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LIGAND INFLUENCE IN ALKYL TIN(IV) HALIDE COMPLEXES

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CONTENTS

A. INTRODUCTION

Although interest in the phenomenon of ligand influence (LI) has stimulated a number of investigations during the past 15 years, the problem can hardly be considered as completely clear. Being a fundamental problem of coordination chemistry, it attracts the attention of chemists who work in the fields of preparative and quantum chemistry, and X-ray analysis.

The importance of the *trans*-influence rule in the coordination chemistry of transition elements is widely known, and the study of similar regularities in the chemistry of main group elements is also appreciated.

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Here we discuss only static LI which is limited to processes in the ground state of a system, as distinct from kinetic LI determined by the excited state characteristics. The latter is evidently influenced by factors other than the ground state properties.

Different indicators for recognizing the LI in main group element compounds have been predicted using various theoretical approaches [1–7]. The effect of LI in transition element complexes can be described solely as *trans* influence. However, in non-transition element compounds, depending on the central atom oxidation state and its position in the Periodic Table, it can be observed as either *cis* weakening, or *trans* weakening, or *cis* weakening accompanied by a relatively smaller *trans* influence, both strengthening and weakening being in principle possible for the last.

Here we consider hexacoordinate tin complexes of the type $SnHal_6$ or $SnHal_4 \cdot 2L$ where the tin atom is in its highest oxidation state and either one or two acidoligands (Hal) are substituted for σ-donor groups (Alk), which considerably exceed the halogen ligands in donating power. The σ-level energies of the substituents are then close in value to those of the p levels of the central atom, while the σ-level energies of the acidoligands are close in value to those of the s levels of the Sn atom [4]. In such systems a weakening of the Sn–Hal bonds at the *cis* position to the σ-donor substituents (*cis* weakening) has been predicted, as compared with the strength of the Sn–Hal bonds in unsubstituted compounds. The *cis* weakening is accompanied by a relatively smaller *trans* influence, either weakening or strengthening [3,4,6].

Further progress in understanding the nature of the phenomenon requires reliable experimental data on the direction of the *trans* influence in the compounds discussed, as well as on the quantitative comparison of the *trans* and *cis* influences in these systems.

The results of X-ray studies are conventionally considered as the most unambiguous evidence in favour of or opposed to theoretical predictions. The variation in interatomic distances as a result of the introduction of "influencing" ligands serves in this experiment as a measure of LI. X-ray data are now available for nearly all the compounds discussed in this review, and their analysis together with the spectroscopic nuclear quadrupole resonance (NQR) data appeared to be helpful to outline the limitations in the use of interatomic distances as a measure of LI.

A characteristic can be used as a measure of LI if it satisfies at least two requirements, namely, it characterizes a system in its ground state and it changes value predominantly under the LI [3]. In this respect NQR spectroscopic parameters seem to be quite suitable, since, firstly, they are ground state characteristics of a system, and secondly, they are directly related to the electron density distribution in the vicinity of a quadrupolar nucleus.

Indeed, the quadrupole coupling constant, QCC = e^2Qq_{zz}/h, and asymmetry parameter, $\eta = |(q_{xx} - q_{yy})/q_{zz}|$, of the electric field gradient (EFG) are known to depend on the electric field potential U at the site of the quadrupolar nucleus as $e^2Qq_{zz}/h = e^2Q/h(\partial^2U/\partial z^2)$ and $\eta = |\partial^2U/\partial x^2 - \partial^2U/\partial y^2)/\partial z^2|$. A high sensitivity of these parameters to subtle variations in electron density in the systems under study is also known. It is therefore expected that even weak electron density changes due to the introduction of "influencing" ligands will be clearly and adequately reflected in the NQR spectra.

To our knowledge, no systematic NQR data have previously been available on LI in main group element compounds. X-ray analysis has been carried out to check the spectroscopic assignments as well as to draw conclusions about how both sets of results conform to the theoretical predictions.

B. EXPERIMENTAL RESULTS

The ^{35}Cl and ^{81}Br NQR spectra measured in the chloro and bromo compounds studied are listed in Table 1. The ^{127}I NQR spectra together with the Sn–I bond distances are given in Table 2. The assignment of frequencies as well as the identification of isomer configurations rely on both spectral patterns (multiplicity and relative intensities of resonances) and X-ray data, which greatly reduced any uncertainty in spectral determinations.

A linear correlation of the type $y = a + bx$ between the halogen resonance frequencies and the Sn–Hal bond distances has been observed (Figs. 1–3, Table 3). Relatively higher NQR frequencies were assumed to correspond to relatively shorter Sn–Hal distances, as is usually accepted for singly coordinate halogen atoms, purely σ-bonded to their partners in compounds with nominally isolated structural units. We have, however, decided to discuss the results not in terms of NQR frequencies or quadrupole coupling constants, but in terms of the more physically meaningful effective charges (δ) located on the halogen atoms. The magnitudes of the charges are easily calculated from experimentally measured frequencies (ν) within the approximations of the Townes–Dailey theory [8]. For chloro and bromo complexes the following relationship was used, assuming pure σ-bonding and ignoring sp hybridization of the halogen atom valence np_z orbitals:

$$\delta = \frac{2\nu(1 + \eta^2/3)^{-1/2}}{e^2Qq_0/h} - 1 \tag{1}$$

Here e^2Qq_0/h is the atomic quadrupole coupling constant produced by a single electron in the halogen atom np_σ orbital.

TABLE 1

^{35}Cl and ^{81}Br resonance frequencies (ν (MHz)) of tin(IV) chloro and bromo compounds [a] (relative intensities of lines in parentheses)

Compound	T (K)	ν (MHz)	Ref.	Compound	T (K)	ν (MHz)	Ref.
$(NMe_4)_2SnCl_6$	292	16.683	9	$(NMe_4)_2SnBr_6$	300	115.070	14
	77	16.70			77	117.21 (1)	
		17.51				117.46 (1)	
$(NMe_4)_2EtSnCl_5$	77	11.804				118.10 (2)	
		12.953		$(NMe_4)_2BuSnBr_5$	77	77.14	
		12.093				78.04	
		13.268				81.77	
		18.407				90.83	
trans-$SnCl_4\cdot2HMPT$	77	17.775	10			133.36	
		18.039		*trans*-$SnBr_4\cdot2HMPT$	77	127.75	11
$EtSnCl_3\cdot2HMPT$	77	–		$BuSnBr_3\cdot2HMPT$	77	92.06	
		–				95.57	
		20.024				132.60	
$Me_2SnCl_2\cdot2HMPT$	77	9.45	11	$Me_2SnBr_2\cdot2HMPT$	77	60.61	12
trans-$SnCl_4\cdot2THF$	110	18.697	10	*trans*-$SnBr_4\cdot2THF$	293	129.92	12
		19.256				134.04	
$MeSnCl_3\cdot2THF$	77	15.36	12	$MeSnBr_3\cdot2THF$	77	103.28	12
		15.55				106.12	
		20.17				141.12	

cis-$SnCl_4 \cdot 2DMSO$	77	18.74	13	*trans*-$SnBr_4 \cdot 2DMSO$	77	128.78	12
		17.98		$Me_2SnBr_2 \cdot 2DMSO$	77	59.46	12
		17.17		*cis*-$SnBr_4 \cdot 2DPSO$	77	116.633	
		16.92				128.340	
$EtSnCl_3 \cdot 2DMSO$	77	13.39		$BuSnBr_3 \cdot 2DPSO$	77	89.127	
		13.50(2)				92.305	
		13.71				102.400	
		16.96(2)		*trans*-$SnBr_4 \cdot 2py$	77	122.66	12
cis-$SnCl_4 \cdot 2TPPO$	77	17.785	13	$Me_2SnBr_2 \cdot 2py$	77	65.76	12
		18.514		$SnBr_4 \cdot 2TMU$	77	123.50	
$EtSnCl_3 \cdot 2TPPO$	77	–				123.70	
		–				125.31(2)	
		20.443		$(HPy)SnBr_6$	77	119.0(2)	14
trans-$SnCl_4 \cdot 2py$	77	17.644	13			120.9(1)	
		17.760				102.4(3)	
trans-$SnCl_4 \cdot 2TMU$	77	18.346		$(HPy)BuSnBr_4 \cdot py$	77	84.14	
		18.142				84.37	
$EtSnCl_3 \cdot 2TMU$	77	13.256				90.80	
		13.683				97.41	
		19.350		$Bu_2SnBr_2 \cdot bipy$	77	74.69	

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[a] HMPT = hexamethylphosphortriamide; THF = tetrahydrofuran; DMSO = dimethyl sulphoxide; TPPO = triphenylphosphine oxide; py = pyridine; TMU = tetramethyl urea; DPSO = diphenyl sulphoxide.

TABLE 2

^{127}I NQR spectra (MHz) of tin(IV) iodo compounds

Compound	T (K)	Transition frequencies		e^2Qq/h	η (%)	Ref.	d(Sn I) (Å)	Ref.
		1/2-3/2	3/2-5/2					
SnI_4	301	203.49	406.91	1456.4	1.2	15(a), 15(b)	2.69(4)	16
		204.47	408.99	1363.3	0.0			
	77	207.683	415.32(3)	1384.4	0.92			
		209.133	418.26(1)	1394.2	0.40			
$SnI_4 \cdot 2HMPT$	77	156.15				12		
		164.61						
$EtSnI_3 \cdot 2HMPT$	77	109.8	219.17	731.3	3.8		2.901(2)	17
		111.3					2.886(2)	
		166.4					2.634(4)	
$Et_2SnI_2 \cdot 2HMPT$	77	70.51	140.26	467.9	6.5		3.016(1)	18
$SnI_4 \cdot bipy$	77	153.68					2.816(2)av	19
		169.29					2.788(2)av	
cis-$SnI_4 \cdot 2DPSO$	77	154.41	305.0	1018.7	9.8		2.806(1)	20
		167.22					2.773(1)	
		163.72					2.781(1)	
		164.58					2.776(1)	
$EtSnI_3 \cdot 2DPSO$ [a]	77	130.5					2.869(1)	20
		136.5	268.0	895.1	12.4		2.840(1)	
							2.821(1)	
$SnI_4 \cdot 2PyO$ [b]	77	152.78(2)						
		157.38(1)						
		161.91(1)						
$SnI_4 \cdot 2TPPO$	77	158.36					2.813(2)av	21
		163.42					2.782(2)av	

[a] In the bulk powder, resonances with frequencies 111.5, 222.10, 114.68 and 228.67 MHZ were also present. These might be evidence for the presence of a mixture of modifications in the sample available. [b] PyO = pyridine-*N*-oxide.

TABLE 3

Correlation parameters $y = a + bx$ (Figs. 1–3) between ^{35}Cl, ^{81}Br, ^{127}I NQR frequencies and Sn–Hal bond distances in the tin(IV) compounds determined according to the least-squares procedure

	a	b	r^2 [a]
Chloro complexes (Fig. 1)	131.87	−47.58	0.939
Bromo complexes (Fig. 2)	917.66	−311.29	0.922
Iodo complexes (Fig. 3)	1342.08	−423.2	0.981

[a] r^2, correlation coefficient.

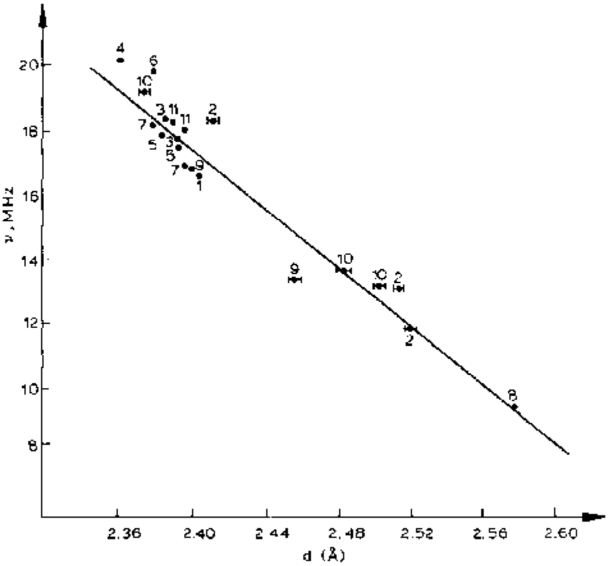

Fig. 1. Correlation between ^{35}Cl NQR frequencies (ν (MHz)) and interatomic Sn–Cl distances (d (Å)) in tin (IV) chloro complexes: 1, $(NMe)_2SnCl_6$; 2. $(NMe_4)_2EtSnCl_5$; 3, $SnCl_4 \cdot 2TPPO$; 4, $EtSnCl_3 \cdot 2TPPO$; 5, $SnCl_4 \cdot 2HMPT$; 6, $EtSnCl_3 \cdot 2HMPT$; 7, $SnCl_4 \cdot 2DMSO$; 8, $Me_2SnCl_2 \cdot 2HMPT$; 9, $EtSnCl_3 \cdot 2DMSO$; 10, $EtSnCl_3 \cdot 2TMU$; 11, $SnCl_4 \cdot 2TMU$.

The NQR results thus give information on the amount of σ-electron density on the halogen atoms in the positions *cis* and *trans* with respect to the alkyl substituent. Since we are interested in the estimation of the extent of the electron density change caused by substitution of the "influencing" ligand, we have to separate out the contribution from frequency changes in factors having no relation to such a substitution.

C. MAIN SOURCES OF ERRORS IN NQR EXPERIMENTAL MEASUREMENTS AND IN DERIVATION OF SPECTRAL PARAMETERS

(i) Accuracy of frequency measurements

The experimental error in the resonance frequency measurement is approximately determined as $\epsilon \approx \Delta\nu/2(s/n)$, where $\Delta\nu$ is a resonance line half-width and s/n is a signal-to-noise ratio. The main contribution to the linewidth in the compounds discussed is inhomogeneous broadening, so that $\Delta\nu/\nu \approx 10^{-3}$. Typical values for the s/n ratio appeared to be of the order of 10–15. This gave $\epsilon \approx (\nu/2.5) \times 10^{-4}$ which produces frequency shifts of ca.

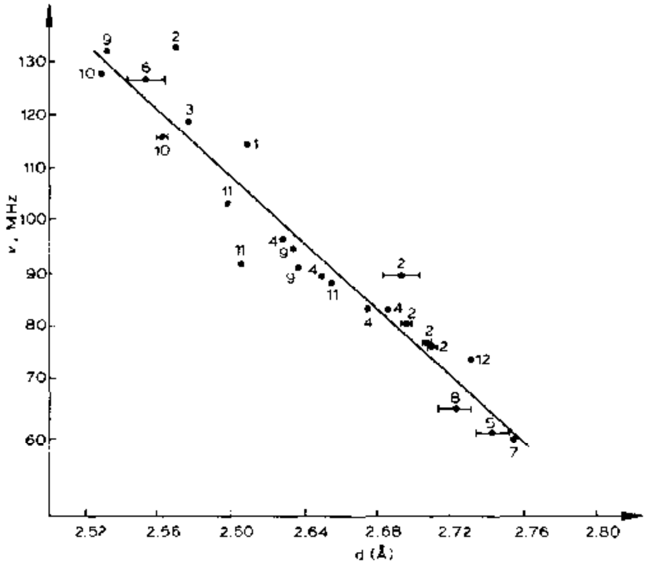

Fig. 2. Correlation between ^{81}Br NQR frequencies (ν (MHz)) and interatomic Sn–Br distances (d (Å)) in tin (IV) bromo complexes: 1, $(NMe_4)_2SnBr_6$; 2, $(NMe_4)_2BuSnBr_5$; 3, $(HPy)_2SnBr_6$; 4, $(HPy)BuSnBr_4 \cdot Py$; 5, $Me_2SnBr_2 \cdot 2HMPT$; 6, $SnBr_4 \cdot 2HMPT$; 7, $Me_2SnBr_2 \cdot 2DMSO$; 8, $Me_2SnBr_2 \cdot 2Py$; 9, $BuSnBr_3 \cdot 2HMPT$; 10, $SnBr_4 \cdot 2DPSO$; 11, $BuSnBr_3 \cdot 2DPSO$; 12, $Bu_2SnBr_2 \cdot bipy$.

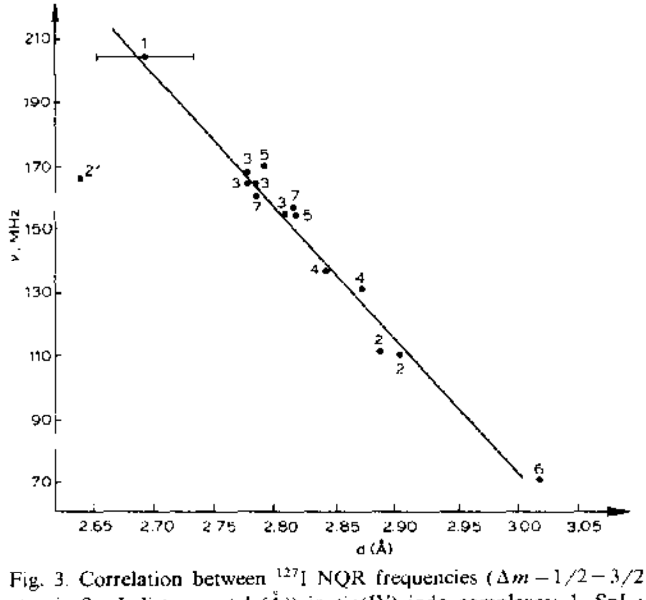

Fig. 3. Correlation between ^{127}I NQR frequencies ($\Delta m - 1/2 - 3/2$) (ν (MHz)) and interatomic Sn–I distances (d (Å)) in tin(IV) iodo complexes: 1, SnI_4; 2, $EtSnI_3 \cdot 2HMPT$; 3, $SnI_4 \cdot 2DPSO$; 4, $EtSnI_3 \cdot 2DPSO$; 5, $SnI_4 \cdot bipy$; 6, $Et_2SnI_2 \cdot 2HMPT$; 7, $SnI_4 \cdot 2TPPO$.

TABLE 4

Ligand influence as found by NQR ($\Delta\delta$ (%))[a] and X-ray analysis (Δd (%))[a]; *cis* weakening, $+\Delta\delta(+\Delta d)$ (%); *trans* strengthening, $-\Delta\delta(-\Delta d)$ (%)

Compound	Assignment	δ(Hal) (average)	($+\Delta\delta$, $-\Delta\delta$) (%)	d(Sn–Hal) (Å) (average)	Ref.	($+\Delta d$, $-\Delta d$) (%)
$(NMe_4)_2SnCl_6$	Cl–Sn–Cl	−0.696	+10.9	2.402(3)	23	
$(NMe_4)_2EtSnCl_5$	Cl–Sn–Cl	−0.772	+10.9 (+11.7[b])	2.516(10)	23	+4.8
	Cl–Sn–C	−0.665	−4.5 (−3.8[b])	2.407(3)		−0.2
trans-$SnCl_4\cdot2HMPT$	Cl–Sn–Cl	−0.674		2.388(1)	24	
$EtSnCl_3\cdot2HMPT$	Cl–Sn–Cl	–		2.491	25	+4.3
	Cl–Sn–C	−0.635	−5.7	2.379(1)		−0.4
$Me_2SnCl_2\cdot2HMPT$	Cl–Sn–Cl	−0.828	+22.8	2.57(1)	24, 26	+7.6
cis-$SnCl_4\cdot2TPPO$	Cl–Sn–Cl	−0.662		2.383(1)	25	
	Cl–Sn–O	−0.676		2.393(1)		
$EtSnCl_3\cdot2TPPO$	Cl–Sn–Cl	–		2.492(1)	25	+4.6
	Cl–Sn–C	−0.627	−5.3	2.361(1)		−0.9
$Et_2SnCl_2\cdot2TPPO$	Cl–Sn–Cl	–		2.603(4)	27	+9.2
cis-$SnCl_4\cdot2DMSO$	Cl–Sn–Cl	−0.690		2.387(1)	13	
	Cl–Sn–O	0.669		2.386(1)		
$EtSnCl_3\cdot2DMSO$	Cl–Sn–O	−0.753	+12.6	2.456(4)	28	+2.9
	Cl–Sn–C	−0.690	−0.0	2.398(3)		−0.5
trans-$SnCl_4\cdot2TMU$	Cl–Sn–Cl	−0.668		2.391(1)		
$EtSnCl_3\cdot2TMU$	Cl–Sn–Cl	−0.755	+13.0	2.491(4)		+4.2
	Cl–Sn–C	−0.647	3.1	2.374(4)		−0.7
trans-$SnCl_4\cdot2THF$	Cl–Sn–Cl	−0.654				
$MeSnCl_3\cdot2THF$	Cl–Sn–Cl(O)	−0.718	+9.7			
	Cl–Sn–C	−0.632	−3.4			
$SnI_4\cdot2HMPT$	I–Sn–I(O)	−0.534				
$EtSnI_3\cdot2HMPT$	I–Sn–O	−0.681	+27.5 (+34.0[c])	2.894(2)	17	+3.8[c]
	I–Sn–C	−0.516	−3.4 (−6.7[c])	2.634(4)		−6.5[c]
$Et_2SnI_2\cdot2HMPT$	I–Sn–I	−0.797	+49.3	3.016(1)	18	+7.1[c]
cis-$SnI_4\cdot$bipy	I–Sn–I	−0.553		2.816	19	
	I–Sn–N	0.508		2.788		
cis-$SnI_4\cdot2DPSO$	I–Sn–I	−0.523		2.779(1)	20	
	I–Sn–O	−0.556		2.790(1)		
$EtSnI_3\cdot2DPSO$	I–Sn–I	−0.615	+17.6	2.855(1)	20	+2.7
	I–Sn–O			2.821(1)		

[a] Calculated using eqns. (2) and (3). [b] Determined using ^{35}Cl NQR data for $[SnCl_6]^{2-}$ at 77 K. [c] Compared with the data for $SnI_4\cdot$bipy.

4×10^{-3} of the measured value, or 1–5 KHz at the ^{35}Cl and ^{81}Br transition frequencies.

(ii) Temperature variation of the resonances

Most of the NQR data cited in this paper were obtained at 77 K in order to reduce the contributions of thermal motion to the spectroscopic parame-

TABLE 5

Ligand influence as shown by NQR ($\Delta\delta$ (%)) [a] and X-ray analysis (Δd (%)) [a]: *cis* weakening, $+\Delta\delta(+\Delta d)$ (%); *trans* strengthening, $-\Delta\delta(-\Delta d)$ (%)

Compound	Assignment	δ(Br) (average)	($+\Delta\delta$, $-\Delta\delta$) (%)	d(Sn–Br) (Å) (average)	Ref.	($+\Delta d$, $-\Delta d$) (%)
$(NMe_4)_2SnBr_6$	Br–Sn–Br	−0.642		2.605(1)	23	
$(NMe_4)_2BuSnBr_5$	Br–Sn–Br	−0.745	−16.0 (+17.5) [b]	2.699(5)	23	−3.6
	Br–Sn–C	−0.584	−8.9 (−7.9) [b]	2.566(2)		−1.5
$(HPy)_2SnBr_6$	Br–Sn–Br	−0.634 [c]		2.574 [c]	14	
$(HPy)BuSnBr_4 \cdot py$	Br–Sn–Br	−0.723	+14.0 (+15.2) [b]	2.657(1)	29	+3.2
trans-$SnBr_4 \cdot 2HMPT$	Br–Sn–Br	−0.603		2.55(1)	24	
$BuSnBr_3 \cdot 2HMPT$	Br–Sn–O	−0.709	+17.7	2.633(1)	30	+3.3
	Br–Sn–C	−0.589	−2.3	2.529(1)		−0.8
$Me_2SnBr_2 \cdot 2HMPT$	Br–Sn–Br	−0.810	+34.6	2.74(1)	24	+7.4
cis-$SnBr_4 \cdot 2DPSO$	Br–Sn–Br	−0.637		2.561(1)	31	
	Br–Sn–O	−0.600		2.529(2)		
$BuSnBr_3 \cdot 2DPSO$	Br–Sn–Br	−0.718	+12.7	2.627(1)	31	+2.6
	Br–Sn–O	−0.681	+13.5	2.595(1)		+2.6
$SnBr_4 \cdot 2THF$	Br–Sn–Br(O)	0.588				
$MeSnBr_3 \cdot 2THF$	Br–Sn–Br(O)	−0.674	+14.6			
	Br–Sn–C	−0.561	−4.6			
trans-$SnBr_4 \cdot 2DMSO$	Br–Sn–Br	−0.599				
$Me_2SnBr_2 \cdot 2DMSO$	Br–Sn–Br	−0.815	+36.1	2.752(1)	24	
trans-$SnBr_4 \cdot 2py$	Br–Sn–Br	−0.618				
$Me_2SnBr_2 \cdot 2py$	Br–Sn–Br	−0.795	+28.6	2.72(1)		
$Bu_2SnBr_2 \cdot bipy$	Br–Sn–N	−0.767		2.656 2.729		

[a] Calculated using eqns. (2) and (3). [b] Determined using ^{81}Br NQR data for $[SnBr_6]^{2-}$ at 77 K. [c] Average values assigned to halogen atoms that do not form hydrogen bonds.

ters. Data at elevated temperatures have been used only when the changes in spectroscopic multiplicities pointed to the existence of phase transitions in the interval between room temperature and 77 K, as in the $(NMe_4)_2SnHal_6$ compounds (Table 1). Cubic at room temperature, they undergo phase transitions to less symmetrical structures on cooling (chloro complexes to 168 K [9] and bromo complexes to 90 K [22]). The results of low temperature X-ray studies are not yet available. It is then clear that the NQR data on substituted $[AlkSnHal_5]^{2-}$ anions should also be examined at elevated temperatures. However, according to the X-ray results on $(NMe_4)_2AlkSnHal_5$ (Alk = C_2H_5, Hal = Cl; Alk = C_4H_9, Hal = Br [23]), disordering of the alkyl group and cationic $(NMe_4)^+$ crystallographic positions exists at room temperature, resulting in a determination of the Sn–Hal distances with highly increased standard deviations. The same reason seems to be responsible for the rapid vanishing of NQR signals with increasing temperature, so that they are already unobservable at 175–180 K. The comparison of effective charges on atoms in $[AlkSnHal_5]^{2-}$ calculated at 77 K with those in $[SnHal_6]^{2-}$ determined at room temperature will evidently give results (Tables 4 and 5) overestimating the *cis* weakening and underestimating the *trans* strengthening of the Sn–Hal bonds owing to the introduction of the alkyl group. The extent of the temperature variation of charges in $(NMe_4)_2SnHal_6$ appeared, however, not to be very important, contributing an error of about 1% (Tables 4 and 5).

(iii) Cation influence on resonance frequencies

Some of the compounds discussed have ionic structures, and we have to discuss the importance of the cation charge contribution to the EFG at the halogen site. The influence of cation charges on the halogen NQR frequency in ionic compounds of general formula R_2SnHal_6 with the K_2PtCl_6 structure type has been considered [32] to result from interionic repulsion acting through the change in the halogen inner electron shell polarization (the Sternheimer antishielding). This antishielding depends on the anion–cation and anion–anion distances between the neighbouring octahedra. With increasing size of the cation, the interionic Hal–Hal distances increase, the repulsion between them weakens and the Sternheimer antishielding factor γ_∞, determining the contribution of external charges to the EFG at the halogen site (Q_{ext}), decreases. Since Q_{ext} has a sign opposite to that of the contribution produced by the intra-anion charge distribution (Q_{int}), the NQR frequency must increase; this increase was observed experimentally within the series R_2MHal_6 (R = K, NH_4, Rb, Cs; M = Sn, Re, Pt; Hal = Cl, Br) [32].

Calculations using the point charge model [32] led to the conclusion that the external charge contribution to the EFG at the site of the halogen associated with the direct electrostatic effect (Q_{dir}) is much smaller than the indirect effect (Q_{ind}) originating from polarization of the halogen core electron shells by external ions. The direct electrostatic effect is thus enhanced by the Sternheimer antishielding factor, giving rise to a large indirect effect responsible for the NQR frequency variations observed experimentally in complexes with the relatively small cations mentioned above:

$$Q_{ext} = Q_{dir} + Q_{indir} = Q_{dir} + Q_{dir}(1 - \gamma_{\infty})$$

According to X-ray results [23] all Hal · · · Hal interanionic distances in the compounds $(NMe_4)_2SnHal_6$ and $(NMe_4)_2AlkSnHal_5$ are longer than the corresponding sums of the van der Waals radii, so that their unit cell dimensions are determined by the anion–cation distances. Only equatorial Cl atoms in $(NMe_4)_2EtSnCl_5$ were found to make Cl · · · CH_3 contacts shorter than the sum of the van der Waals radii. The relative lengthening of the Sn–Cl′ bonding in one of the linear Cl′–Sn–Cl″ fragments (due probably to the presence of shortened Cl · · · N and Cl′ · · · CH_3 contact [23]) is, however, accompanied by the shortening of the Sn–Cl″ bonding in the same fragment. Hence the average magnitudes of the Sn–Cl distances for both equatorial linear fragments Cl–Sn–Cl are practically the same, and the corresponding points deviate insignificantly from the linear correlation (Fig. 1), the average frequencies being unaffected by external charges. In both tetramethylammonium hexachlorostannate(IV) and hexabromostannate(IV), interionic distances are much longer than in similar complexes of the same composition with alkali metal cations.

The volume of the formula unit in the compound $(NMe_4)_2SnBr_6$ is $V = a_0^3/Z = 614.4$ Å^3 compared with $V = 315.8$ Å^3 in Cs_2SnBr_6; for the corresponding chloro complexes they are equal to $V = 532.3$ Å^3 and $V = 277.6$ Å^3 respectively. In monoalkyl-substituted complexes they are also large: $V = 527.6$ Å^3 in $(Me_4N)_2EtSnCl_5$ and $V = 589.9$ Å^3 in $(Me_4N)_2BuSnBr_5$.

While within the series K_2SnCl_6, $(NH_4)_2SnCl_6$, Rb_2SnCl_6 and $(Me_4N)_2SnCl_6$ the difference in cation contribution to the EFG at the chlorine site is responsible for a ^{35}Cl frequency shift of about 14% and no correlation exists between the ^{35}Cl NQR frequencies and the Sn–Cl bond distances [32], the decrease in cation contribution in the compounds with the cations of larger size leads to such a correlation taking place (Figs. 1–3) [14]. This shows that the halogen frequency is mostly determined by intra-anionic electron distribution, i.e. by the ionic character of the Sn–Hal bonding in the compounds studied.

In molecular adducts of composition $SnHal_4 \cdot 2L$ the frequency shifts due to complexation are also produced mainly by intramolecular electron effects.

This was convincingly shown in ref. 13(a) where a linear correlation exists between the halogen NQR frequencies in the linear fragments Hal–Sn–Hal and Hal–Sn–L and the enthalpies of their formation in the gaseous phase.

(iv) Neglect of the asymmetry parameter values at the chlorine and bromine sites and sp *hybridization of the halogen valence orbitals*

A factor responsible for the increase in estimated electron density on the halogen atom is neglect of the asymmetry parameter value (η) in eqn. (1). This neglect changes the magnitude of δ by an insignificant amount, namely, by $3\nu \times 10^{-3}/e^2Qq_0$ for values of η up to $\eta \approx 30\%$, which makes the change equal to $3\nu \times 10^{-4}$ at most. There is no reason to expect the magnitude of η to exceed 30% in the compounds discussed, since the X-ray data available show that their structures are built of nominally isolated fragments in most cases, the Sn–Hal distances possessing typically ordinary bond lengths (see references in Tables 4 and 5). The selected η values experimentally measured in iodo compounds (Table 2) confirm this expectation.

As mentioned above, eqn. (1) also neglects the contribution of s hybridization of the halogen atom np_z orbitals to chemical bonding. This was originally assumed [8] to be 15% when the halogen atom is bonded to an atom more electropositive than the halogen by as much as 0.25. However, taking into account that more recent experimental data provide much evidence that this contribution hardly exceeds 5% for Cl atoms and is reduced further for Br and I atoms we, in agreement with the currently accepted view, neglected this value. Since we are interested not in absolute magnitudes of charges but in their variation over a series of related compounds, such neglect will evidently have no effect on the final conclusions.

D. SOME RELIABILITY ASPECTS OF MEASUREMENTS AND CALCULATIONS IN X-RAY EXPERIMENTS

The main source of error in the X-ray determination of atomic positions is a truncation of the Fourier series. The parameter ($\sin \theta/\lambda$) reaches the magnitude of 0.7 Å^{-1} only rarely, varying as a rule within 0.5–0.6 Å^{-1}. This was due to poor quality of the crystals, which were very difficult to grow in the sizes required for X-ray analysis. The truncation of the Fourier series gave rise to the appearance of many weak false maxima on the electron density maps, affecting the coordinates of the electron density maxima assigned to the real atoms of the crystal structure. In addition, the functions minimized according to the least-squares procedure had false local minima.

The systematic error due to neglect of X-ray absorption by the crystals was insignificant, since, firstly, the single crystals used were small and, secondly, molybdenum irradiation was applied. The latter gave relatively small values for linear absorption coefficients (μ). The value of μR, where R is the radius of a crystal approximated to a sphere, did not exceed six.

The correction for extinction generally did not influence the accuracy of atomic coordinate determination, although in several cases it improved the R factor. The most important correction was that for thermal motion of the atoms. The magnitudes of interatomic distances had a smaller scatter after this correction was applied.

Compounds with statistically disordered crystallographic positions of atoms or atomic groups gave the most serious difficulty for the X-ray study. For instance, in $CH_3SnHal_3 \cdot 2HMPT$ (Hal – Cl, Br) one of the halogen atoms and one methyl group substitute each other statistically, so that the carbon and halogen atom maxima in the electron density maps cannot be distinguished. As a result, the Sn–Hal and Sn–C distances cannot be measured, which means that not only the magnitude but even the direction of the LI is impossible to determine. In such cases the necessary information is derived from a comparison with structures of different compounds, as in ref. 7.

In compounds with no statistical positional disorder, the accuracy of the atomic position measurements is lowered by defects in the crystal lattice. The overall contribution of random and systematic errors affects the accuracy of the determination of interatomic distances in such a way that in chlorides it lies, as a rule, below the level of electronic effects produced by LI, and in bromides it is also often below this level.

In addition, many reasons exist for changes in interatomic distances. Caution is therefore required before ascribing these changes to LI. In this respect the use of NQR data seems to be highly appropriate.

E. EVIDENCE FOR LIGAND INFLUENCE IN NQR SPECTRA AND X-RAY DATA

As mentioned above, quantum chemical considerations predict *cis* weakening of the Sn–Hal bonds accompanied by a relatively smaller *trans* influence when going from unsubstituted to monoalkyl-substituted tin(IV) halides and a further increase in *cis* weakening in dialkyl-substituted compounds [1–7]. We have examined experimentally the validity of these predictions using NQR. The spectral data also give a clear idea of the extent to which the σ-electron density varies as a result of substitution. The weakening of the Sn–Hal bond occurring as a result of substitution evidently leads to an increase in σ-electron density ($N_{p_\sigma} - 1 + |\delta|$) on the corresponding halogen atom. This will cause a lowering of the NQR frequency (eqn. (1)). If the bond is strengthened as a result of substitution, the σ-electron density decreases, which means there is an increase in the NQR frequency with respect to the unsubstituted compound (eqn. (1)).

From an estimation from NQR spectra of the δ values on the halogen atoms, firstly in unsubstituted $SnHal_6$ complexes and $SnHal_4 \cdot 2L$ adducts and then in monoalkyl- and dialkyl-substituted systems, we determined the relative variations in the σ-electron density on the halogen atoms at positions *cis* and *trans* to the alkyl substituent as follows:

$$\pm \Delta\delta(\mathrm{Hal}) = \frac{\delta(\mathrm{AlkSnHal_3 \cdot 2L}) - \delta(\mathrm{SnHal_4 \cdot 2L})}{\delta(\mathrm{SnHal_4 \cdot 2L})} \times 100\% \qquad (2)$$

Similarly, the relative lengthening (shortening) of the Sn–Hal bond (Δd(Sn–Hal)%) was estimated from the X-ray results as

$$\pm \Delta d(\mathrm{Sn{-}Hal}) = \frac{d(\mathrm{AlkSnHal_3 \cdot 2L}) - d(\mathrm{SnHal_4 \cdot 2L})}{d(\mathrm{SnHal_4 \cdot 2L})} \times 100\% \qquad (3)$$

In both cases the ligands L include as the limiting case the anions Hal^-, if the initial unsubstituted compound is $[SnHal_6]^{2-}$. The sign "plus" corresponds evidently to a relative weakening (lengthening) of the Sn–Hal bond, while "minus" corresponds to a relative strengthening (shortening) of the appropriate bonds.

The results obtained are listed in Tables 4 and 5.

As seen from Tables 1 and 2, the influence of the alkyl group is reflected in the NQR spectra in unexpectedly large NQR frequency shifts compared with the unsubstituted compounds. Being expressed in terms of σ-electron density changes, they provide evidence for a profound reorganization in electron distribution as a result of the introduction of the alkyl substituent (Tables 4 and 5). Thus introduction of an ethyl group into a regular $[SnCl_6]^{2-}$ octahedron with a singlet ^{35}Cl NQR spectrum results in a difference between the charge values on equatorial and axial Cl atoms of 0.10 e on average, which corresponds to a spectroscopic splitting of the order of 6 MHz. The influence of a butyl substituent introduced into $[SnBr_6]^{2-}$ is reflected in the difference in charges on the Br atoms at positions *cis* and *trans* with respect to this substituent reaching 0.16 e, or in a splitting of the corresponding ^{81}Br NQR frequencies of the order of 51 MHz.

The substitution of both halogen ligands in the linear fragment Hal–Sn–Hal of the complex *trans*-$SnHal_4 \cdot 2HMPT$ by methyl groups increases the σ-electron density on the halogen atoms in the other fragment by 0.21 e in the bromo complex (the corresponding ^{81}Br resonance being lowered by 67 MHz) and by 0.15 e in the chloro complex (the lower frequency shift being 8.5 MHz). These frequency shifts evidently greatly exceed those produced by the contributions analysed in Section C.

(i) Cis *weakening as reflected in spectroscopic and structural data*

As seen from Tables 1, 2, 4 and 5 the prevailing effect characterizing LI in the compounds studied is a weakening (lengthening) of the Sn–Hal bonds at position *cis* to the alkyl substituents, i.e. *cis* weakening. Its magnitude ($+\Delta\delta$%) depends considerably on the nature of the acidoligand and amounts to 10–13% in monoalkyl-substituted chlorides, 14–18% in the analogous bromides and ca. 28% in the I–Sn–O fragment in $EtSnI_3 \cdot 2HMPT$.

The second alkyl substituent increases the *cis* weakening approximately additively, making the effect in the complexes of type $Alk_2SnHal_2 \cdot 2HMPT$ about 23%, 35% and 50% in the chloride, bromide and iodide respectively. This means that the *cis*-weakening influence of alkyl groups on Sn–Hal bonding increases according to NQR in the order Cl < Br < I.

Variation of ligands L in bromo complexes of the type $Me_2SnBr_2 \cdot 2L$ revealed the contribution of the ligands L to the *cis* influence, combined with the influence of alkyl ligands. Thus $\Delta\delta \approx 36\%$ for L = DMSO, $\Delta\delta \approx 35\%$ for L = HMPT and $\Delta\delta \approx 29\%$ for L = Py, which reflects an increase in σ-electron density on the Br atoms by 0.216 e, 0.208 e and 0.177 e respectively. The corresponding ^{81}Br lower frequency shifts with respect to $SnBr_4 \cdot 2L$ gave 69.3 MHz, 67.1 MHz and 56.9 MHz respectively.

As to the appropriate changes in interatomic Sn–Hal distances, the X-ray data give a *cis* lengthening of about 0.1 Å when going from $SnHal_4 \cdot 2HMPT$ to $AlkSnHal_3 \cdot 2HMPT$. This makes $\Delta d = 4.3\%$ for the chloro, $\Delta d = 3.3\%$ for bromo and $\Delta d = 3.8\%$ for the I–Sn–O fragment of the iodo complex. (In the last case the *cis* weakening was estimated with respect to $SnI_4 \cdot$ bipy since the structure of $SnI_4 \cdot 2HMPT$ is not yet known.)

In dialkyl tin substituted complexes, $Alk_2SnHal_2 \cdot 2HMPT$, when the second alkyl group occupies a position *trans* with respect to the first, the relative *cis* lengthening ($+\Delta d$ (%)) becomes 7.6%, and 7.4% for the chloro compound and bromo compound respectively and 7.1% for the iodo compound (also with respect to $SnI_4 \cdot$ bipy). The X-ray results therefore do not detect the dependence of *cis* lengthening on the nature of the acidoligand.

(ii) Trans *strengthening in chloro and bromo complexes according to data from two methods*

The *trans* influence is reflected in X-ray data as a not very significant change in the corresponding Sn–Hal distance. In adducts of chloro compounds they are not observed within the standard deviation values. Only in $[EtSnCl_5]^{2-}$ was the effect noted as a *trans* shortening of the order of 1.3% after thermal motion corrections were applied [23]. Shortening by approximately 0.05 Å of the Sn–Br bonds at the position *trans* to the alkyl substituent has also been found for $[BuSnBr_5]^{2-}$ and $EtSnBr_3 \cdot 2TPPO$, which makes $\Delta\delta \approx 1.5\%$ for the former complex (Table 5).

The *trans* influence is, however, reliably detected in all the compounds studied by NQR spectroscopy. The only direction of the effect observed was *trans* strengthening. It consisted of a decrease by 3–6%, with respect to the unsubstituted precursors, of the σ-electron density on the halogen atom at the position *trans* to the alkyl substituent. The greatest *trans* strengthening ($\Delta\delta \approx 9\%$) was observed in $[BuSnBr_5]^{2-}$, which gave rise to a high frequency shift of 18 MHz in the ^{81}Br resonance with respect to the unsubstituted $[SnBr_6]^{2-}$ anion. The deficiency in the experimental data available does not unfortunately enable us to establish any regularities in *trans* strengthening, such as, for example, the relative contribution to the effect of various alkyl groups, or its dependence on acidoligands.

As seen from Tables 4 and 5, *trans* strengthening to an approximately similar extent is observed in alkyl tin trichloride (3–6%) and alkyl tin tribromide (4–5%) complexes.

(iii) *Results for iodo complexes*

An unusually large *trans* shortening has been found by X-ray analysis [17] in $EtSnI_3 \cdot 2HMPT$ ($\Delta d = 0.17$ Å if the Sn–I bond distance at the *trans* position to the ethyl group is compared with that in the I–Sn–I fragment of $SnI_4 \cdot bipy$). The *trans*-shortened Sn–I bond distance in $EtSnI_3 \cdot 2HMPT$ was reported [17] to become even shorter than in SnI_4. The NQR results (Tables 2 and 4), however, showed that the *trans* shortening in $EtSnI_3 \cdot 2HMPT$ does not exceed similar effects in the related chloride and bromide. The amount of σ-electron density on the *trans* iodine atom was found to be noticeably higher in $EtSnI_3 \cdot 2HMPT$ (1.52 e assuming $\eta = 0$) than in SnI_4 (1.4 e). According to NQR the effect of *trans* strengthening in $EtSnI_3 \cdot 2HMPT$ when calculated, as in the X-ray analysis [17], with respect to $SnI_4 \cdot bipy$ (6.7%) exceeded by a factor of almost two that calculated with respect to its parent adduct $SnI_4 \cdot 2HMPT$ (3.4%). The complex $EtSnI_3 \cdot 2HMPT$ is at present the only compound where X-ray analysis finds such a strong *trans* shortening, the *cis* lengthening lying within ordinary limits. Taking into account that NQR does not show any unusual *trans* strengthening in this sample, one should refrain from drawing final conclusions on this compound until consistent results from the two methods become available.

F. CONCLUDING REMARKS

As the results of NQR show, the ligand influence in hexacoordinate alkyl tin(IV) halogen complexes consists of a profound electron reorganization of all the tin–halogen bonds, owing to the introduction of a substituent with strong σ-donor properties (alkyl group) into $[SnHal_6]^{2-}$ or $SnHal_4 \cdot 2L$. In agreement with theoretical predictions the NQR spectra as well as the X-ray results provide evidence for a considerable increase in σ-ionic character of the Sn–Hal bonds at positions *cis* to the alkyl substituent, accompanied by their lengthening with respect to the corresponding parent compounds (*cis* weakening). Using NQR, regularities in *cis* weakening have been studied in a quantitative manner, i.e. the relative extent of ligand influence on the electron density on the halogen atoms, is dependent on the type of donor ligand L, the acidoligand and the number of alkyl substituents.

The *trans* influence has been identified by NQR only as a decrease in σ-electron density on the halogen atoms at the position *trans* to the alkyl group (*trans* strengthening). The relative importance of both the *cis* and the *trans* influence has been compared on a quantitative scale in terms of variations in σ-electron density on the appropriate halogen atoms with respect to the parent compounds. It appears that *cis* weakening is characterized on average by an increase in the σ-electron density by 0.08 e and 0.1 e on Cl and Br atoms respectively, while *trans* strengthening was measured as a decrease in the σ-electron density on the halogen atoms by 0.02–0.04 e, reaching nearly 0.06 e in $[BuSnBr_5]^{2-}$.

X-ray analysis, however, finds no structural evidence within the standard deviations for *trans* influence in chloro complexes, except for $[EtSnCl_5]^{2-}$ where *trans* shortening of the order of 1.3% could be ascertained after thermal motion corrections were applied. *Trans* shortening of the order of 1.5% was also observed in $[BuSnBr_5]^{2-}$. X-ray data for strong *trans* shortening in $EtSnI_3 \cdot 2HMPT$ are inconsistent with the NQR results.

As NQR shows, the ligand influence is governed by the electron effects, those responsible for the *cis* influence being particularly strong. The effects of the *trans* influence, which are 2–5 times weaker were, however, also readily reflected in the NQR spectra, the corresponding frequency shifts exceeding the errors of measurement by orders of magnitude.

In general, the analysis of the variation in bond distance is a less direct way to study the phenomenon, the necessary information being masked by various lattice contributions influencing the interatomic distances. These might be the reason for the apparent discrepancies between the X-ray and spectroscopic results concerning, for example, the dependence of *cis* weakening on the nature of the acidoligand.

The NQR parameters, directly determined by electron density distribution, reflect the effects of LI more adequately, being at the same time more sensitive to electron effects than the interatomic distances. However, X-ray data on the spatial arrangement of atoms and atomic groups, especially in the isomers of monoalkyl-substituted adducts, are very helpful for the correct assignment of resonance lines and hence for reliable conclusions on ligand influence.

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