Synthesis and Structural Studies by Infrared and Mössbauer Spectroscopy of Adducts of Tin(IV) and Organotin(IV) Derivatives with 2,2′-azopyridine

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Abstract

A number of complexes have been prepared by the reaction between 2,2′-azopyridine(AZP) and tin-(IV) halides and organotin(IV) halides, and characterized by elemental analysis and infrared and variable temperature ^{119}Sn Mössbauer spectroscopies. All of the new compounds have 1:1 stoichiometry, with the AZP ligand occupying two coordination sites by bonding through one of the ring and one of the azo group nitrogen atoms, to give rise to distorted octahedral structures. In the diorganotin complexes the two organic groups occupy trans positions. The infrared and Mössbauer spectroscopic data suggest that these compounds are monomeric in the solid state.

Introduction

As part of a research program planned with the aim of investigating the structures, reactivity and pharmacological applications of tin(IV) and organotin(IV) complexes with heterocyclic nitrogen bases, the present research has been carried out and concerns the syntheses and solid state configuration of a series of adducts of Sn^{IV}, RSn^{IV}, and R_2Sn^{IV} with 2,2′-azopyridine.

We have previously investigated the solid state polymers $RSnCl_3pyz$ (R = Me, Bu^n, n-octyl, Ph or Cl; pyz = pyrazine) [1]; the ligand 2,2′-azopyridine, AZP (Fig. 1), a potentially tetradentate base, present in the *trans* isomeric form [2], has now been studied in greater detail since it would be expected to be more versatile than pyrazine in the formation of molecular adducts as well as polymers, the latter potentially originating through the bridging action of the nitrogen atoms [3–7]. Adducts with 1:1 stoichiometry have been synthesized, and have been studied in the solid state by I.R. and variable temperature ^{119}Sn Mössbauer spectroscopy in order
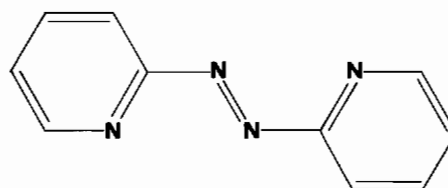

Fig. 1. 2,2′-azopyridine.

to elucidate the coordinating behaviour of the ligand. The monomeric or polymeric nature of the compounds has been studied by means of the temperature dependence of the ^{119}Sn recoil free fraction.

Experimental

Organotin reagents were gifts from Schering AG (Bergkamen) and Ciba-Geigy (Marienberg) and were used as received. The solvent cyclohexane (C. Erba, Milano) was dried with molecular sieves prior to use.

The ligand AZP can be prepared by literature methods [3, 8]. The following procedure has been employed: 2-aminopyridine (5 g) was dissolved in cold water. Sodium hypochlorite (400 ml, 8 wt.%) cooled in salt-ice bath was then added. Rapid stirring and cooling for 10 min gave a deep red solution which was immediately extracted with diethyl ether. The extract was dried with anhydrous sodium sulphate, filtered and the solvent evaporated to give a brown oil. The oil was treated with petroleum ether and orange needles from the solution crystallized. M.P. 55–58 °C, uncorrected, lit. 81 and 85 °C [2a, 3] (yield 22%). This difference in observed and reported melting points will be discussed below. The purity of the ligand was first checked by elemental analysis %found (calcd.): C 64.99 (65.22); H 4.51(4.35); N 30.49(30.43). Moreover, the crude product submitted to T.L.C., with

TABLE I. Analytical Data Found (Calcd) %.

Compound[a] (colour)	M.p. (°C)	C	H	N
$SnCl_4 \cdot AZP$ (yellow)	150(dec.)	27.12 (27.01)	2.01 (1.81)	12.73 (12.60)
$SnBr_4 \cdot AZP$ (orange)	180(subl.)	19.48 (19.29)	1.52 (1.30)	9.18 (9.00)
$MeSnCl_3 \cdot AZP$ (yellow)	220	31.14 (31.23)	2.71 (2.61)	13.03 (13.21)
$MeSnBr_3 \cdot AZP$ (yellow)	190(dec.)	23.56 (23.69)	1.93 (1.99)	10.08 (10.05)
$Bu^nSnCl_3 \cdot AZP$ (yellow)	137–140	35.47 (35.06)	3.58 (3.67)	11.77 (12.01)
$Oct^nSnCl_3 \cdot AZP$ (yellow)	118–125 (dec.)	40.78 (41.38)	4.69 (4.82)	10.59 (10.72)
$Me_2SnCl_2 \cdot AZP$ (orange)	125–130	36.06 (35.49)	3.60 (3.49)	14.09 (13.87)
$Me_2SnBr_2 \cdot AZP$ (orange)	133–138	28.97 (29.25)	3.05 (2.86)	11.13 (11.37)

[a]AZP is 2,2'-azopyridine, Fig. 1.

ethyl acetate 95% and methanol 5% as eluent, has shown a single spot with $R_f \sim 0.47$.

The tin and organotin adducts were prepared by mixing equimolar cyclohexane solutions of the reagents under stirring and by filtering off the resulting yellow or orange solids. Analytical data are summarized in Table I.

Infrared spectra have been obtained using Perkin-Elmer Mod. 457, 580 and 983 I.R. spectrometers in the 4000–200 cm^{-1} region on nujol or hexachlorobutadiene mulls between CsI disks as well as in the range 400 to 4800 cm^{-1} on nujol mulls of the samples confined between KBr disks using an IBM Instrument IR/32 Fourier transform spectrometer. In the latter spectra, 100 interferometer scans were coadded, using a 2 cm^{-1} resolution, and ratioed against a KBr blank. Good agreement was observed between the spectra obtained using the dispersive and the interferometer based instrumentation. Relevant bands are listed below (s = strong; m = medium; w = weak, bd = broad; sh = shoulder). Some reasonable assignments are in parentheses, while absorptions due to the coordinated ligand are underlined. In the spectrum of free AZP, the underlined frequencies correspond to values reported in the literature (see *e.g.* [6, 7]).

AZP: 3319w,bd; 3164w,bd; 3100–3000 group of bands; 1645m; 1598m; <u>1579s</u>; 1560m; 1489m; 1460s; 1440m; <u>1425s</u>; 1329w; 1264m; 1220w; 1143w; <u>1096m</u>; 1038m; <u>992s</u>; 960m; 905w; 895w; 863w; 840w; <u>799vs</u>; 778m; <u>739vs</u>; 725sh; <u>626m</u>; 575w; 560m, 527m; 438m; <u>409m</u>.

SnCl$_4$AZP: 3417w,bd; 3336w,bd; 3220–3080 group of bands; 1663m,s; 1627m; 1606m; <u>1586m</u>, 1496m; 1466m,s; 1446s; 1436s; <u>1425m</u>; 1379w;

1323m,w; 1313m; 1290w; 1219m; 1184w; 1160w; 1156w; <u>1100m,w</u>; 1049m; 1023s; <u>994m</u>; 975w; 955w; 906w; <u>795vs</u>; 783m; 745sh; <u>741m,s</u>; 705w; 645m; <u>624w</u>; 580w; 563w; 544w; 515w,bd; 480w,bd; <u>428m</u>; <u>415w</u>; 395w; 337vs,bd $\nu(SnCl_n)$; 310m, sh $\nu(SnCl_n)$.

SnBr$_4$AZP: The spectrum is similar to that of SnCl$_4$AZP in the 4000–350 cm^{-1} region.

MeSnCl$_3$AZP: 3100–2900 group of bands; 1663w; 1605m; <u>1584s</u>; 1580sh; 1497m; 1468s; 1448vs; <u>1439vs</u>; 1312m; 1218s; 1185w; 1175w; 1157s; <u>1100s</u>; 1049m; 1021s; <u>995s</u>; 953w; 916w; <u>800vs</u>; 790vs; 777s; <u>744s</u>; 730m; 722m; 645s; <u>623m</u>; 562m; 547m $\nu(Sn-C)$; <u>434m</u>; <u>411w</u>; 377w; 283vs, bd $\nu(SnCl_n)$; 260m $\nu(SnCl_n)$.

MeSnBr$_3 \cdot$AZP: The spectrum is similar to that of MeSnCl$_3 \cdot$AZP in the 4000–350 cm^{-1} region.

Bu^{n}SnCl$_3$AZP: 3400–2900 group of bands: 1665s; 1625m,bd; 1605m; <u>1582m</u>; 1543w; 1501w; 1467s; 1450sh; <u>1444s</u>; <u>1415m</u>; 1382m; 1340m; 1321m; 1312m; 1222s; 1180w; 1161m; 1140m; <u>1105w</u>; 1091w; 1080w; 1044m; 1022s; 1013m; <u>994m</u>; 974w; 950w; 924w; 872w; 848w; <u>796vs</u>; 765s; <u>747s</u>; 728m; 720m; 690m; 642m,s; <u>623m</u>; 600w; 581w; 560m; 545m; 512w; <u>439m</u>; <u>405w</u>; 287vs,bd $\nu(SnCl_n)$; 257s, bd $\nu(SnCl_n)$.

Oct^{n}SnCl$_3 \cdot$AZP: 3400–2850 group of bands; 1659s; 1606m; <u>1585m,s</u>; 1565w; 1545w; 1505w; 1468vs; 1450s; <u>1436vs</u>; <u>1420m</u>; 1379m; 1327m; 1310m; 1225s; 1155s; 1140w; <u>1105w</u>; 1094w; 1049m; 1025m; <u>995m</u>; 970w; 955w; 910w, <u>799vs</u>; 790m; 771m; <u>742s</u>; 725m; 687m; 642m; <u>624m</u>; 605w; 585w; 560m; 548m; <u>434m</u>; <u>411m</u>; 286s, bd $\nu(SnCl_n)$.

Me$_2$SnCl$_2 \cdot$AZP: 3060–2920 group of weak bands; 1595sh; <u>1589m,bd</u>; 1511w; 1480w; 1461m; 1451m; <u>1439s</u>; 1405sh; 1310m; 1300sh; 1222m,bd; 1152m; <u>1090m</u>; 1050sh; 1042m; 1004m,s; 993m; 940w; 895w; <u>799vs</u>; <u>743s</u>; <u>631m,s</u>; 624sh; 578m $\nu(SnC_2)_{as}$; 572m; 554m; 544m $\nu(SnC_2)_s$; 513w; <u>420m</u>; <u>410w</u>; 296s,bd $\nu(Sn-Cl_2)_{as}$; 253s,bd $\nu(SnCl_2)_s$.

Me$_2$SnBr$_2 \cdot$AZP: The spectrum is nearly similar to that of Me$_2$SnCl$_2 \cdot$AZP except for Sn–Cl vibrations. A few slight differences are noted near 1000 and 800 cm^{-1} perhaps due to a different resolutions of the spectrum. A single absorption at 998 cm^{-1} is present in Me$_2$SnBr$_2$AZP in place of the two bands (1004 and 993 cm^{-1}) in the chloride. Three bands at 810m, 799s and 785s respectively are present in Me$_2$SnBr$_2$AZP in place of a single absorption (799 cm^{-1}) in the chloride derivative. In the range 600–400 cm^{-1} the following absorptions are present: 574m, $\nu(SnC_2)_{as}$ + ligand; 551 m $\nu(SnC_2)_s$ + ligand; 513w; 418m.

Variable temperature ^{119}Sn Mössbauer effect spectra have been obtained using the spectrometers described previously [1a, 9]. Data reduction was effected using a matrix inversion least squares fitting

TABLE II. Mössbauer Data of AZP Adducts.

Compound[a]	M.W.	I.S.[b] (mm sec^{-1}, ±0.01)	Q.S.[b] (mm sec^{-1}, ± 0.01)	$-d\ln A/dT$[c] ($\times 10^{-2}$ K^{-1}, ±0.05)
SnCl$_4$·AZP	444.70	0.39	–	1.33
SnBr$_4$·AZP	622.53	0.57	–	1.14
MeSnCl$_3$·AZP	424.29	1.01	1.83	1.10
Bu^{n}SnCl$_3$·AZP	465.36	1.13	1.80	1.27
Oct^{n}SnCl$_3$·AZP	522.48	1.23	1.77	1.49
MeSnBr$_3$·AZP	557.66	1.18	1.71	1.21
Me$_2$SnCl$_2$·AZP	403.87	1.48	3.80	2.10
Me$_2$SnBr$_2$·AZP	492.78	1.59	4.06	1.97

[a]Ligand code as in Table I.   [b]Isomer shift with respect to R.T. Ca^{119}SnO$_3$, and nuclear quadrupole splitting, both at liquid N$_2$ temperature. These parameters are independent from temperature in the ranges of Fig. 3.   [c]'A' = total area under the resonant peaks normalized to the liquid N$_2$ value. 'A' is proportional to the recoil free fraction f$_a$, see [9].

routine. The samples typically contained ~7 × 10^{17} ^{119}Sn atoms per square centimeter and comprised optically 'thin' samples (*i.e.*: t = nσ_of$_a$ ≅ 1.5) so that no saturation corrections were applied to the data, even at the lowest temperatures used in the present study. All isomer shifts are reported with respect to the center of a BaSnO$_3$ absorber spectrum obtained at 295 ± 2 K using the same ^{119}Sn Mössbauer source. Spectrometer calibration was effected using the magnetic hyperfine splitting of metallic iron at 295 ± 2 K. The results of these spectroscopic studies are summarized in Table II.

Results and Discussion

The AZP ligand, obtained as the stable trans isomer [2], exhibits ν(N=N) at about 1500 cm^{-1}, Raman active [6]; in trans azobenzene, ν(N=N) is located at 1419 cm^{-1} in Raman [10]. This ligand can be regarded as 2-substituted pyridine, and extensive infrared correlations have been made in this context [3, 6 and refs. therein]. Pertinent literature on vibrational spectra of AZP and its complexes [6, 7] employs the notation of the normal vibrations of benzene [11a], extended to pyridine and related compounds [11b]. In the AZP spectrum here reported (see Experimental), as well as in the spectra of a series of samples of AZP prepared in our laboratory during the present research, all relevant literature bands in the range 1600–400 cm^{-1} have been detected. There are many other absorptions, which may correspond to several spectral data of pyridine [11b]; some other bands seem to be overtones, *e.g.* the 1645 and 1595 cm^{-1} absorptions, not cited in Refs. [6] and [7], which may be corresponding to pyridine combination bands at 1627 and 1593 cm^{-1} [12]. These fact, in conjunction with replicated analytical and T.L.C. measurements, strongly indicate the purity

of our AZP samples despite the fact that their M.P. differ from literature values (see Experimental).

Bands of the coordinated ligand in Me$_2$Snhal$_2$-AZP, AlkSnhal$_3$AZP and Snhal$_4$AZP, for the ring modes (in the middle frequency range) selected in [6] and [7], are generally doubled, one band being nearly coincident with the corresponding one of the free ligand and the other occurring at a higher frequency (*e.g.*, bands at 1579, 1425, 626 and 409 cm^{-1} of free AZP). This is analogous to results reported for some Mhal$_2$(AZP)$_2$ complexes [3, 6, 7], where the data have been interpreted in terms of coordination by one only pyridine moiety. In fact, some pyridine ring modes have been observed to shift to higher frequency upon complex formation [12]; moreover, coordination of pyridine to metal centres may be regarded as a halfway step to protonation, and in the latter case pyridine vibrations increase in energy [11]. The same bonding could accordingly be assumed for our complexes, as far as the interaction with the AZP ligand is concerned, especially for the pyridine modes. As far as the possible further coordination by a nitrogen atom of the azo group of the AZP is concerned, it must be taken into account that ν(N=N) is infrared inactive in the free ligand while occurring around 1500 cm^{-1} in the infrared spectrum of AZP chelating through pyridine and azo nitrogen atoms [6]. In our AZP complexes, this mode has not been identified, probably due to the presence of the ligand band at 1489 cm^{-1} (which corresponds to ν_{19a} of pyridine at 1482 cm^{-1} [11b]), so that no definite conclusion may be extracted in the present context from the vibrational spectroscopic data.

The bands at about 1625 and 1660 cm^{-1} in the spectra of AlkSnhal$_3$AZP and Snhal$_4$AZP require additional comments. These bands have not previously been discussed for metal–AZP complexes [3, 6, 7]; they may correspond to combination

bands of the free ligand (see the preceding), at least for the $MeSnCl_3$ derivative, and appear also in pyridine complexes as low intensity absorptions. However, these pyridine bands occur at a consistently lower frequency [12] (a band at 1660 cm^{-1} is also cited [12]). In the case of Bu^nSnCl_3, Oct^nSnCl_3, and $Snhal_4AZP$ complexes these bands at 1660 cm^{-1} are very strong and cannot be attributed with any certainty to ligand combination bands as far as their appearance is concerned; no reasonable assignments seem to be possible in the present context.

In the 600–200 cm^{-1} region the occurrence of Sn–C, Sn–hal and Sn–N vibrational modes is expected. The $\nu(SnC_n)$ modes are difficult to assign unambiguously due to the presence of ligand bands, e.g. at 575, 560, 527 cm^{-1} (which are not pyridine bands [11], and have not been previously discussed for AZP [3, 6, 7]). Concerning the band intensities, it seems quite probable that both $\nu(SnC_2)_{s,as}$ vibrations are present in Me_2Snhal_2AZP spectra (see Experimental, this paper). In this context it should be noted that additional data obtained for samples from a series of different synthetic batches, and measured by different spectrometers (including both dispersive and FTIR instruments) have yielded essentially identical results, indicating that the CSnC bond angle appears to be non linear in the latter complex (see later in this paper). The $SnCl_n$ vibrations appear as double broad bands below 350 cm^{-1} for all adducts; it does not seem possible to infer configurations of $SnCl_n$ groups from these data, although a cis-Cl_2 structure is suggested for Me_2SnCl_2AZP complex (see Experimental; further spectra on different samples gave same results). Finally, no bands attributable to $\nu(SnN)$ modes have been identified with reasonable certainty, presumably being obscured by the broad intense $SnCl_n$ modes.

Structural informations can be extracted from the Mössbauer spectra primarily from the isomer shifts, I.S., and quadrupole splitting, Q.S., hyperfine interaction parameters which are summarized in Table II. For all of the compounds reported in the present study, the I.S. is typical of quadrivalent tin in inorganic and organometallic compounds, and lies in the range 0.39 to 1.59 mmsec^{-1}, the exact value depending on both the coordination number and the nature of the ligands bonded to the metal atom. The two $Snhal_4$ adducts of AZP show isomer shifts which are less positive by 0.45 (hal = Cl) and 0.56 (hal = Br) mmsec^{-1} than that observed for the corresponding $Snhal_4$ compounds [13], indicating a decrease in the s-electron density on going from the four- to the six-coordinated species, and is consistent with a decrease in the bond covalency (Sn–hal) on AZP coordination.

The ^{119}Sn Mössbauer spectra of the two $Snhal_4$-AZP complexes show a single broad resonance

maximum, having a full width at half maximum of 1.40 ± 0.05 mmsec^{-1}, indicative of an unresolved quadrupole hyperfine interaction of approximately 0.4 mm sec^{-1}. This hyperfine interaction is due to a distortion from ideal O_h symmetry in the adducts and can arise from two probable contributions. The first of these is related to the differences in the electron withdrawing properties of AZP compared to halide, which causes a non negligible rehybridization of the six sp^3d^2 orbitals used by the tin atom in achieving a six-coordinate structure. The second contribution from ideal O_h symmetry of the charge distribution around the metal atom can originate in the steric demand of the AZP ligand, which causes the N–Sn–N' 'bite angle' to deviate from 90° and thus distorts the geometry of the other ligands attached to Sn from an ideal six-coordinate structure. Both of these effects are likely to be present in the AZP complexes under discussion and the available spectroscopic data do not permit individual evaluation of these effects which must ultimately be achieved by a single crystal X-ray diffraction study of these materials.

The ^{119}Sn Mössbauer spectra of the organotin AZP complexes all show the characteristic doublet structures associated with molecules having a symmetry lower than O_h or T_d, with one or more tin–carbon bonds. The full width at half maximum of these resonance absorptions are approximately 0.85 to 0.92 mm sec^{-1} and are characteristic of a single metal atom site in the structure. A typical spectrum is shown in Fig. 2 from which it is noted that the two components of the resonance doublet have different intensities (the ratio of the area under the two resonance maxima does not correspond to unity). This intensity asymmetry, which is designated as R = A(+)/A(−), where A(+) and A(−) are the areas under the component at velocities greater and lesser than the spectrum centroid, respectively, can arise from two major sources: (a) crystal orientation effects, and (b) vibrational anisotropy effects. The first of these arises from the accidental preferred orientation of the sample crystallites with respect to the optical axis of the Mössbauer spectrometer, and is temperature independent. The second contribution to R (the so-called Gol'danskii-Karyagin Effect) arises from a dependence of the recoil-free fraction on the angle between the direction of the gamma ray absorption and the molecular symmetry axis (or, more accurately, the direction of the principal field gradient axis), and is a temperature dependent quantity which should approach unity in the low temperature limit.

With respect to the three $AlkSnCl_3AZP$ compounds reported in the present investigation, the intensity asymmetry is essentially temperature independent for Alk = CH_3 but has a pronounced thermal coefficient for Alk = C_4H_9 and C_8H_{17} as is
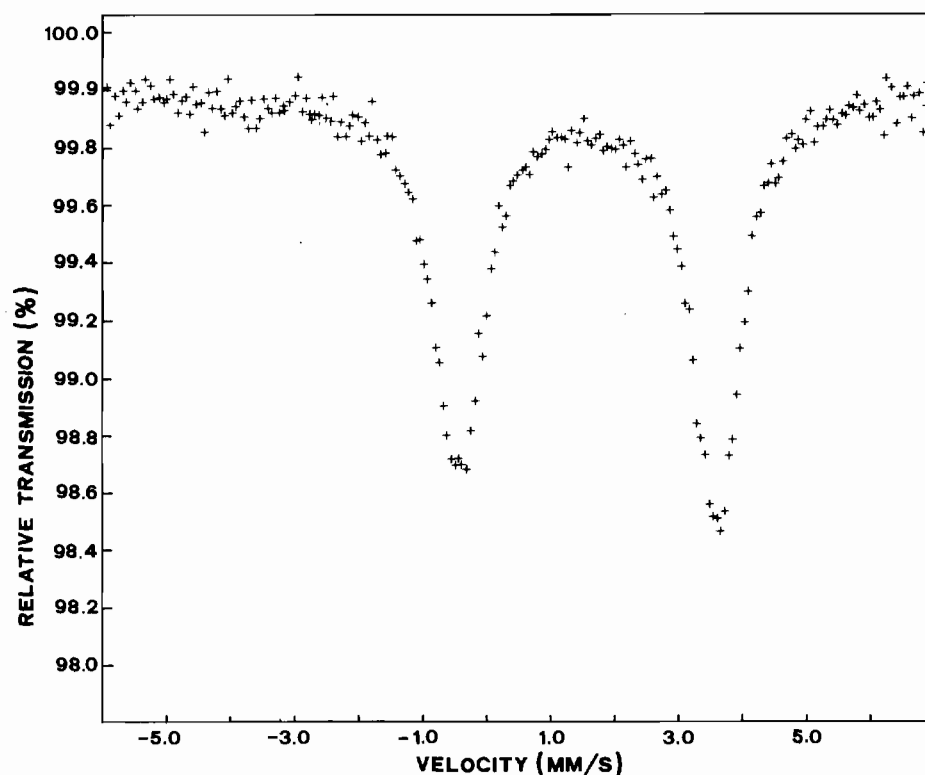
Fig. 2. Mössbauer spectrum, at liquid N_2 temperature, of $Me_2SnBr_2 \cdot AZP$. The asymmetry of the two components of the resonance doublet is evidenced.
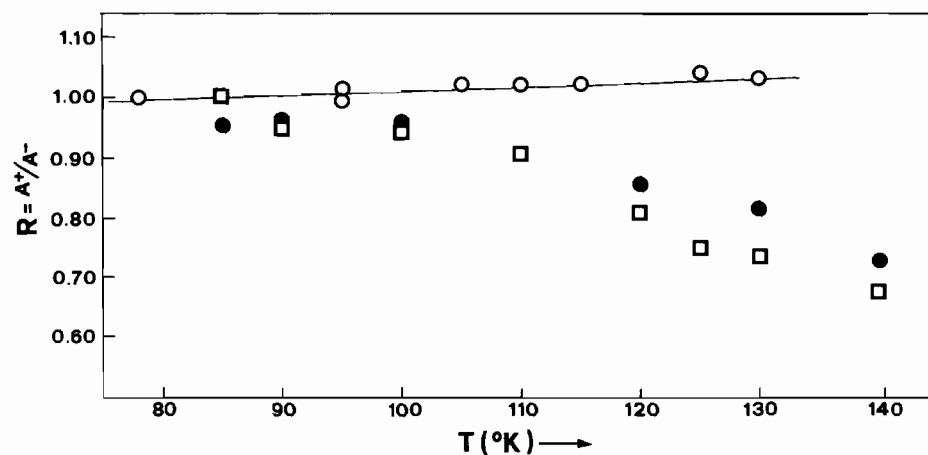
Fig. 3. Temperature dependence of $R = A(+)/A(-)$ for $AlkSnCl_3 \cdot AZP$. o = $MeSnCl_3 \cdot AZP$; • $Bu^nSnCl_3 \cdot AZP$; □: $Oct^nSnCl_3 \cdot AZP$.

summarized graphically in Fig. 3. Since, as will be discussed more fully below, all of the organotin AZP complexes are believed to be monomeric in the solid state, the temperature dependent intensity asymmetry must be related to the amplitude of the vibrational motion of the metal atom parallel and perpendicular to the Sn—C bond. Contrary to a priori expectation, this vibrational anisotropy is larger for the larger organic groups (and experi-

mentally unobservable for the methyl derivative) and thus must be related to the stacking of the molecules in the solid and the influence of the steric requirements of the alkyl moiety on the vibrational motion of the metal atom.

The Q.S. interaction in the three $AlkSnCl_3AZP$ compounds are the same within experimental error (± 0.03 mmsec^{-1}), and independent of the nature of the alkyl group. This observation is
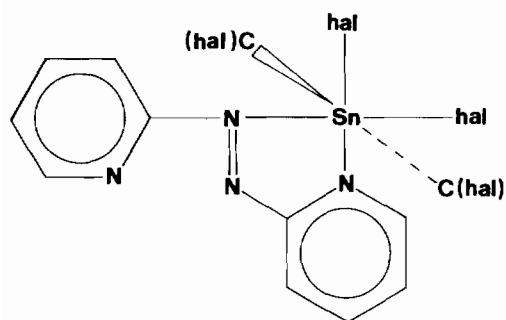
Fig. 4. The proposed configuration of 2,2'-azopyridine adducts. **Ia**: AlkSnhal$_3$·AZP, fac-hal$_3$; **Ib**: AlkSnhal$_3$·AZP, mer-hal$_3$; **Ic**: Me$_2$Snhal$_2$·AZP, trans-Me$_2$.

Fig. 5. The I.R. spectra of (a): 2,2'-azopyridine; (b): Me$_2$-SnCl$_2$·AZP; (c): Me$_2$SnBr$_2$·AZP.

consistent with literature values [14] which show that the contribution of alkyl groups to the electric field gradient tensor are identical regardless of the length of the alkyl chain. It is, however, interesting to note that the Q.S. for MeSnBr$_3$AZP is ~0.12 mmsec^{-1} smaller than that for corresponding chloride compound, consistent with the smaller electronegativity of the bromide as compared to the chloride ligand, leading to a slightly more symmetrical charge distribution about the metal atom in the former compared to the latter.

The magnitude of the Q.S. interactions in the AlkSnhal$_3$AZP compounds are all consistent with a six-coordinate structure, which in principle can be of one of two types, *e.g.* the alkyl group can be co-axial with one of the halogens (**Ia**) or with one of the two nitrogen atoms of the AZP ligand (**Ib**) (see Fig. 4) giving in either case a molecule which (ignoring the asymmetry of the AZP ligand itself) has only a mirror plane element of molecular symmetry. In the absence of a single crystal X-ray diffraction study it is not possible, on the basis of the presently available data, to decide between the two above possibilities.

Turning next to the two diorganotin(IV) AZP complexes, Table II, these differ in two major ways in their Mössbauer parameters from their mono-organotin(IV) homologues. The I.S. increases by ~0.4 mmsec^{-1} on replacement of a Sn–hal bond by a Sn–C bond. Since the latter is appreciably more covalent than the former, the increased s-electron density of the metal atom nucleus is clearly a consequence of the greater covalency of the metal–carbon bonding interaction compared to the metal–halogen bond, which increases the overlap between the sigma bond of the ligand and the sp^{3}d^2 hybrid orbital of the metal.

It is also noted that the Q.S. interaction observed for the two diorganotin(IV) complexes is approximately twice as large as that observed in the spectra of the monoalkyl compounds and is unambiguously indicative of a trans octahedral configuration of the
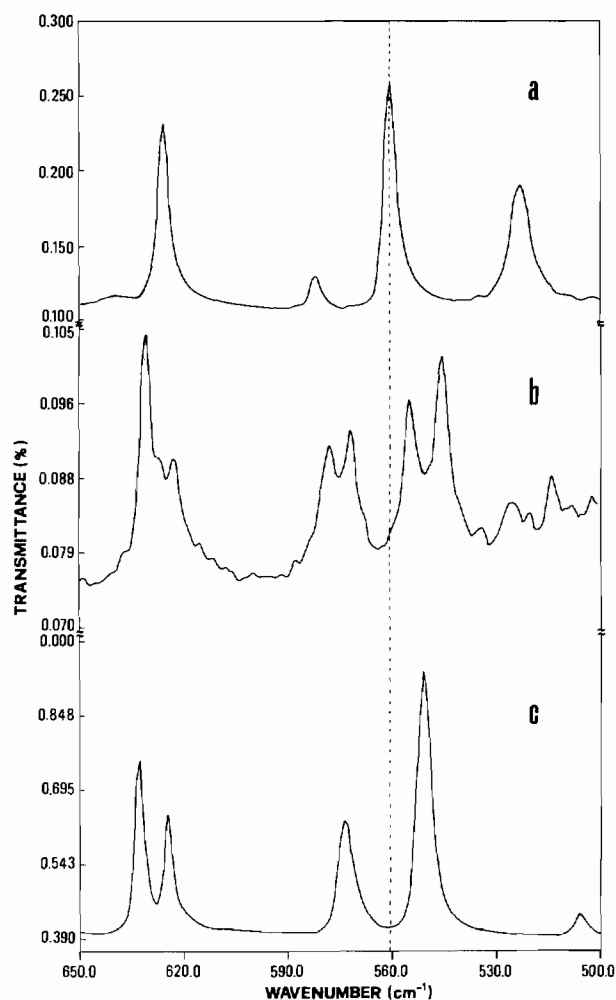
two organic groups in the former, as shown in structure **Ic** (Fig. 4).

Finally, it is of interest to comment on the temperature dependence of the recoil-free fraction as elucidated from the temperature dependence of the area under the resonance curve, as summarized in Table II. It is noted from these data that d lnA/dT is appreciably larger for the Me$_2$Snhal$_2$AZP compounds than for the other members of the series here reported, indicating a larger mean square amplitude of vibrations of the metal atom in those compounds where the organic groups occupy trans axial position. This softening of the solid as halogens are replaced by organic groups is consistent with the observation, referred to above, that a Gol'danskii-Karyagin asymmetry is observed for the larger alkyl groups, but not when Alk = CH$_3$, for the mono-organotin(IV) complexes. In the case of the diorgano-tin(IV) complexes, replacing two of the equatorial chlorine atoms by the heavier bromine ligands again permit the eduction of a temperature dependent

intensity asymmetry from the ^{119}Sn Mössbauer data. Because of the relatively large temperature dependence of the recoil-free fraction, the accessible temperature range over which the Mössbauer effect can be observed in these compounds is severely limited. Under these conditions the vibrational asymmetry can just be extracted from the data for Me₂SnBr₂-AZP, but not for the corresponding chlorine homologue. These results are again indicative of a *trans* octahedral structure of the two organic groups in these molecules.

The structural inferences extracted from the Mössbauer spectroscopic data for Me₂Snhal₂AZP are confirmed by the infrared spectra for these compounds which are summarized in Fig. 5 for the spectral range 500 to 650 cm^{-1}. The most intense band due to the uncoordinated ligand in this region is observed at 560 cm^{-1}, with somewhat weaker absorptions at ~627 and 523 cm^{-1} and a very weak band at ~580 cm^{-1}, Fig. 5a. In Me₂SnCl₂AZP the intense AZP ligand band is symmetrically split into a doublet, accompanied by two bands which arise from $\nu(SnC_2)_s$ and $\nu(SnC_2)_{as}$ vibrations, giving rise to a quartet of absorptions, Fig. 5b. In Me₂SnCl₂ infrared spectra the two tin–carbon vibrations are observed at 520 and 571 cm^{-1} so that it is probable that the absorptions at 544 and 578 cm^{-1} correspond to $\nu(SnCl_2)_s$ and $\nu(SnC_2)_{as}$ respectively, while the 554 and 572 cm^{-1} absorptions reflect the lifting of the degeneracy of the band observed at 560 cm^{-1} in AZP. This assignment is reasonable in view of the known bonding interaction between AZP and Sn(IV) compounds in which one coordination site is occupied by a ring nitrogen atom, while the other is occupied by one of the azo nitrogen atoms of the ligand, Fig. 4.

The infrared spectrum observed in this region for the Me₂SnBr₂AZP complex (Fig. 5c) shows only two absorption maxima at 551 and 574 cm^{-1}. This observation can be understood on the basis of an accidental degeneracy between the lower frequency ligand mode and $\nu(SnC_2)_s$ at 500 cm^{-1} and between the higher frequency ligand mode and $\nu(SnC_2)_{as}$ at 574 cm^{-1}. Thus, the absorption envelope between 530 and 590 cm^{-1} in the spectrum of Fig. 5b and c is actually that of a quartet of absorption bands (as in the case of the chloride complex) in which the accidental degeneracy superimposes two of the bands in each case.

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