in tin s-character of the tin-carbon bonds in the divinyl and diphenyl compounds.

The difference in isomer shifts for the $Et_2SnCl₄²⁻$ and $Vin_2SnCl₄²⁻$ anions, $_{11}^{11}$ I and III, and for the Bu₂Sn(NCS)₄²⁻ and Vin₂Sn(NCS)₄²⁻ anions, IV and V, for which the quadrupole splittings indicate a *trans* configuration, is 0.3 mm s⁻¹, the same as the average difference in δ for a number of pairs of trans octahedral $\frac{1}{6}$ dialkyl and diphenyl tin(IV) complexes. The isomer shift for the Vin₂SnCl₄²⁻ anion is 0.29 mm s^{-1} larger than for the corresponding tetraisothiocyanate anion. **'pThe decrease in S from dichloro to diisothiocyanate octahedral** tin(W) compounds has been noted previously $[10]$, and is evident from the values for corresponding pairs of these compounds listed in Table 2.

Dimethyldiisothiocyanatotin(IV) **has been shown to have a distorted** $\ddot{ }$ **3 octahedral sulfur-bridged polymeric structure with a C-Sn-C angle of 146° , [11, 12]. The values of** δ **and** ΔE_{Ω} **for this compound are 1.48 and 3.87 mm s⁻¹** I [**131. The corresponding dibutyl, diphenyl** and divinyl compounds are also expected to be polymeric and this is indicated for the first two compounds by infrared and Mössbauer data [10]. A polymeric structure for solid divinyldiisothiocyanatotm(IV) is indicated by NCS absorption at 2108 cm^{-1} and by strong Mössbauer absorption at room temperature. The large quadrupole splitting, 4.28 mm s⁻¹, and the relatively large isomer shift, 1.52 mm s⁻¹, indicate a significantly larger $C-Sn-C$ bond angle than that found for the dimethyl compound. NCS absorption shifts to 2055 cm⁻¹ in ethanol, indicate a breaking of the sulfur bridges in solution. $\,$

The large quadrupole splittings obtained for all V in₂SnCl₂L₂ and Vin₂Sn- $(NCS)₂L₂$ complexes (Table 2), reveal a *trans* arrangement of vinyl groups. The fact that quadrupole splittings obtained for the isothiocyanates are larger than those for the corresponding chlorides is consistent with a decreased electron

density for tin in the \sum_{s_n} . \diagup \diagup plane. The isomer shift for $\mathrm{ Vin}_2\mathrm{Sn(NCS)}_2$ - $2\mathrm{TMTL}$

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1.26 mm s-'. is appreciably larger than the values for compleses XVIII and XIX, which have ligands with osygen donors. Infrared absorption associated with the N-C-N antisymmetric stretching vibration occurs at 1579 cm⁻¹ for $\text{Vir}_2\text{SnCl}_2$ \cdot TMTU in a KBr disk and in 1,2-dichloroethane solution, compared to 1550 cm^{-1} (the usual value for $1/2$ complexes) for $Vin_2Sn(NCS)_2(TMTU)_2$ in KBr. The ΔE_Q value for the dichloride, 2.82 mm s⁻¹, suggests a coordination number **of five for tin in this compound.**

The relatively small quadrupole splittings for V in₂Sn(NCS)₂ · *o*-phen and (Vin) ₂Sn(NCS)₂ \cdot dipy, 2.63 and 2.24 mm s⁻¹, indicate a *cis* arrangement of carbon-tin bonds. This cis configuration is also indicated for divinylbis(tropolonato)tin(IV) and divinylbis(2-pyridinethiolato 1-oxide)tin(IV) by the quadrupole splittings, 1.93 and 1.78 mm s^{-1} . The four corresponding diphenyltin(IV) com**plexes also have a** *cis* configuration, whereas quadrupole splittings reveal a *trans* configuration for all dibutyltin(IV) complexes with the above ligands. The isomer shifts for the *cis* complexes are 0.6 mm s⁻¹ lower than the values for the corresponding *tram* dibutyl compounds [14, 151. This large difference has been attributed to the decrease in tin s-character with decrease in the $C-Sn-C$ bond angle $[1]$.

Previous work by the authors has indicated a *trans* arrangement of C-Sn-C

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^a Ref. 24. ^b Ref. 13. C Ref. 10. ^d Ref. 1 C Melts without decomposition.

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bonds in Vin₂Sn(picolinate)₂, with δ and ΔE_0 values of 1.18 and 4.02 mm s⁻¹, and **a** *cis* arrangement **for the corresponding diphenyl compound, with values of 0.80 and 1.94 mm s-'. Vin,Sn(SSCNMe,), (XXX) has an isomer shift of 1.35** and a quadrupole splitting of 2.74 mm s⁻¹, compared to values of 1.07 and 1.64 **for the diphenyl compound [161, indicating distorted** *truns* **and** *cis* **configuratioq [171 respectively for the complexes with this anisobidentate [181 Ugand. The above comparisons appear to rule out steric and unsaturation factors as causes for differences in configurations of diorganotin(IV) complexes. We are unaware of any satisfactory explanation for these differences.**

The large quadrupole splitting, 3.96 mm s⁻¹, for divinyl(chloranilato)tin(IV**indicates a** *tram* **arrangement of vinyl groups, similar to that indicated for the dialkyl and djphenyl compounds, with planar polymer chains.** The relatively large isomer shift, 1.33 mm s⁻¹, suggests a C-Sn-C bond angle close to 180[°]. The quadrupole splitting for $[Vin_2Sn(NCS) \cdot \text{terpyridyl}]^* [BPh_4]^2$, 3.73 mm s⁻¹, indicates trans C-Sn-C bonds, as in the diphenyl compound [2]. Axial C-Sn-Q **bonds, as in the corresponding dialkyl and diphenyl compounds [Z], are indicatel by the value of the quadrupole splitting for Vin₂Sn(NCS)₂ · terpyridyl, in which** tin is seven-coordinate. A significant deviation from 180° for this C-Sn-C bond **angle is indicated by the isomer shift and quadrupole splitting, 1.17 and 3.89 mr** compared to 1.29 and 4.18 mm s⁻¹ for the diphenyl compound. The C-Sn-C bond angle in Me₂Sn(NCS)₂ · *terpyridyl*, with δ and ΔE_{Ω} values 1.32 and 4.29 **mm s-! [Z], is 173.7" [19].**

Reichle [201 has interpreted a number of physical properties of dibutyltin oxide and diphenyltin oxide as indicating that these compounds are polymeric. The values of δ and $\Delta E_{\mathbf{Q}}$ for divinyltin oxide, 0.90 and 2.11 mm s⁻¹, compare **with 1.04 and 2.09 mm s-'** for di-n-butyltin oxide [Zl] and 0.89 **and 2.00 mm s'** for diphenyltin oxide [22]. None of these compounds shows appreciable Möss**bauer absorption at room temperature.**

Infrared spectra

Peruzzo and coworkers [231 have assigned absorptions in the 480-580 cm-' region in the spectrum of trivinyltin(IV) acetates to $Sn-C$ **stretching vibrations.**

Fig. 2. Infrared spectra in the C-Sn-C stretching region. (A) $\text{Vir}_2\text{SnCl}_2(\text{pyndine N-oxide})$? **(B)Vii2Sn(NCS)?** - dirwridyL

Absorptions in this region for the divinyltin(IV) complexes are listed in Table 2. **it is evident that all cis compounds absorb at lower frequencies than trans. The absorption patterns are illustrated in Fig. 2. The frequencies of absorptions in ;his region offer a means of disting?lishing between cis and trarx configurations for divinyitin(IV)** complexes.

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