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THE EFFECT OF SOLVENT UPON THE RATES AND MECHANISMS OF ORGANOMETALLIC REACTIONS

III. NQR SPECTRA AND STRUCTURES OF MOLECULAR COMPLEXES OF METHYLTIN HALIDES AND TIN TETRAHALIDES

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SUMMARY

NQR spectra have been obtained for molecular complexes of methyltin halides or tin tetrahalides containing various electron-donating molecules. The structures have been shown to be a function of the number of methyl groups and halogens present in the methyltin halides and of the nature of the electron donor. An anomalous temperature dependence of the NQR frequencies has been observed in some cases.

INTRODUCTION

The reported structures of organotin complexes[1] and the elemental analyses of methyltin halides complexed with various electron donors[2] suggest that trialkyltin halides form $R_3SnX\cdot L$ complexes with monodentate ligands and $2R_3SnX\cdot L$ complexes with bidentate ligands, whereas dialkyltin dihalides, alkyltin trihalides and tin tetrahalides form $R_nSnX_{4-n}\cdot 2L$ complexes with monodentate ligands and $R_nSnX_{4-n}\cdot L$ complexes with bidentate ligands.

It has been demonstrated[3,4] that the technique of nuclear quadrupole resonance (NQR) spectroscopy is quite promising for the study of molecular complexes of metal halides since NQR frequencies are very sensitive to the electron-density distribution in the molecule. NQR spectra of such complexes reflect, firstly, the extent of charge transfer and, secondly, the arrangement of the halogen atoms in the complex. We have used NQR spectroscopy to study molecular complexes of methyltin halides prepared as described previously[2] thus extending such studies of Sn–Hal bonds[5-8].

RESULTS AND DISCUSSION

1. Complexes of the type $Me_3SnBr\cdot L$ and $2Me_3SnBr\cdot L$

Table 1 contains the ^{81}Br and ^{79}Br NQR parameters for Me_3SnBr and its molecular complexes while Fig. 1 is a schematic representation of the spectra ob-

TABLE 1

^{81}Br AND ^{79}Br NQR SPECTRA OF Me_3SnBr COMPLEXES

System	*Temp.* (K)	$\nu(^{81}Br)$ (*MHz*)	*Signal/noise ratio*	$\nu(^{79}Br)$ (*MHz*)	$\nu_{av}(^{81}Br)$ (*MHz*)	$\delta(\nu_\chi)^a$ (%)
Me_3SnBr	77	93.50	100	111.92	93.50	
	293	95.47	30	114.29	95.47	2.1
$Me_3SnBr\cdot DEE$	77	89.28	20	106.90	89.28	4.5
$2\ Me_3SnBr\cdot$dioxane	77	82.53	50	98.78	82.53	11.7
$Me_3SnBr\cdot Me_2CO$	77	79.95	10	95.74	80.85	13.5
		81.75	10	97.89		
$Me_3SnBr\cdot DME$	77	79.86	50	95.51	76.86	14.6
$Me_3SnBr\cdot THF$	77	76.48	10	91.55	76.48	18.2
$Me_3SnBr\cdot DMF$	77	67.34	50	80.64	67.34	28.0
	293	70.25	10	84.12	70.25	24.9
$Me_3SnBr\cdot HMPT$	77	64.87	50	77.64	64.87	30.6
$Me_3SnBr\cdot Py$	77	62.57	30	74.91	61.46	34.3
		62.28	30	74.55		
		59.54	30	71.27		
	293	65.26	10	78.15	65.26	30.2
$Me_3SnBr\cdot DMSO$	77	56.32	30	67.42	56.32	39.8
$2\ Me_3SnBr\cdot TMED$	77	55.02	30	65.87	55.02	41.1

[a] $\delta(\nu_\chi) = \dfrac{\nu_{av}(\chi) - \nu(Me_3SnBr)}{\nu(Me_3SnBr)} \times 100$ represents the shift with respect to Me_3SnBr.

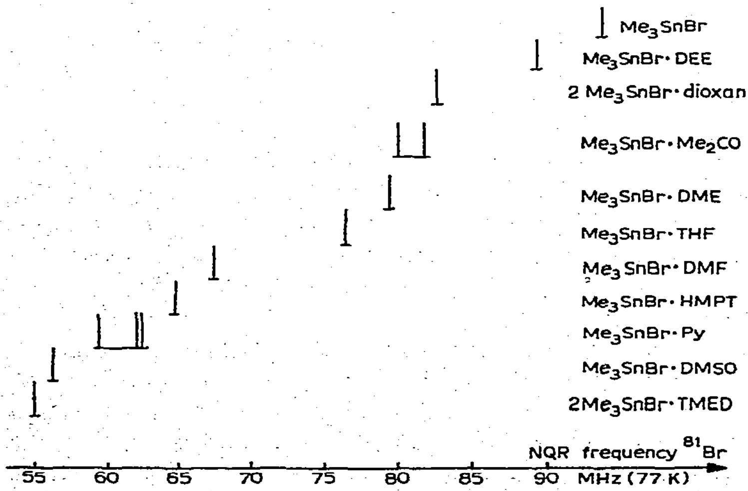
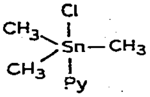


Fig. 1. ^{81}Br NQR spectra of Me_3SnBr complexes.

tained. Generally, the spectra consist of one line which demonstrates the existence of one crystallographically independent molecule in the elementary cell. The splittings in the spectra of $Me_3SnBr\cdot Me_2CO$ and $Me_3SnBr\cdot Py$ are low, indicating that they are of a crystallographical nature, as is verified by the fact that the splittings vanish at room temperature.

The shape of the NQR spectrum of Me_3SnBr solution in DME depends on the ratio of components present. At a ratio of 1/1, one line is observed (Table 1, Fig. 1) which may be characteristic of the donor strength of the DME oxygen with respect to Me_3SnBr. At a ratio of 2/1, additional lines appear [$\nu(^{81}Br)$ 89.28; $\nu(^{79}Br)$ 106.90] which are difficult to assign in an unambiguous manner.

The Townes–Dailey model[9] assumes that the halogen NQR frequency is a function of the order of the M–Hal bond, of its ionic character and of the extent of halogen *sp*-hybridisation. For the compounds studied here, it is not unreasonable to assume that the double-bond contribution is insignificant while the halogen *sp*-hybridisation is low and invariable. If this is the case, then the variation in the NQR frequency caused by complex formation may be attributed to the variation in the ionic character of the bond. Our data demonstrate that the bromine resonance frequencies in all the compounds studied are lower than those in solvent-free Me_3SnBr, and that this may be attributed to a greater ionic character of the Sn–Br bonds in the complexes compared with those in the solvent-free species. This conclusion agrees well with IR spectra recorded for solutions of Me_3SnHal[10,11] and with X-ray data[12] which reveal that $Me_3SnCl \cdot Py$ is a trigonal bipyramid (I) with the Sn–Cl bond longer than that in gaseous Me_3SnCl[13].



(I)

The complexes are donor–acceptor in character with the coordinating ligand being the donor, while the halogen NQR frequency shift is proportional to the charge transferred[3,4]. For this reason the bromine frequency shift may be a measure of the variation in the donor activity of the ligands. NQR data show that complexes of the type $Me_3SnBr \cdot L$ exhibit the following series of donor activity for monodentate ligands:

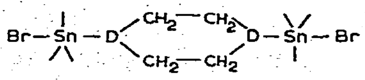
DEE < acetone < THF ⩽ DMF < HMPT < Py < DMSO

For bidentate ligands, the following series applies:

dioxane < DME ⩽ TMED

Since structure (II) (only one donor atom per Me_3SnBr molecule) may be expected for Me_3SnBr complexes containing bidentate ligands, the following series may be constructed to describe the donor activities of ligands with respect to Me_3SnBr:

DEE < dioxane < acetone < DME < THF ⩽ DMF < HMPT < Py <
DMSO < TMED



(II)

The first five ligands in the series are weak donors while the remaining five are strong donors.

II. Complexes of the type $Me_2SnHal_2 \cdot 2L$ and $Me_2SnHal_2 \cdot L$

Five structures (see Fig. 2 and the spectra expected for them) may be assumed for octahedral complexes of dimethyltin dihalides containing two monodentate ligands or one bidentate ligand.

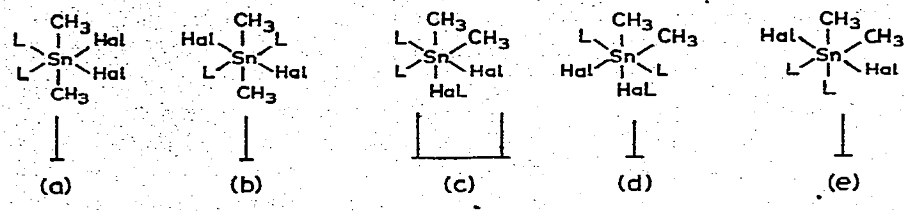


Fig. 2.

TABLE 2

^{81}Br AND ^{79}Br NQR SPECTRA OF Me_2SnBr_2 COMPLEXES

System	*Temp.* (K)	$\nu(^{81}Br)$ (*MHz*)	*Signal/noise ratio*	$\nu(^{79}Br)$ (*MHz*)	$\nu_{av}(^{81}Br)$ (*MHz*)	$\delta(\nu_\chi)^a$ (%)
Me_2SnBr_2	77	109.98	100	131.66	110.57	
		111.17	80	133.08		
	293	110.92	45	132.78	111.52	0.8
		112.12	40	134.21		
$Me_2SnBr_2 \cdot$ dioxane	77	104.82	50	125.50	104.89	5.1
		104.96	50	125.65		
	293	105.97	80	126.85	105.97	4.2
$Me_2SnBr_2 \cdot 2THF$	77	99.04	50	118.56	99.04	10.4
$Me_2SnBr_2 \cdot 2Me_2CO$	77	93.72	30	112.16	93.88	15.1
		94.05	30	112.62		
$Me_2SnBr_2 \cdot DME$	77	89.84	40	107.48	89.84	18.7
$Me_2SnBr_2 \cdot 2Py$	77	65.76	20	78.72	65.76	40.5
	293	64.74	5	77.50	64.74	41.4
$Me_2SnBr_2 \cdot 2HMPT$	77	60.61	30	72.57	60.61	45.2
$Me_2SnBr_2 \cdot 2DMF$	77	60.02	20	71.85	60.02	45.7
	293	59.74	5	71.47	59.74	46.0
$Me_2SnBr_2 \cdot 2DMSO$	77	59.46	30	71.20	59.46	46.2

[a] $\delta(\nu_\chi) = \dfrac{\nu_{av}(\chi) - \nu_{av}(Me_2SnBr_2)}{\nu_{av}(Me_2SnBr_2)} \times 100$ represents the shift with respect to Me_2SnBr_2.

In Table 2 are listed the ^{81}Br and ^{79}Br NQR parameters for Me_2SnBr_2 and its molecular complexes while Fig. 3 is a schematic representation of the spectra obtained.

Structure (c) may be ruled out immediately since only singlets or slightly split doublets (crystallographic non-equivalence of the halogens) are observed in all the spectra. On the other hand, the Mössbauer quadrupole splittings found in spectra of the same complexes[14] demonstrate (*cf.* ref. 15) that the CH_3 groups are arranged *trans* in these complexes, *i.e.* the complexes possess either structure (a) or (b) (Fig. 2). The

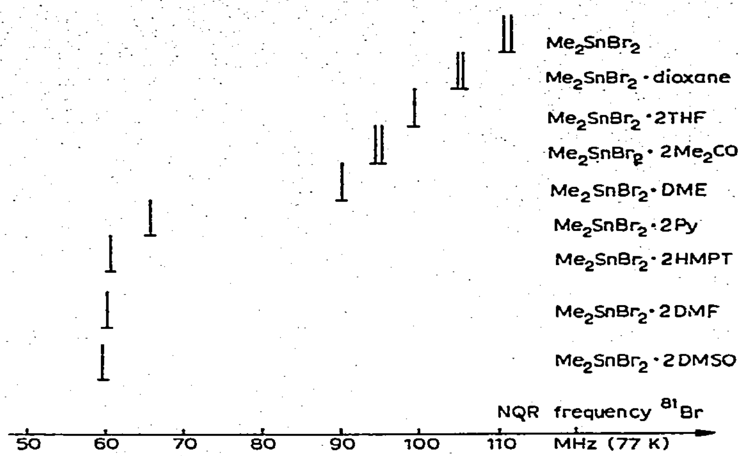


Fig. 3. ^{81}Br NQR spectra of Me_2SnBr_2 complexes.

frequency shifts observed for the bromines with respect to solvent-free Me_2SnBr_2 (Table 2) enable the donors to be subdivided into those which are relatively weak (dioxane, THF, acetone, DME) and those which are stronger (Py, HMPT, DMF, DMSO). The spectrum of $Me_2SnBr_2\cdot$2DEE coincides with the spectrum of solvent-free Me_2SnBr_2 and this may be explained by assuming that the solvent-free species is frozen out of its solution in DEE at 77 K.

Unfortunately, Me_2SnCl_2 is only sparingly soluble in ethers. This, together with the low sensitivity of the instrument in the frequency range employed, has considerably limited the number of $Me_2SnCl_2\cdot$2L complexes examined (Table 3, Fig. 4). The spectrum of solvent-free Me_2SnCl_2, as well as the spectrum of the dioxane complex, consists of a singlet, *i.e.* the complex may be assumed, as for Me_2SnBr_2, to possess either structure (a) or (b) (Fig. 2). On the other hand, the DME complexes (1/1) and, especially, the acetone complexes (1/2) exhibit larger splittings which point to the

TABLE 3

^{35}Cl NQR SPECTRA OF Me_2SnCl_2 COMPLEXES

System	*Temp.* *(K)*	$\nu(^{35}Cl)$ *(MHz)*	*Signal/noise ratio*	$\nu_{av}(^{35}Cl)$ *(MHz)*	$\delta(\nu_\chi)^a$ (%)
Me_2SnCl_2	77	15.46	80	15.46	
	293	15.71	30	15.71	1.6
$Me_2SnCl_2\cdot$dioxane	77	15.09	10	15.09	2.4
	293	15.19	4	15.19	1.7
$Me_2SnCl_2\cdot 2Me_2CO$	77	13.71	5	15.68	2.5
		16.45	5		
$Me_2SnCl_2\cdot$DME	77	13.16	7	13.75	11.1
		14.35	7		

[a] $\delta(\nu_\chi) = \dfrac{\nu_{av}(\chi)-\nu(Me_2SnCl_2)}{\nu(Me_2SnCl_2)} \times 100$ represents the shift with respect to Me_2SnCl_2.

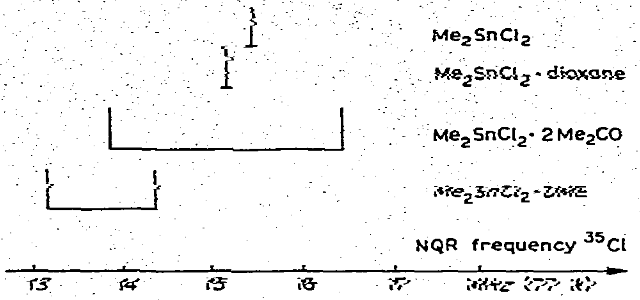


Fig. 4. ^{35}Cl NQR spectra of Me_2SnCl_2 complexes.

non-equivalence of the halogens, *i.e.* structure (c) may be present in this case. For $Me_2SnCl_2 \cdot DME$ the resonance frequencies found for both the chlorines are lower than the frequency observed in solvent-free Me_2SnCl_2 whereas the spectrum of $Me_2SnCl_2 \cdot 2Me_2CO$ exhibits one line at a higher frequency relative to that of the solvent-free compound. This may be explained in terms of the appreciable self-association of solid Me_2SnCl_2, this leading to an increase in the ionic character of the Sn–Cl bond in the resulting associated complex and to a respective decrease in the NQR frequency. This conclusion agrees with X-ray data obtained for crystalline Me_2SnCl_2[16] which indicate that the Sn–Cl bonds in the associated complex are longer than those in gaseous Me_2SnCl_2[13]. The data also demonstrate that DME is a stronger electron donor than acetone in agreement with Mössbauer spectroscopic data on the systems[14].

III. Complexes of the type $MeSnHal_3 \cdot 2L$ and $MeSnHal_3 \cdot L$

Three octahedral structures may be assumed for methyltin trihalide complexes containing two monodentate, or one bidentate, ligand (Fig. 5).

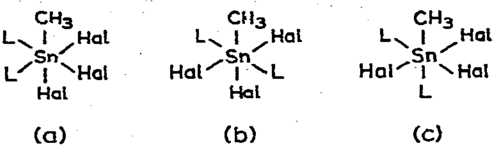


Fig. 5.

Tables 4 and 5 contain the NQR parameters of the complexes studied while Figs. 6 and 7 present schematic representations of the spectra obtained.

The splitting is more than 7% in the spectrum of solvent-free $MeSnBr_3$. This is significantly greater than the values possible for molecular crystals which lie in the range 1.5 to 2%[17]. It is probable that so great a non-equivalence may be explained by assuming that self-association occurs in the solid state leading to the formation of a six-coordinate tin compound. This agrees well with the NQR intensity ratio. Normally, the formation of associated complexes leads to the NQR frequencies of the bridged halogens being lower than those of the terminal halogens[18]. The fact that the intensity of the lower-frequency line is twice the intensity of the higher-

TABLE 4

^{81}Br AND ^{79}Br NQR SPECTRA OF MeSnBr$_3$ COMPLEXES

System	*Temp.* (K)	$\nu(^{81}Br)$ (*MHz*)	*Signal/noise ratio*	$\nu(^{79}Br)$ (*MHz*)	$\nu_{av}(^{81}Br)$ (*MHz*)	$\delta(\nu_x)^a$ (%)
MeSnBr$_3$	77	138.02	20	165.24	141.46	
		148.34	10	177.54		
	293	135.43	20	162.18	139.39	1.5
		143.35	10	171.66		
2MeSnBr$_3$·dioxane	77	124.61	40	149.15	142.54	0.76
		151.50	80	181.32		
MeSnBr$_3$·2THF	77	103.28	10	123.50		17.4
		106.12	10	127.00	116.84	
		141.12	10	168.96		

^{a} $\delta(\nu_x) = \dfrac{\nu_{av}(\chi) - \nu_{av}(\text{MeSnBr}_3)}{\nu_{av}(\text{MeSnBr}_3)} \times 100$ represents the shift with respect to MeSnBr$_3$.

TABLE 5

^{35}Cl NQR SPECTRA OF MeSnCl$_3$ COMPLEXES

System	*Temp.* (K)	$\nu(^{35}Cl)$ (*MHz*)	*Signal/noise ratio*	$\nu_{av}(^{35}Cl)$ (*MHz*)	$\delta(\nu_x)^a$ (%)
MeSnCl$_3$	77	19.43	20	20.24	
		21.85	10		
	293	19.14	6	19.73	2.5
		20.92	3		
MeSnCl$_3$·2DEE	77	20.97	3	21.03	3.9
		21.13	2–1.5		
MeSnCl$_3$·2THF	77	15.36	10		
		15.55	10	17.02	18.9
		20.17	10		
MeSnCl$_3$·dioxane	77	15.95	20		
		16.12	10	17.59	15.1
		16.20	10		
		20.67	20		

^{a} $\delta(\nu_x) = \dfrac{\nu_{av}(\chi) - \nu_{av}(\text{MeSnCl}_3)}{\nu_{av}(\text{MeSnCl}_3)} \times 100$ represents the shift with respect to MeSnCl$_3$.

frequency line reveals that there are two bridged, and one terminal, halogen in each MeSnBr$_3$ molecule. A similar state of affairs exists in MeSnCl$_3$. Thus, the solvent-free methyltin trihalides possess either structure (a) or (b) (Fig. 5), L being the bridged halogen belonging to adjacent molecules. For a five-coordinate tin compound, the intensity ratio would have been opposite to that described above.

The signals for MeSnHal$_3$·2THF and MeSnCl$_3$·dioxane are shifted to lower frequencies relative to those of the spectra of solvent-free MeSnHal$_3$. The more intense signal, which is associated with two halogens, is shifted much further than the one associated with one halogen, *i.e.* the different ligands affect the ionic character of

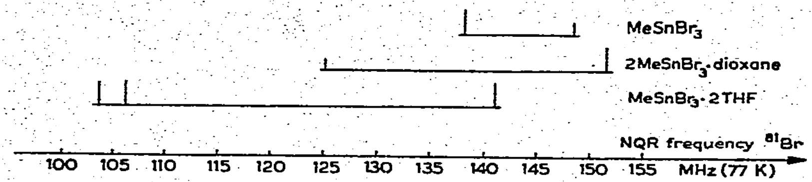


Fig. 6. ^{81}Br NQR spectra of MeSnBr$_3$ complexes.

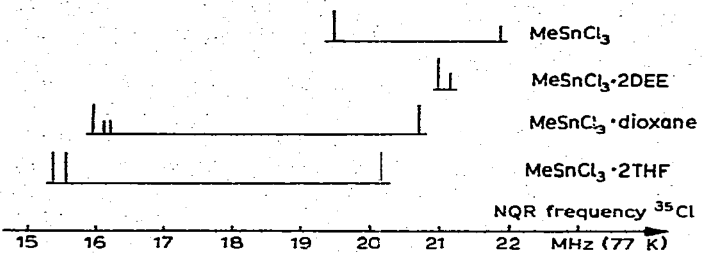


Fig. 7. ^{35}Cl NQR spectra of MeSnCl$_3$ complexes.

the tin–halogen bonds to a different extent. Hence, structure (b), in which all three halogen atoms should be equally affected by the presence of ligands, can be ruled out. For this reason, it is probable that the complexes under discussion possess structure (a). In this structure the total *cis* and *trans* effect of the ligands upon the ionic character of the Sn–Hal bonds lying in the octahedral plane is greater than their respective total *cis* effect upon the ionic character of the tin–halogen bonds associated with the halogens positioned *trans* relative to the methyl groups, *i.e.* the *trans* effect in octahedral complexes of methyltin halides is stronger than the *cis* effect (*cf.* ref. 19). The spectrum of a five-coordinate complex such as 2MeSnBr$_3$·dioxane[2,14] corresponds to that of a trigonal bipyramid with two bromines being located in the plane and one at the apex.

The spectrum of MeSnBr$_3$·2DEE is identical with that of solvent-free MeSnBr$_3$, again because the associated complex of MeSnBr$_3$ is frozen out of its solution in DEE at 77 K. The spectrum of MeSnCl$_3$·2DEE, in which all three halogen atoms are equivalent, may be explained in terms of the monomeric MeSnCl$_3$ being frozen out of solution in DEE at 77 K.

IV. Complexes of the type SnHal$_4$·2L and SnHal$_4$·L (Hal=Br, I)

It has already been shown[20] that SnCl$_4$ complexes containing various donors may possess either structure (a) or (b) below depending on the nature of L. The structures, and the spectra expected for them, are presented in Fig. 8. Calculations show that in structure (b) the electron density localised over the equatorial halogens is

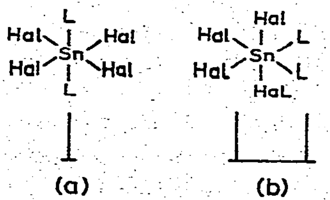


Fig. 8.

greater than that over the axial halogens.

The ^{81}Br and ^{79}Br NQR spectra of $SnBr_4$ complexes and the ^{127}I NQR spectra of SnI_4 complexes containing various mono- or bidentate ligands have been

TABLE 6

^{81}Br AND ^{79}Br NQR SPECTRA OF $SnBr_4$ COMPLEXES

System	*Temp.* (*K*)	$\nu(^{81}Br)$ (*MHz*)	*Signal/noise ratio*	$\nu(^{79}Br)$ (*MHz*)	$\nu_{av}(^{81}Br)$ (*MHz*)	$\delta(\nu_\chi)^a$ (%)
$SnBr_4$ phase I	77	162.03	30	193.96		
		165.21	30	197.77	164.57	
		165.40	30	198.00		
		165.64	30	198.28		
	285.5^b	157.84	10	188.93		
		160.62	10	192.26	160.08	
		160.73	10	192.39		
		161.15	10	192.90		
phase II	77	164.79	100	197.26	164.79	
$SnBr_4 \cdot$DME	77	135.82	10	162.59		
		136.47	10	163.37	136.62	17.0
		136.92	10	163.91		
		137.27	10	164.33		
$SnBr_4 \cdot$dioxane	77	136.20	10	163.04	136.20	17.3
$SnBr_4 \cdot$2DEE	77	135.31	10	161.98	135.43	17.8
		135.58	7	162.30		
$SnBr_4 \cdot$2THF	77	128.28	10	153.63		
		131.26	10	157.11	132.44	19.6
		134.30	10	160.70		
		135.93	10	162.72		
	293	129.92	10	155.52	131.98	
		134.04	10	160.46		19.8
$SnBr_4 \cdot$2DMSO	77	128.78	3	154.38	128.78	21.8
$SnBr_4 \cdot$2HMPT	77	118.18	5	141.37	122.94	25.3
		127.70	5	152.97		
$SnBr_4 \cdot$2Py	77	122.66	3	146.86	122.66	25.5

^{a} $\delta(\nu_\chi) = \dfrac{\nu_{av}(\chi)-\nu_{av}(SnBr_4)}{\nu_{av}(SnBr_4)} \times 100$ represents the shift with respect to $SnBr_4$. ^{b} Ref. 21.

TABLE 7

^{127}I NQR SPECTRA OF SnI_4 COMPLEXES AT 77 K

System	$\nu[^{127}I(\frac{1}{2}-\frac{3}{2})]$ (*MHz*)	*Signal/noise ratio*	$\nu_{av}(^{127}I)$	$\delta(\nu_\chi)^a$ (%)
$SnI_4{}^b$	207.68	10	208.40	
	209.13	10		
$SnI_4 \cdot$2Py	162.66	2.5	162.66	22.1
$SnI_4 \cdot$2HMPT	164.61	5		
	156.15	5	160.38	23.0

^{a} $\delta(\nu_\chi) = \dfrac{\nu_{av}(\chi)-\nu_{av}(SnI_4)}{\nu_{av}(SnI_4)} \times 100$ represents the shift with respect to SnI_4. ^{b} Ref. 21.

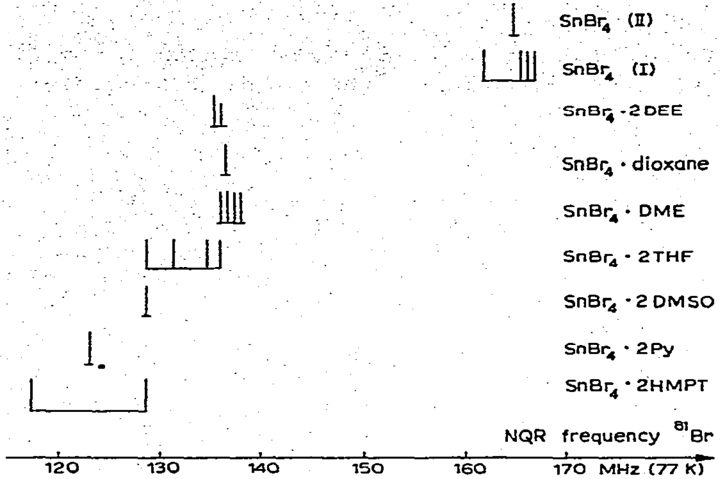


Fig. 9. ^{81}Br NQR spectra of $SnBr_4$ complexes.

studied in this instance. The data obtained are summarised in Tables 6 and 7. The spectra are shown diagrammatically in Fig. 9.

The spectra of $SnBr_4$ complexes containing DEE, dioxane, DME, Py, or DMSO, as well as the ^{127}I NQR spectrum of $SnI_4 \cdot 2Py$ agree with structure (a) whereas the spectra of $SnBr_4 \cdot 2HMPT$ and $SnI_4 \cdot 2HMPT$ indicate a *cis* arrangement of the ligands as in the structure (b). The splitting in the structure (a) complexes is at or below the value characteristic of the crystallographical splitting. For solvent-free $SnBr_4$, the spectrum exhibits the usual[21] quartet attributable to the five-coordinate associated complex together with a singlet which appears after $SnBr_4$ has been kept in Dry-Ice for some time (Table 6, Fig. 9). The singlet suggests that the compound may exist in another crystalline phase in which the four bromines are all equivalent. It is interesting that the same phase is formed after the addition of $POCl_3$, $PhNO_2$, or $PhCH_2Cl$ to $SnBr_4$, materials which do not form complexes with $SnBr_4$.

Finally, the NQR spectra of some of the compounds studied ($MeSnBr_3$, $Me_3SnBr \cdot DMF$, $Me_3SnBr \cdot Py$, Me_2SnBr_2, $Me_2SnBr_2 \cdot$dioxane, Me_2SnCl_2 and $Me_2SnCl_2 \cdot$dioxane) indicate that the frequencies exhibit a positive temperature dependence.

Usually, the NQR frequency decreases with an increase in temperature, this being attributed to torsional vibrations of the molecule or its local sites[22]. The anomaly observed here may be attributed to a decrease in charge transfer due to the increased interatomic distances within the molecules.

EXPERIMENTAL

The syntheses of solid complexes of methyltin halides with dioxane, HMPT, Py, DMF, DMSO, or TMED, and of solid $SnBr_4$ and SnI_4 complexes have already been described previously[2].

Liquid complexes were obtained by mixing the necessary stoichiometric amounts of the components.

NQR spectra were measured on an ISSh-1 pulse NQR spectrometer at liquid nitrogen temperature (77 K) or at room temperature (293 K).

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