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

IV. MÖSSBAUER SPECTRA AND STRUCTURES OF MOLECULAR COMPLEXES OF METHYLTIN HALIDES

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SUMMARY

The Mössbauer techniques have been employed to study intermolecular interactions of methyltin halides with electron-donor solvents. For dimethyltin dihalides, the quadrupole splittings have been found to be most informative whereas with methyltin trihalides the isomer shifts are of considerable importance.

INTRODUCTION

The importance of structural studies for the study of molecular complexes of organotin compounds has already been emphasised in earlier papers in this series[1-3] which have described the synthesis and NQR investigation of molecular complexes of methyltin halides.

In the present work, Mössbauer techniques have been applied to a study of intermolecular interactions of methyltin halides with electron donors used as solvents in organometallic chemistry *i.e.* diethyl ether (DEE), dimethoxyethane (DME), tetrahydrofuran (THF), dioxane, acetone, dimethylformamide (DMF), dimethyl sulphoxide (DMSO), tetramethylethylenediamine (TMED), hexamethylphosphoric triamide (HMPT) and pyridine (Py).

RESULTS AND DISCUSSION

I. Complexes of dimethyltin dihalides

The spectra of Me_2SnCl_2 and Me_2SnBr_2 dissolved in methylene chloride, and to which various electron-donor solvents have been added, have been measured. For each solvent added, quadrupole splitting (QS) and isomer shift (IS) have been obtained as a function of the molar ratio, $n = [\text{donor}]/[Me_2SnHal_2]$ ($n = 1, 2, 5$), spectra being also obtained for the dihalides dissolved in the electron-donor solvents alone or in neat methylene chloride. The spectral parameters are listed in Tables

TABLE 1

MÖSSBAUER SPECTRAL PARAMETERS FOR Me_2SnCl_2 DISSOLVED IN VARIOUS SOLVENTS

Solvent	*[Donor]/[Me_2SnCl_2]*							
	1/1		2/1		5/1		*Neat donor*	
	Δ	*δ*	*Δ*	*δ*	*Δ*	*δ*	*Δ*	*δ*
Solvent-free							3.60	1.59
CH_2Cl_2							3.55	1.64
DEE	3.75	1.75	3.81	1.78	3.80	1.73	3.80	1.75
DME	4.05	1.74	4.05	1.74	4.05	1.74	4.05	1.74
THF	3.75	1.61	3.92	1.61	4.04	1.66	3.92	1.66
Dioxane	3.70	1.67	3.75	1.67	3.77	1.67	3.77	1.67
Acetone	3.61	1.69	3.85	1.75	3.85	1.75	3.85	1.75
DMF	3.68	1.66	4.30	1.69	4.30	1.69	4.25	1.66
DMSO	3.91	1.60	4.33	1.64	4.33	1.64	4.40	1.60
HMPT	4.05	1.55	4.45	1.54	4.45	1.50	4.36	1.50
TMED	3.98	1.58	3.98	1.58	3.98	1.58	3.86[a]	1.60
Pyridine	3.84	1.63	4.05	1.60	4.05	1.60	4.05	1.60

[a] The *QS* value for the solution in pure TMED differs sharply from the value found for solutions with *n* equal to 1, 2 and 5; this is attributed to decomposition of the complex formed in TMED.

TABLE 2

MÖSSBAUER SPECTRAL PARAMETERS FOR Me_2SnBr_2 DISSOLVED IN VARIOUS SOLVENTS

Solvent	*[Donor]/Me_2SnBr_2]*							
	1/1		2/1		5/1		*Neat donor*	
	Δ	*δ*	*Δ*	*δ*	*Δ*	*δ*	*Δ*	*δ*
Solvent-free							3.40	1.62
CH_2Cl_2							3.64	1.64
DEE	3.63	1.81	3.63	1.81	3.57	1.78	3.57	1.78
DME	4.14	1.70	4.22	1.70	4.22	1.70	4.22	1.70
THF	3.57	1.79	3.92	1.79	3.98	1.82	3.86	1.87
Dioxane	3.55	1.56	3.62	1.52	3.62	1.52	3.63	1.59
Acetone	3.61	1.80	3.82	1.86	3.82	1.86	3.85	1.81
DMF	3.61	1.63	4.36	1.77	4.36	1.77	4.30	1.75
DMSO	3.63	1.64	4.49	1.64	4.32	1.64	4.40	1.58
HMPT	3.84	1.08	4.40	1.56	4.45	1.56	4.40	1.56
TMED	3.93	1.72	3.98	1.75	3.98	1.75	3.57[a]	1.72
Pyridine	3.76	1.74	3.90	1.67	3.98	1.70	3.98	1.63

[a] The *QS* value for the solution in pure TMED differs sharply from the value found for solutions with *n* equal to 1, 2 and 5; this is attributed to decomposition of the complex formed in TMED.

1 and 2 and in addition *QS* and *IS* as a function of *n* are presented in Figs. 1–4 where the reference compounds used for indicating the effect of complex formation upon the spectral parameters were the solvent-free dimethyltin dihalides whose structures in the solid state indicate molecular association, the resulting complexes possessing distorted octahedral structures[4,5].

Tables 1 and 2 demonstrate that the *IS* values are, within experimental error, all identical for the systems studied and are very close to the values found for the solvent-free dihalides. For this reason, this spectral parameter is not sufficiently sensitive to enable its use in the study of donor–acceptor effects occurring in these systems.

QS measurements are much more sensitive. The *QS* values found were of the order of 3.77 to 4.40 $\text{mm}\cdot\text{s}^{-1}$ for the Me_2SnCl_2 complexes and 3.63 to 4.40 $\text{mm}\cdot\text{s}^{-1}$ for the Me_2SnBr_2 complexes. In both the cases, *QS* increased according to the addition of electron-donor solvent in following sequence:

dioxane $\leqslant$ DEE $\leqslant$ acetone $<$ THF $<$ TMED $<$ Py $\leqslant$ DME $<$ DMF $<$ DMSO $<$ HMPT

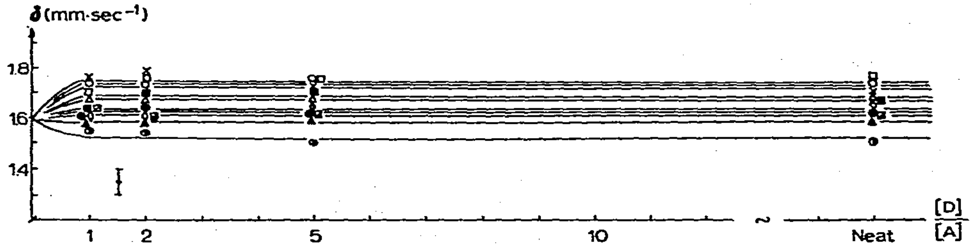

Fig. 1. Plot of *IS* against *D*/*A* for $(CH_3)_2SnCl_2$. Notation here and in other Figures: × DEE, □ acetone, ◇ THF, ○ DME, △ dioxane, ◑ HMPT, ◪ pyridine, ● DMSO, ▲ TMED, ■ DMF.

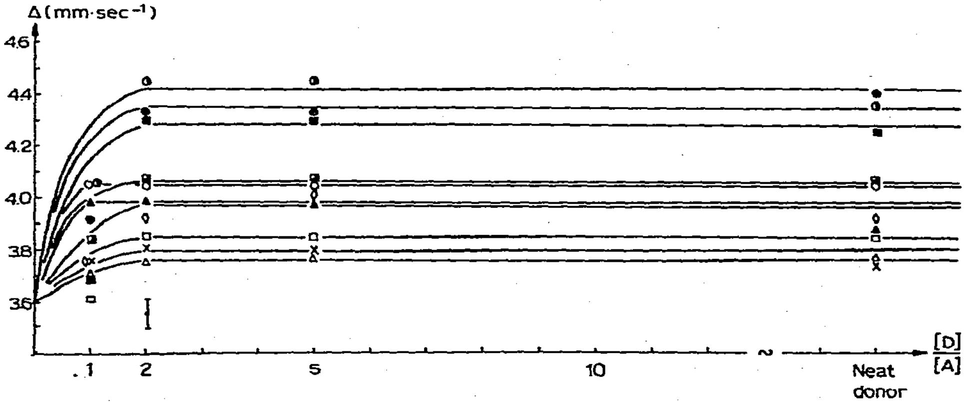

Fig. 2. Plot of *QS* against *D*/*A* for $(CH_3)_2SnCl_2$.

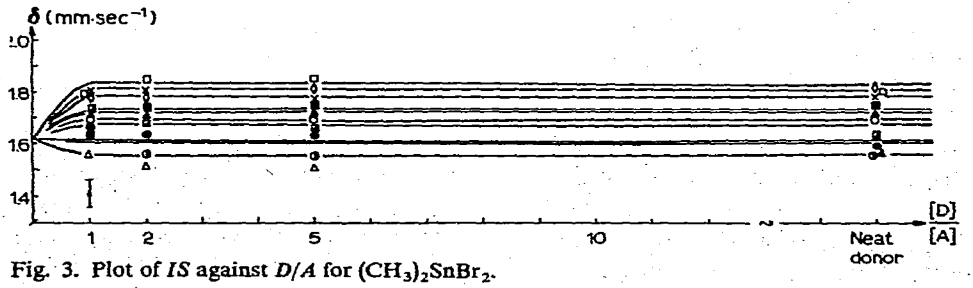

Fig. 3. Plot of *IS* against *D*/*A* for $(CH_3)_2SnBr_2$.

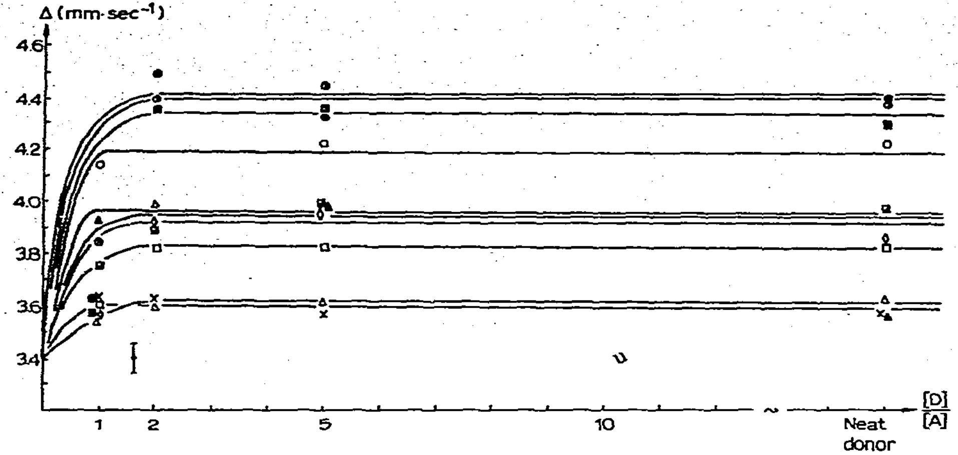

Fig. 4. Plot of *QS* against *D*/*A* for $(CH_3)_2SnBr_2$.

A similar series was observed earlier during a study of complex formation in dibutyltin dichloride systems[6].

Figs. 2 and 4 show that the *QS* values for the systems studied here correspond to the plateau value observed for the neat donor when *n* is equal to 2 for monodentate ligands (THF, acetone, DMF, HMPT, DMSO) and when *n* is 1 for bidentate ligands (TMED, dioxane, DME). This observation is in agreement with the stoichiometry[2] of these complexes.

The modern explanation[7] of *QS* and the relationship between *QS* and structure[4,5] suggests that the observed *QS* values correspond to an octahedral arrangement of the ligands at the tin atom, the methyl group being in a *trans* arrangement. The observed increase in the value of *QS* may be explained in the following way. Initially, complex formation leads to an increase in the ionic character of the Sn–Hal bonds, the increase being proportional to the extent of charge transfer from the donor to the acceptor[3], *i.e.* for a given acceptor the increase is proportional to the donor strength of the added electron-donor solvent. This is accompanied by an increasing difference between the ionic characters of the tin–ligand σ-bonds (mainly, Sn–C and Sn–Hal) and hence *QS* increases[8]. In terms of this explanation, the observed quadrupole splitting should be proportional to the donor strength of a ligand. However, the value of *QS* also increases when the distorted octahedral structure whose CSnC angle is close to tetrahedral is replaced by a regular octahedral structure where the CSnC angle[5] is ca. 180°. Although formation of a regular structure is usually accompanied by strong donor–acceptor interactions, it is also possible that steric effects may interfere with such a rearrangement and lead to lower *QS* values which no longer reflect the donor–acceptor interaction strength.

Tables 1 and 2 indicate that the largest *QS* values were obtained for Me_2SnHal_2 complexes with DMF, DMSO, or HMPT; this may be taken as evidence in favour of a regular octahedral structure for these complexes with the structure resembling that of $Me_2SnCl_2 \cdot 2DMSO$[10], *i.e.* with a significant difference between the tin–ligand σ-bond polarities. It should be noted that ^{81}Br NQR data[3] indicate that Me_2SnBr_2 complexes with DMF, DMSO or HMPT possess the greatest ionic character for the Sn–Br bond among the complexes studied. When it is also recalled that QS is 4.32 mm·s^{-1} for the anion[11] $[Me_2SnCl_4]^{2-}$, it is not unreasonable to assume that a Δ value equal to 4,40 mm·s^{-1} corresponds to the formation of complexes for which the difference between the tin–ligand σ-bond polarities is a maximum and where the structure is a regular octahedron.

The somewhat lower QS values obtained for $Me_2SnHal_2 \cdot 2Py$ and $Me_2SnHal_2 \cdot TMED$ do not necessarily indicate that pyridine possesses a lower donor activity since the ^{81}Br NQR frequency observed[3] for $Me_2SnCl_2 \cdot 2Py$ is almost equal to that for the complexes with DMSO, DMF, and HMPT. It is assumed, therefore, that in this case formation of a distorted octahedral structure occurs involving considerable charge transfer.

The lower QS values (3.57 to 4.05 mm·s^{-1}) obtained for complexes with DEE, THF, DME, acetone or dioxane indicate that charge transfer is much lower in these cases and that significant distortion occurs in the octahedral structures formed.

The QS value of a dilute solution of Me_2SnCl_2 in methylene chloride is equal to the QS value for the solvent-free dihalide whereas the QS value for a solution of Me_2SnBr_2 in methylene chloride is 0.2 mm·s^{-1} greater than the QS value for the solvent-free compound. This suggests, therefore, that interaction occurs between Me_2SnBr_2 and methylene chloride. It is probable that the methylene chloride molecules form hydrogen bonds with the halogen atoms attached to the tin[12], the latter being a stronger acceptor towards hydrogen than the halogen atom towards the carbon. Hydrogen bond formation leads to further polarisation of the tin–halogen bond and, from the discussion above, to an increase in the value of QS. The above mechanism is also favoured by the fact that, judging from the QS data, Me_2SnBr_2 which contains an easily polarisable bromine atom interacts with methylene chloride to a greater extent than Me_2SnCl_2 whose chlorine atoms are less polarisable.

II. Complexes of methyltin trihalides

Tables 3 and 4 summarise the Mössbauer spectral parameters obtained for solutions of $MeSnCl_3$ and $MeSnBr_3$ in methylene chloride containing various electron-donor solvents. For each solvent, values of IS and QS have been plotted as a function of $n = [\text{donor}]/[MeSnHal_3] = 1, 2, 5, 10$, and, in addition, spectra of $MeSnHal_3$ dissolved in the electron-donor solvent alone or in neat methylene chloride have also been measured. Plots of IS and QS *versus* n are given in Figs. 5–8 where the reference compounds used were the solvent-free trihalides which, according to NQR data[3], exist in the solid state as molecular associates possessing six-coordinate octahedral structures.

The data show that, unlike the dihalides (and, even less like the monohalides, see below), IS for the trihalides is more sensitive towards intermolecular coordination, and quite informative. For $MeSnBr_3$ complexes with weaker donors (DEE, DME, THF, dioxane, acetone), the IS values obtained coincide, to all intents and purposes, with those obtained for solvent-free $MeSnBr_3$. IS values for solutions involving strong donors are on the average 0.4 mm·s^{-1} lower than the IS values for solvent-free $MeSnBr_3$. The relative values of IS for different electron-donor solvents added to solutions of $MeSnBr_3$ in methylene chloride follow the sequence:

$$\text{DEE} \approx \text{acetone} \approx \text{dioxane} \approx \text{THF} \approx \text{DME} > \text{TMED} > \text{DMSO} \approx \text{HMPT} > \text{Py} \approx \text{DMF}$$

TABLE 3

MÖSSBAUER SPECTRAL PARAMETERS FOR $MeSnCl_3$ DISSOLVED IN VARIOUS SOLVENTS

Solvent	*[Donor]/[MeSnCl$_3$]*									
	1/1		2/1		5/1		10/1		*Neat donor*	
	Δ	*δ*	*Δ*	*δ*	*Δ*	*δ*	*Δ*	*δ*	*Δ*	*δ*
Solvent-free									2.07	1.32
CH_2Cl_2									1.94	1.36
DEE	2.18	1.19	2.14	1.21	2.21	1.14	2.18	1.16	2.15	1.18
DME	2.43	1.18	2.40	1.12	2.40	1.12	2.43	1.18	2.40	1.12
THF	2.08	1.21	2.37	1.15	2.34	1.12	2.37	1.15	2.37	1.15
Dioxane	2.44	1.15	2.44	1.15	2.50	1.18	2.46	1.15	2.43	1.14
Acetone	2.30	1.15	2.40	1.16	2.44	1.18	2.40	1.16	2.44	1.18
DMF	2.08	1.14	1.97	0.98	1.92	0.94	1.94	0.94	1.89	0.89
DMSO	2.03	1.05	1.96	0.91	1.96	0.88	1.99	0.92	1.97	0.90
HMPT	2.00	1.03	2.17	0.80	2.17	0.80	2.35	0.85	2.35	0.89
TMED	1.78	0.97	1.75	0.95	1.68	0.95	1.72	1.00	1.74	0.98
Pyridine	1.91	1.01	1.89	0.95	1.94	0.97	1.91	0.93	1.86	0.93

TABLE 4

MÖSSBAUER SPECTRAL PARAMETERS FOR $MeSnBr_3$ DISSOLVED IN VARIOUS SOLVENTS

Solvent	*[Donor]/[MeSnBr$_3$]*									
	1/1		2/1		5/1		10/1		*Neat donor*	
	Δ	*δ*	*Δ*	*δ*	*Δ*	*δ*	*Δ*	*δ*	*Δ*	*δ*
Solvent-free									1.75	1.44
CH_2Cl_2									1.94	1.36
DEE	1.96	1.37	2.07	1.39	2.07	1.39	2.10	1.34	2.14	1.39
DME	2.43	1.32	2.46	1.33	2.48	1.37	2.46	1.34	2.46	1.33
THF	2.12	1.32	2.37	1.27	2.37	1.27	2.39	1.30	2.42	1.34
Dioxane	2.18	1.34	2.18	1.34	2.22	1.35	2.11	1.38	2.18	1.34
Acetone	2.14	1.36	2.25	1.37	2.32	1.34	2.36	1.36	2.36	1.36
DMF	1.88	1.18	1.88	0.96	1.83	0.97	1.83	1.02	1.77	0.94
DMSO	1.99	1.34	2.03	1.05	2.00	1.06	1.96	1.12	1.96	1.08
HMPT	2.10	1.12	2.25	1.12	2.27	0.93	2.34	0.98	2.31	1.05
TMED	1.75	1.16	1.75	1.16	1.69	1.16	1.75	1.16	1.75	1.16
Pyridine	1.77	1.05	1.74	1.03	1.83	1.05	1.83	1.02	1.74	0.98

With $MeSnCl_3$, which is a stronger Lewis acid, the *IS* values vary in a somewhat different way. For all the electron donors studied, the *IS* values obtained in methylene chloride solution are invariably lower than the value for the solvent-free species, the following series applying for the relative influence of various electron-donor solvents:

DEE $\approx$ acetone $\approx$ dioxane $\approx$ DME $\approx$ THF $>$ TMED $>$ DMSO $\approx$ HMPT $\approx$
$\approx$ Py $\approx$ DMF

The conventional explanation for this behaviour is that a decrease in the isomer shift corresponds to a decrease in the *s*-electron density at the tin caused either by an increase in the Sn–Hal polarity (with reference to the initial halide)[13] or by increased shielding due to involvement of the 5*d* orbitals during coordination[14]. Both the

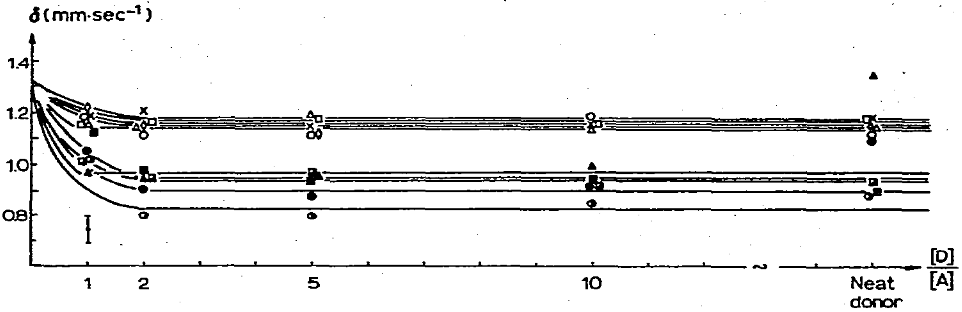

Fig. 5. Plot of *IS* against *D*/*A* for CH_3SnCl_3.

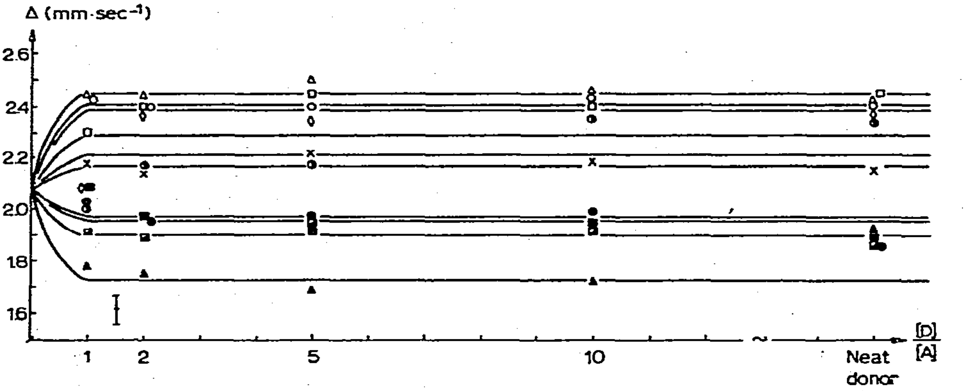

Fig. 6. Plot of *QS* against *D*/*A* for CH_3SnCl_3.

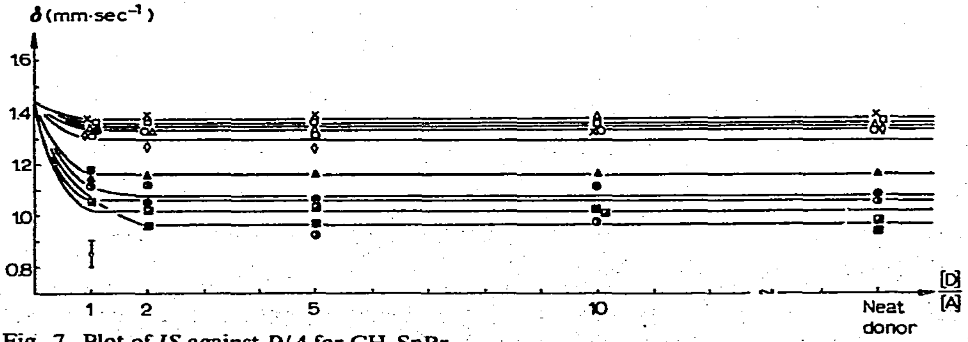

Fig. 7. Plot of *IS* against *D*/*A* for CH_3SnBr_3.

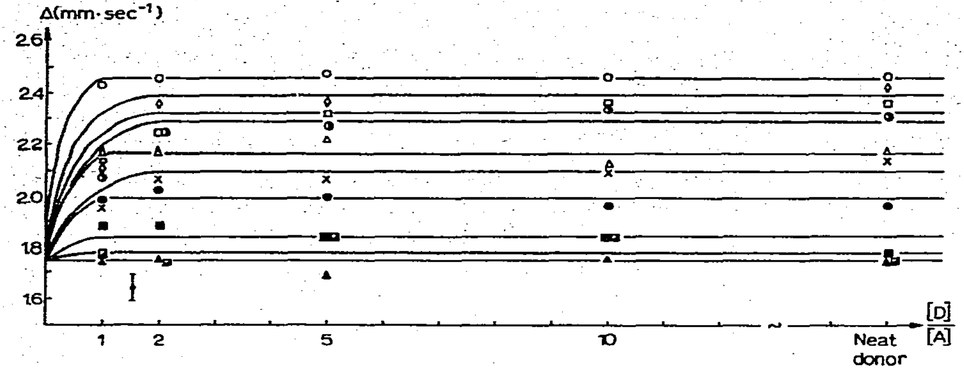

Fig. 8. Plot of *QS* against *D*/*A* for CH_3SnBr_3.

ionic character of the Sn–Hal bond and the extent to which the *5d* orbitals are occupied are proportional to the extent of charge transfer, and for this reason, whatever the mechanism of the observed variation in *IS* value, a decrease in the isomer shift reflects the extent of charge transfer from donor to acceptor for complexes having equal coordination numbers whereas for a given acceptor it reflects the donor strength of the added ligands. On the basis of this explanation, the series quoted above may be taken as a measure of the relative donor activities of the solvents studied with respect to $MeSnCl_3$ or $MeSnBr_3$. The *IS* value of solvent-free $MeSnBr_3$ indicates that the extent of charge transfer in the molecular associates present in the solid is of the same order as in complexes containing ethers or acetone, whereas it is much lower in comparison to complexes containing strong donors (DMF, DMSO, etc.). The *IS* value of solvent-free $MeSnCl_3$ reveals that intramolecular interaction in the solvent-free compound is lower than in any of the complexes studied. Although the observed data again emphasise that $MeSnCl_3$ is a stronger Lewis acid than $MeSnBr_3$, they give no indication whatsoever as to whether $MeSnBr_3$ is associated to a greater extent than $MeSnCl_3$.

The *QS* behaviour observed for the trihalides differs from that observed for the dihalides. Tables 3 and 4 show that the observed *QS* range (1.74–2.44 mm·s^{-1}) agrees, on average, with the value (ca. 2 mm·s^{-1}) predicted for $RSnL_5$ on the basis of a point-charge model[11]. However, the variations in *QS* are opposite to the variations observed for the dihalides, the *QS* values for both trihalides being shifted towards lower values on addition of solvents which exhibit strongly solvating properties. The *QS* variations observed may be arranged in the following series:

For $MeSnCl_3$:

acetone ≈ dioxane ≈ DME ≈ THF ≈ HMPT > DEE > solvent-free $MeSnCl_3$ > DMSO > DMF ≈ TMED ≈ Py,

For $MeSnBr_3$:

DME ≈ THF > acetone ≈ HMPT > dioxane ≈ DEE > DMSO > DMF ≈ TMED ≈ Py ≈ Solvent-free $MeSnBr_3$

NQR studies have shown[3] that in six-coordinate complexes or molecular associates of $MeSnCl_3$ two of the Sn–Hal bonds are invariably more ionic than the third. This has been attributed to the *trans* effect of the ligands involved in the respective complexes or, alternatively, to the presence of chlorine or bromine bridges in the molecular associates. The difference between the ionic characters of the Sn–Hal bonds has been shown to be 12.5% for $MeSnCl_3$ while the corresponding value for $MeSnBr_3$ is 7.5%, *i.e.*, the difference in the ionic character of the various Sn–Cl bonds is 5% greater than that for the various Sn–Br bonds. This difference should be reflected by the respective *QS* values and indeed the *QS* value for $MeSnBr_3$ is in fact 0.32 $mm \cdot s^{-1}$ lower than the *QS* value for $MeSnCl_3$. In addition, the NQR spectra of the systems demonstrate that the ionic character of the Sn–Hal bond increases when the molecular associates initially present in the system are replaced by complexes, the increase being such that the differences between the ionic character of the non-equivalent Sn–Hal bonds increases, thus leading to an increase in the *QS* value. Unfortunately, no NQR spectra could be obtained[3] for $MeSnHal_3$ complexes containing stronger donors, but other data[15] suggest that the difference between the ionic characters of the Sn–Hal bonds should decrease as the extent of charge transfer increases, *i.e.* the *QS* value should be lower for complexes containing stronger donors, which has in fact been observed in this work.

The complex containing one of the strongest donors, HMPT, has a *QS* value much greater than that of other complexes containing strong donors. This may be explained by assuming that the structure involving this donor deviates strongly from octahedral, a reasonable explanation in view of the very large size of the HMPT molecule.

The *QS* value for the $MeSnBr_3 \cdot$dioxane complex is, on the average, 0.25 $mm \cdot s^{-1}$ lower than the *QS* value for complexes of $MeSnBr_3$ with DME, acetone or THF. We believe that this is due to the formation of a five-coordinate structure, in agreement with the ^{81}Br NQR spectrum[3] and with elemental analysis[2], rather than to a greater donor activity of dioxane with respect to $MeSnBr_3$.

The lower *QS* value found for solutions in DEE may be due to the fact that solvent-free $MeSnHal_3$ is frozen out of such solutions at 78 K. This has also been observed in NQR experiments.

III. Complexes of trimethyltin halides

The spectra of Me_3SnCl and Me_3SnBr have been studied only for a limited number of solvents, the spectral parameters being rather insensitive to intermolecular coordination with the result that they have not been studied as a function of the molar ratio *n*. The results (Table 5) show that the *IS* values obtained for Me_3SnCl or Me_3SnBr dissolved in donor solvents are, within experimental accuracy, equal to the values found for the solvent-free species. The *QS* values found for the various solutions are also apparently independent of the nature of the donor being practically the same as the *QS* value of the initial molecules. The latter *QS* value (ca. 3.5 $mm \cdot s^{-1}$) corresponds to that predicted for five-coordinate tin compounds[4] on the basis of a point-charge model. The *QS* value found for solutions involving the strongest donor studied, HMPT, is practically independent of the nature of the halogen present (3.52 and 3.54) whereas the values obtained for the initial trimethyltin halides are distinctly different. This may be explained by assuming that the halogen effect is averaged out with regular five-coordinate complexes containing strong donors while, in contrast, the initial halides are self-associated to different extents.

TABLE 5

MÖSSBAUER SPECTRAL PARAMETERS FOR Me_3SnCl OR Me_3SnBr DISSOLVED IN VARIOUS SOLVENTS

Solvent	*Me_3SnCl*		*Me_3SnBr*	
	Δ	δ	Δ	δ
Solvent-free	3.52	1.66	3.37	1.51
CH_2Cl_2	3.48	1.69	3.47	1.57
Dioxane	3.42	1.60	3.60	1.63
Acetone	3.60	1.63	3.54	1.66
HMPT	3.52	1.60	3.54	1.66

EXPERIMENTAL

Mössbauer spectra were recorded on an electrodynamic instrument using $^{119m}SnO_2$ as the source of resonance gamma quanta. This source was kept at room temperature while the absorbers (solutions or individual compounds) were kept at liquid nitrogen temperature. The measured *IS* and *QS* values were accurate to within ± 0.04 to ± 0.08 mm·s^{-1}.

The preparation of the samples and purification of the solvents have already been described[2]. To obtain a desired ratio, *n*, a weighed portion (0.020 g tin per 1 cm^2 of the carrier surface) was dissolved in methylene chloride (total volume of the solution 2 ml) followed by addition of the electron-donor solvent. The solution was poured into a Teflon cell and frozen at liquid nitrogen temperature.

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