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ORGANOTIN(IV) AZIDO AND MIXED AZIDOTHIOCYANATO COMPLEX ANIONS; A MÖSSBAUER AND VIBRATIONAL SPECTROSCOPIC STUDY

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Summary

Tetraphenylarsonium and tetramethylammonium salts of the complex anions $Ph_3Sn(N_3)_2^-$, $Ph_3Sn(N_3)(NCS)^-$, $Me_2Sn(N_3)_4^{2-}$ and $Ph_2Sn(N_3)_2(NCS)_2^{2-}$ have been synthesized, and the solid state configuration of the complex anions has been studied by Mössbauer and vibrational spectroscopies. Trigonal bipyramidal structures are advanced for the Ph_3Sn^{IV} derivatives, with equatorial SnC_3 and apical pseudohalide ligands, while the R_2Sn^{IV} compounds are assumed to be *trans*-octahedral species. The NCS^- ligands are observed to be N-bonded to Sn^{IV}. Conductance and PMR (for the Me_2Sn^{IV} compound) data suggest the presence of the complex anions also in solution phases.

Introduction

The architecture and bonding of tri- and di-organotin(IV) azides [1,2] and thiocyanates [3-5] have been widely explored by ^{119m}Sn Mössbauer spectroscopy. The pseudohalide groups generally bridge organotin(IV) moieties [except N_3^- in $R_2Sn(N_3)_2$]; the idealized configuration of R_3SnX ($X = N_3$, NCS; T 80 K for N_3 derivatives) is trigonal bipyramidal with R_3Sn^{IV} located in the trigonal plane, while that of $R_2Sn(NCS)_2$ is *trans*-octahedral [1-5]. The crystal and molecular structures of $Me_2Sn(NCS)_2$ [6,7] and R_3SnNCS [8] (R = Me, Ph) show that the inferences concerning configurations of these compounds extracted from Mössbauer spectroscopy are essentially correct.

Neutral organotin(IV) pseudohalides are likely to be further coordinated by pseudohalide ligands, forming complex anions [9]. The environment of the tin atom in species such as $R_3SnX_2^-$ and $R_2SnX_4^{2-}$ (X^- = pseudohalide) is expected to correspond to that of the related polymeric neutral derivatives [10, 11], with interesting differences arising from the nature of the ionic crystal lattice in which the organotin(IV) complex anions are electrostatically coupled through their counterions. The aim of the present research is to extend the knowledge of organotin(IV) pseudohalide complex anions of the type referred to above. Salts of $Ph_3Sn(N_3)_2^-$, $Ph_3Sn(N_3)(NCS)^-$, $Me_2Sn(N_3)_4^{2-}$ and $Ph_2Sn(N_3)_2(NCS)_2^{2-}$, taken as representative members, were synthesized, and subsequently investigated by Mössbauer, infrared and Raman spectroscopies, which permitted an assessment of their probable configurations in the solid. Solution phase investigations, complementary to the above, were carried out by conductivity measurements and proton magnetic resonance studies.

Experimental

Pure (or purified by standard procedures) chemicals were used throughout the work. The salts Ph_4As SCN[12], Me_4NN_3 [13] and Me_4N SCN [14] were obtained by literature methods.

The compound Ph_4AsN_3 was prepared from a concentrated aqueous solution of Ph_4As Cl and NaN_3. Needle-like crystals of Ph_4AsN_3 precipitated and were collected, dried and recrystallized from ethanol/ether (m.p. 228-230°C). The general synthetic method for Ph_3SnN_3 and $Ph_2Sn(NCS)_2$ consisted of refluxing, for several hours, a solution of the corresponding chloride (Fluka product) with an excess of the appropriate sodium pseudohalide (typically: organotin chloride 15 mmole, sodium pseudohalide 50 mmole). The solid residue (NaCl and the excess of NaN_3) was filtered off the warm solutions, and the crystalline organotin(IV) pseudohalides were recovered by cooling, then purified through recrystallization. Benzene was the solvent used in the synthesis and recrystallization of $Ph_2Sn(NCS)_2$, and 2/1 n-hexane/benzene for Ph_3SnN_3 (n-hexane for recrystallization). Elemental analyses were satisfactory and the melting points corresponded to literature values (where reported).

The salts of the complex anions $Ph_3Sn(N_3)_2^-$, $Ph_3Sn(N_3)(NCS)^-$ and $Ph_2Sn(N_3)_2(NCS)_2^{2-}$ were recovered as white crystalline solids by cooling solutions of Ph_3SnN_3 and $Ph_2Sn(NCS)_2$ containing the stoichiometric amount of the appropriate tetraorgano-ammonium or -arsonium salt, followed by recrystallization (typically: for $[Me_4N][Ph_3Sn(N_3)(NCS)]$ 2.3 mmole of Ph_3SnN_3 and Me_4N SCN dissolved in 15 ml of warm solvent, and the same solvent volume employed for recrystallization). The solvents used for solution and recrystallization were absolute ethanol for Ph_3Sn^{IV} derivatives, and acetonitrile for the salt of Ph_2Sn^{IV}. The complex $[Ph_4As]_2[Me_2Sn(N_3)_4]$ was prepared by refluxing for several hours 2.3 mmole of Me_2SnCl_2 and 4.6 mmole of Ph_4AsN_3 in 30 ml of acetonitrile, in the presence of an excess of NaN_3. After filtering off the warm solution and cooling the filtrate, a white crystalline solid precipitated. This was recrystallized from 20 ml of acetonitrile. Table 1 reports m.p. and analytical data for these compounds.

The ^{119m}Sn Mössbauer spectra were obtained at liquid nitrogen temperature, using the BTL type constant acceleration spectrometer described earlier [15]. Temperature measurements were effected by use of a pre-calibrated thermocouple and the reported values are uncertain by ±1° over the time interval of the Mössbauer data accumulation (10 to 20 h). Spectrometer

TABLE 1. ANALYTICAL DATA AND MOLAR CONDUCTANCES IN METHANOL

Compound	Emp. formula	M.p. (°C)	Analysis found (calcd.)(%) C	H	N	S	Molar conductances Λ_m Concn. (mM)	(ohm^{-1} cm^2 mole^{-1})
I	$C_{50}H_{46}As_2N_{12}Sn$	205-206	55.19	4.37	15.71		4.13	155
			(55.43)	(4.28)	(15.51)		0.41	181
II	$C_{22}H_{27}N_7Sn$	184-185	51.74	5.48	19.04			
			(51.99)	(5.30)	(19.29)			
III	$C_{42}H_{35}AsN_6Sn$	173-174	61.83	4.56	10.20		3.39	79
			(61.71)	(4.32)	(10.28)		0.39	91
IV	$C_{20}H_{30}N_5SSn$	148-149	52.45	5.37	13.21	6.05		
			(52.69)	(5.19)	(13.36)	(6.12)		
V	$C_{43}H_{35}AsN_4SSn$	157-158	61.83	4.31	6.58	4.00	3.84	86
			(61.97)	(4.23)	(6.72)	(3.85)	0.38	103
VI	$C_{62}H_{50}N_8S_2Sn$	237-239	59.92	3.91	9.21	5.25	0.33	206
			(60.07)	(4.07)	(9.04)	(5.17)		

TABLE 2. MÖSSBAUER PARAMETERS[a](mm/sec; T = 81 ± 1 K), RELEVANT VIBRATIONAL BANDS[b](cm^{-1}) AND ASSIGNMENTS

Compound	IS[c]	QS[d]	Γ_{ave}[e]	ν_{as}(N$_3$ and/ or NCS)	Other bands	
$[Ph_4As]_2[Me_2Sn(N_3)_4]$ (I)	1.23	3.61	0.88	2040 s	555m[f] 497m s[g]	$\nu_{as}(SnC_2)$ $\nu_{sym}(SnC_2)$
$[Me_4N][Ph_3Sn(N_3)_2]$ (II)				2050 s 2070(sh)		
$[Ph_4As][Ph_3Sn(N_3)_2]$ (III)	1.20	2.75	0.83	2040 s 2055 s		
$[Me_4N][Ph_3Sn(N_3)(NCS)]$ (IV)				2020(sh) 2060 s 2070(sh)	472 w; 478 w 305 w	δ(NCS) ν(Sn NCS)?
$[Ph_4As][Ph_3Sn(N_3)(NCS)]$ (V)	1.21	2.97	0.90	2042(sh) 2060 s 2070(sh)	302 w	ν(Sn NCS)?
$[Ph_4As]_2[Ph_2Sn(N_3)_2(NCS)_2]$ (VI)	1.10	3.72	0.84	2050 s 2065(sh)		

[a] For typical compounds; the effect of the cation is not investigated. [b] Infrared bands unless otherwise stated, s, strong; m, medium; w, weak; (sh), shoulder. [c] Isomer shift with respect to the center of a $BaSnO_3$ spectrum at 294 K, ± 0.02 mm/sec. [d] Quadrupole splitting. [e] Average full width at half height of the absorption peaks (uncorrected for sample thickness broadening effects). [f] Raman inactive. [g] Raman band, inactive in the infrared.

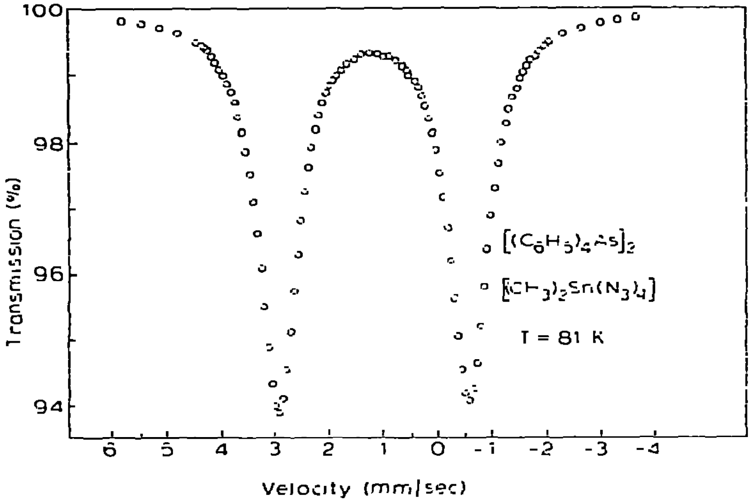


Fig. 1. Mössbauer spectrum of $[C_6H_5)_4As]_2[(CH_3)_2Sn(N_3)_4]$ at 81 K. The isomer shift scale is with respect to the center of a room temperature $BaSnO_3$ absorption spectrum as discussed in the text. The statistical (counting) errors of ± 0.1% are indicated by the size of the circles representing the data points.

calibration was effected [15, 16], using 0.8 mil NBS SRM iron foil at room temperature. All isomer shift data reported herein with respect to a room temperature $BaSnO_3$ absorber spectrum obtained using the same source. Data reduction was effected using the Rutgers IBM 360/67 computer and a program [17] which assumes a Lorentzian line shape, leaving the line position, effect magnitude and full width at half maximum as independent parameters for each of the *n* specified scattering maxima. The Mössbauer parameters are summarized in Table 2 and a representative Mössbauer spectrum (normalized by a least squares fitting program to 100% transmission for the base line) is shown in Fig. 1.

Infrared spectra were obtained for Nujol mull samples in the range 4000 to 250 cm^{-1} on a Perkin—Elmer 457 spectrometer, using CsI plates, and on KBr pellets (~ 0.8% by weight) over the same wavelength range using a Perkin—Elmer 225 spectrometer. Raman spectra were obtained on a Cary 82 spectrometer employing a Kr/Ar mixed gas laser (Coherent Radiation Laboratories model 52MG) at room temperature. The vibrational data are reported in Table 2.

The solution chemistry was investigated by conductance measurements in methanol at 26°C, with an LKB 5300 B instrument (cell constant 4.9 cm^{-1} with NaCl), and by PMR spectroscopy in CD_3OD at 25°C, TMS as internal standard, with a JEOL C60 spectrometer operating at 60 MHz. Conductance data are summarized in Table 1.

Results and discussion

The compositional formulations of the compounds investigated are given in Table 1 and are consistent with the elemental analysis data obtained experimentally. The melting point data, as well as the constancy of the composition results on recrystallization, exclude the presence of mixtures (of reactants) having the same overall stoichiometry, as well as serving as preliminary confirmatory evidence for the formulation of these species as complexes of organotin(IV) anions, as shown. These assumptions have been further tested by Mössbauer and vibrational spectral data analysis to be discussed below.

The ^{119m}Sn Mössbauer resonance results are tabulated in Table 2 for four of the subject compounds. Since the minimum observable line width in ^{119m}Sn spectra (2Γ) is ~ 0.63 mm/sec, the data in Table 2 reflect the fact that each of these compounds contains a unique tin atom and there is no evidence for unresolved hyperfine interactions present in these absorbers. The *IS* values at liquid nitrogen temperature are consistent with a formulation of the metal atoms as being present in the oxidation state IV [15].

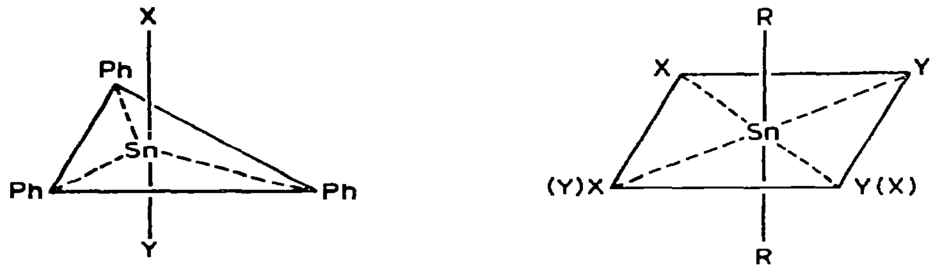
As will be discussed further below, the stereochemistry of the ligands around the metal atom in compounds I and VI corresponds to an octahedral configuration. This is also suggested by the *IS* [15] value of I, which, being larger than 1.20 mm/sec, indicates a *trans*-Me$_2$ octahedral structure [18]. The difference of ~ 0.13 mm/sec in the two isomer shifts (being larger for the dimethyl compound than for the diphenyl compound) is comparable to the corresponding differences in the isomer shifts of $(CH_3)_2Sn^{IV}$ and $(C_6H_5)_2Sn^{IV}$ compounds reported in the literature [19]. It is clear from the *IS* data for III and V that the contribution to the total isomer shift of the N_3 ligand and the SCN ligand are essentially identical since the two isomer shifts are the same within experimental error. Thus these data are in complete agreement with the earlier observation concerning the near identity of the isomer shifts in the trigonal bipyramidal compounds $(CH_3)_3SnN_3$(1.43 mm/sec at 82 ± 4 K) and $(CH_3)_3Sn$ NCS(1.40 mm/sec at 80 ± 2 K) [1, 3]. Moreover, it should be noted that this situation is very different in the corresponding dimethyltin(IV) compounds [1,3] in which the *IS* values for $(CH_3)_2Sn(N_3)_2$ (1.06 mm/sec at 82± 4 K) and for $(CH_3)_2Sn(SCN)_2$(1.48 mm/sec at 82 ± 2 K) reflect the tetrahedral molecular structure and non-bridging ligand in the former and the octahedral molecular structure and bridging ligand in the latter.

The relationship between ligand electronegativity and the ^{119m}Sn isomer shift parameter has been well established, although detailed interpretations are still the subject of some controversy [20]. On the basis of extensive studies of isostructural halogen and pseudohalogen compounds by a variety of techniques it has been found that the greater the ligand electronegativity, the smaller the observed *IS* value relative to $BaSnO_3$ or SnO_2. In a previous study [1] it has been shown that the Mulliken electronegativity of 7.66 ± 0.06 can be assigned to a bridging azide moiety and 8.54 ± 0.10 to a terminal azide group. The present data for III and V suggest that the Mulliken group electronegativity for a non-bridging NCS group bonded to tin must be essentially identical to that of a non-bridging N_3 group, since the isomer shift difference between III and V is zero within the error limits of the present data. However, it should be borne in mind that the *IS* parameter of di- and tri-organotin(IV) is, in fact, not very sensitive to small differences in electron demand by different ligands [18], but only to the total effective *s*-electron density at the tin nucleus. This point has been discussed in detail by Huheey et al. [20] who have pointed out the dangers of overinterpretation of the isomer shift—electronegativity correlation.

Turning now to the *QS* [15] parameter, the value observed for I (3.61 mm/sec) confirms the octahedral nature of the anion and places the two methyl groups *trans* with respect to each other, comparable to the structure of $(CH_3)_2$-$Sn(NCS)_2$ (*QS* = 3.87 mm/sec at 80 ± 2 K) which has been elucidated both by Mössbauer [3] and X-ray diffraction techniques [6,7]. (It should be noted that the *QS* of $(CH_3)_2Sn(N_3)_2$ is 2.61 mm/sec at 82 ± 4 K and a distorted tetrahedral geometry has been assigned to this molecule [1].) A similar *trans* configuration of the two phenyl groups must obtain in VI, although the present data are insufficient in themselves to establish the relative stereochemistry of the two types of pseudohalogen ligands. It is also interesting to note that the *QS* parameter for VI is slightly larger than that observed for I under essentially identical conditions, although in most compounds of the type R_2SnA_4 or $R_2SnA_2B_2$ the *QS* for R = alkyl is normally larger than those observed when R = C_6H_5 [18,19]. Since the *QS* parameter reflects both the difference in electron demand between different ligands bonded to the central tin atom as well as the details of the ligand geometry around the metal [15,18] (eg. the A—Sn—A or A—Sn—B bond angles), it is not possible to give a quantitative interpretation to the difference in the *QS* parameter observed in VI compared to I. A possible resolution of the two factors may be derived from an evaluation of the η [= $V_{xx}-V_{yy})/V_{zz}$] parameter [15], by means of a magnetic hyperfine interaction experiment. However, such studies are beyond the scope of the present investigations.

The *QS* values observed for III and V are somewhat smaller than those generally observed for pentacoordinated triorganotin(IV) species [18,19]. Thus, trigonal bipyramidal structures with equatorial SnC_3 moieties and apical ligand groups often have quadrupole splitting values of ~ 3.3 to 3.5 mm/sec [18,19]. On the other hand, the homologous triphenyltin (rather than trimethyltin) complexes show consistently lower *QS* values [19], that of $[(CH_3)_4N]$-$[(C_6H_5)_3SnCl_2]$ being 3.00 mm/sec [21]. On this basis it is reasonable to postulate a trigonal bipyramidal configuration for compounds III and V of the subject series, as well.

The infrared spectra of $[Ph_4As][Ph_3Sn(N_3)_2]$ (III) and $[Ph_4As][Ph_3Sn(N_3)$-$(NCS)]$ (V) are practically identical except for a band at 302 cm^{-1} observed in $Ph_3Sn(N_3)(NCS)^-$, which may be associated with a Sn—NCS bond vibration (Table 2). The bands due to phenyl groups bound to Sn (apart from those obscured by Ph_4As^+ bands) are as expected [22,23]. The envelopes of the $\nu_{as}(N_3)$ and $\nu_{as}(NCS)$ modes (Table 2) occur at a frequency lower than 2100 cm^{-1}, suggesting that NCS^- is N-bonded to Sn in $Ph_3Sn(N_3)(NCS)^-$ [24]. The nature of N- or S-bonded thiocyanato derivatives is better elucidated by the energy of bending modes, δ(NCS), which lie around 470 and 410-440 cm^{-1}, respectively [24]. In $[Ph_4As][Ph_3Sn(N_3)(NCS)]$ (V) the 470 cm^{-1} region is obscured by cation vibrations, while no bands are observed between 400 and 450 cm^{-1}. The latter would exclude S—Sn bonds. On the other hand, the 470 cm^{-1} region is clear of cation bands in the Me_4N^+ salts of $Ph_3Sn(N_3)_2^-$ and $Ph_3Sn(N_3)$-$(NCS)^-$ (II and IV). The IR spectra of these two anions differ in the region of the band at 302 cm^{-1} discussed above, as well as for two bands at 477 and 472 cm^{-1}, all appearing in the spectrum of the mixed complex (Table 2). This is fully consistent with a N-bonded NCS group [24], in consonance with the usual isothiocyanato nature of Group IV organometal derivatives, such as those of R_3Sn^{IV} [8] and Ph_3Pb^{IV} [25].



(II,III) X = Y = N_3

(IV,V) X = N_3, Y = NCS

(I) X = Y = N_3, R = CH_3

(VI) X = N_3, Y = NCS, R = Ph

Fig. 2. Idealized geometries of the organotin(IV) compounds discussed in the text.

The complex anions $Ph_3Sn(N_3)_2^-$ and $Ph_3Sn(N_3)(NCS)^-$ seem to exist also in CH_3OH solution. The respective molar conductances of Ph_4As^+ salts (Table 1) closely correspond to that of $[Me_4N][PhTlCl_3]$ (Λ_m = 98, $c = 1 \times 10^{-3}$ *M* in CH_3OH [26]), which is a 1/1 electrolyte in this solvent [12,26,27] dissociating to give the anion $PhTlCl_3^-$.

The data for $[Ph_4As]_2[Me_2Sn(N_3)_4]$ (I) strongly suggest the presence of the anion $Me_2Sn(N_3)_4^{2-}$, with the *trans*-octahedral configuration shown in Fig. 2. The vibrational spectra show an infrared band at 555 cm^{-1}, Raman inactive, and a Raman frequency at 497 cm^{-1}, infrared inactive, which are safely attributed to $\nu_{as}(SnC_2)$ and $\nu_s(SnC_2)$ respectively, and clearly indicate the occurrence of linear CSnC moieties [11,22] (Table 2) with a center of symmetry. The PMR spectrum in CD_3OD shows a single methyl proton signal at δ 0.75 ppm, with a coupling constant $J(^{119}SnCH_3)$ of 88.5 Hz, which corresponds to about 41% *s* character in the Sn—C bonds [28]. The molar conductance in CH_3OH (Table 1) is comparable to that of $[Me_4N]_2[PhTlCl_4]$(Λ_m = 183, $c = 2.34 \times 10^{-3}$ *M* in CH_3OH[26]), which mainly ionizes in this solvent to give three particles per mole, including the anion $PhTlCl_4^{2-}$[12, 26, 27].

As to $[Ph_4As]_2[Ph_2Sn(N_3)_2(NCS)_2]$(VI), thiocyanate ligands are N-bonded to Sn, as inferred from the IR spectrum (Table 2), where the envelope of $\nu_{as}(N_3)$ and $\nu_{as}(NCS)$ lies below 2100 cm^{-1} and no bands are observed around 410-440 cm^{-1} (which would be typical for δ(NCS) in S-bonded derivatives) [24]. The 470 cm^{-1} region, where the δ(NCS) of isothiocyanates [24] is assumed to occur, is obscured by Ph_4As^+ vibrations. The remaining bands of the mixed complex anion are as expected [22,29], apart from contributions by Ph_4As^+. The molar conductance in CH_3OH (Table 1) suggests the occurrence of a 2/1 electrolyte in this solvent [27].

All experimental data thus point to the presence of *trans*-octahedral anions $Me_2Sn(N_3)_4^{2-}$ and $Ph_2Sn(N_3)_2(NCS)_2^{2-}$ as well as of trigonal bipyramidal species $Ph_3Sn(N_3)_2^-$ and $Ph_3Sn(N_3)(NCS)^-$, perhaps distorted from the idealized geometries of Fig. 2, both in the solid state and in solution.

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