Electronic Characteristics of Sn–Hal Bonds in Hexa- and Pentacoordinate Tin(IV) Adducts of Type $R_nSnHal_{4-n}L_x$ *

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The σ- and π-electron effects of alkyl/phenyl substituents on the Sn–Hal bonds in penta- and hexacoordinate tin(IV) chloro and iodo adducts are discussed based on their ^{35}Cl and ^{127}I NQR spectra. Unexpectedly high ^{127}I EFG asymmetry parameters were found in most dialkyl(phenyl)-substituted adducts of thin(VI) iodides.

Key words: ^{35}Cl and ^{127}I NQR; adducts of tin(IV) halides; the electronic effects of alkyl/phenyl substituents.

Introduction

Earlier, we studied a series of NQR spectra with the aim of examining the redistribution of electron densities upon complexation of main group IV element halides. We were mainly interested in a metal-halogen bond reorganization due to the effects of various donor ligands (substituents) [1–4]:

$MHal_4 \rightarrow MHal_4L \rightarrow SnHal_4L_2 \rightarrow Alk_nSnHal_{4-n}L_2$
(M = Si, Ge, Sn).

Experimental data on ligand effects in the chemistry of main group elements are less extensive than in the coordination chemistry of transition elements. The relation between the donor properties of ligands L and the halogen ligands in tin(IV) complexes of the type $SnHal_4L_2$ being often uncertain, we performed a systematic NQR study of tin(IV) complexes of the type $Alk_nSnHal_{4-n}L_2$, where one or two acido ligands were substituted by σ-donor groups (R) which notably exceeded the halogen ligands in donating power [1–4].

Among various theoretical approaches developed to predict the effects of substituents on main group element complexes, the one developed by Musher [5] and applied by Shustorovich et al. [6] to the compounds of interest is in best agreement with the results of NQR and X-ray experiments [1].

The resulting changes in the M–Hal bonds were found to be sensitive to details of the adduct electronic structure, namely, the AO relative energies for the central metal, halogen, and substituent as well as the oxidation number of the central atom. The theory is based on the model of hypervalent (HV) orbital-deficient bonds and suggests that the central atom valence basis involves only nS and nP orbitals. According to this model, in the parent $SnHal_6$ complex, the 5 S orbital of the tin atom participates in the formation of three equivalent three-center SP hybrid HV bonds Hal–Sn–Hal, each involving only one 5 P orbital of the central atom.

In substituted and especially in disubstituted complexes, occupation of a_1^* MOs occurs, which are antibonding with respect to the equatorial ligands. Because the a_1^* MOs contain a remarkable contribution of the S orbital of the central atom, the s-character of the equatorial bonding orbitals diminishes, so that the bonds weaken with respect to those in the unsubstituted complex. On the other hand, the alkyl substituent R cannot form stable hypervalent bonds with tin, because R is less electronegative than Sn, so that the R–Sn bonds are normal covalent two-center two-electron bonds, which are naturally stronger than the hypervalent bonds.

Thus, this approach [6] predicts a weakening of the Sn–Hal bonds at the *cis* position to R in $RSnHal_5$ ($RSnHal_3L_2$) complexes, that might be accompanied by *trans* influence (presumably strengthening), as com-

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Table 1. ^{35}Cl and ^{127}I NQR spectra of the adducts at 77 K and the Sn–Hal bond characteristics.

Adduct[a]	Assignment[b]	^{35}Cl Res. frs., MHz ^{127}I e^2Qq/h, MHz[c]	η, %	$\Delta n P\pi$ $(nP_{x-n}nP_y)$	$-\delta$, e[d]
1. $SnCl_4(TMU)_2$ *trans* [2]	e	18.26 (2)	7.5	0.017	0.64
2. $EtSnCl_3(TMU)_2$ *trans* [1]	Cl–Sn–C	19.35 (1)	11.0[e]	0.026	0.61
	Cl–Sn–Cl	13.47 (2)	11.0[e]	0.016	0.73
3. $SnI_4(TMU)_2$ *cis*	e	1095.30 (1)	6.0	0.019	0.49
	á	1048.04 (1)	1.9	0.006	0.53
4. $EtSnI_3(HMPT)_2$ *cis*	I–Sn–C	>1101.7 (1)[g]	<8.0	<0.026	>0.48
		<1109.3 (1)	>0.0	>0.0	<0.52
	I–Sn–L	732.4 (2)	11.0	0.023	0.64
5. $Ph_2SnI_2(HMPT)_2$ *trans*	e–1[f]	495.17 (1)	41.2	0.059	0.695
	e–2[f]	504.08 (1)	41.2	0.060	0.69
6. $SnCl_4 \cdot CH_3NO_2$ [3]	e	24.22 (3)	11.0	0.032	0.51
	a	20.21 (1)	4.5	0.011	0.62
7. $SnCl_4 \cdot C_6H_5OCH_3$ [2]	e	23.63 (3)	11.5	0.033	0.52
	a	20.18 (1)	0.9	0.002	0.63
8. $Ph_2SnI_2 \cdot TMU$	e	>1126.75 (1)[g]	<12.0	<0.039	>0.45
		<1130.77	>10.5[e]	>0.035	<0.455
	a	753.14 (1)	0.0	0.0	0.67

[a] The adducts 1–5 are pseudooctahedral, 6–8 are trigonal-bipyramidal; [b] a – axial, e – equatorial halogen site; [c] the number of halogen sites, over which the averaging is performed, is parenthesized; [d] the effective charges at halogen atoms are calculated assuming $nP_y = 2$; [e] taken as an average of all the known η-values in the related adducts; [f] the unit cell comprises two crystallographically independent molecules of the adduct [7]; [g] the ν_2 resonance was not found up to 330 MHz.

pared to the unsubstituted $SnHal_6(SnHal_4L_2)$ compounds.

Using NQR, both effects were observed experimentally and their relative importance was compared; the *trans* influence was always weaker than the *cis* effect and resulted in strengthening of the corresponding Sn–Hal bond [1, 4]. Because only a few measurements of the EFG asymmetry parameters (η) were performed, the NQR results were interpreted assuming $\eta = 0$ and discussed in terms of their consistency with X-ray data available.

Results

Here, we present the NQR results for compounds $R_nSnHal_{4-n}L_x$ (R = Alkyl, Phenyl; Hal = Cl, I), where the measurement of η at halogen sites enabled us to discuss the effects of substitution, with a contribution of π-electron density variation taken into account. We also discussed differences between the Sn–Hal bonds in pseudooctahedral and trigonal-bipyramidal adducts.

The determination of the ^{35}Cl η-values in powder samples was based on the analysis of slow beats of the spin-echo envelope in an external magnetic field, as described in [2]. In tin(IV) iodo adducts, the ^{127}I EFG asymmetry parameters could be found directly, provided both transition frequencies ($\Delta m = 1/2 - 3/2$ and $\Delta m = 3/2 - 5/2$) are measured using a pulse NQR spectrometer operating within 10–330 MHz.

Table 1 lists the ^{35}Cl and ^{127}I NQR spectra of the titled adducts. The effective charges (δ), born by halogen atoms, and variations of their $P\pi$ orbital occupancy difference ($\Delta n\, P\pi$), that resulted from either substitution or spatial rearrangement of the adducts, are estimated. To minimize an uncontrollably varying contribution from ligands L, the data on the adducts with the same ligand (TMU, tetramethyl urea) were preferably cited, wherever available. In cases where the necessary spectroscopic parameters were not available for a certain adduct, those averaged over all the values determined for the related compounds were used. ^{35}Cl NQR frequencies and ^{127}I quadrupole coupling constants ($QCC = e^2Qq/h$) are averaged over crystallographically inequivalent halogen sites.

In the course of our work, we mainly concentrated on the preparation and NQR investigation of new iodo adducts, because these were the least studied.

Discussion

In agreement with previous findings [1], Tables 1 and 2 show that the alkyl groups weaken the Sn–I bonds at *cis* position to the alkyl substituents. In

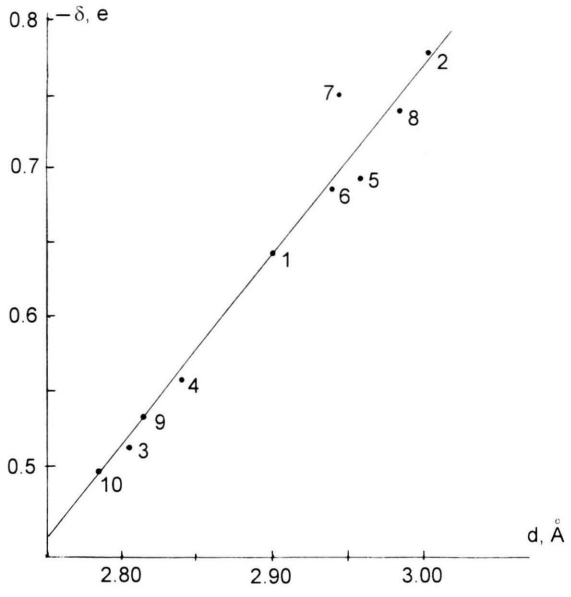

Fig. 1. Correlation between effective charges on the iodine atom ($-\delta$, *e*) and interatomic Sn–I distances (*d*, *Å*) in tin(IV) iodo adducts:
(1) $EtSnI_3([CH_3)_2N]_3PO)_2$; (2) $Et_2SnI_2([CH_3)_2N]_3PO)_2$;
(3) $SnI_4(Ph_2SO)_2$; (4) $EtSnI_3(Ph_2SO)_2$;
(5, 6) $Ph_2SnI_2([CH_3)_2N]_3PO)_2$; (7, 8) $Et_2SnI_2[(CH_3)_2SO]_2$;
(9, 10) $SnI_4([CH_3)_2N])_2CO)_2$.

Table 2. ^{127}I NQR spectra (MHz) of $R_2SnI_2L_2$ at 77 K [8].

Adduct	Res. frqs.		e^2Qq/h	η, %
	1/2–3/2	3/2–5/2		
$Et_2SnI_2(DMSO)_2$	70.83	119.30	409.07	39.1
	79.96	156.34	523.00	13.3
$Ph_2SnI_2(DMSO)_2$	103.17	192.00	647.32	24.3
	107.02	212.04	707.80	8.6
$Et_2SnI_2(HMPT)_2$ [1]	70.51	140.26	467.9	6.5
$Ph_2SnI_2(HMPT)_2$[a]	86.92	144.0	495.17	41.2
	88.46	146.6	504.08	41.2
$Et_2SnI_2(Py)_2$	80.92	149.36	504.35	25.7
	82.01	162.38	542.13	8.8
$Ph_2SnI_2(Py)_2$	98.11	187.68	630.03	18.9

[a] An alternative variant of line assignment ($\eta_1 = 38.9\%$ and $\eta_2 = 43.4\%$) leads to the same values of effective charges at the iodine atoms.

monoalkyl-substituted iodides, the weakening, measured as a relative increase in the effective charge on the appropriate I atoms with respect to that in the parent adduct, amounts to ca. 25%, whereas the second alkyl group increases the effect nearly additively.

The correlation of the effective charges, born by the iodine atoms, with the appropriate Sn–I bond distances (Fig. 1), constructed with regard to the measured η-values ($-\delta = -1.286\,d + 3.088$; $r^2 = 0.019$), shows that the 0.1-Å elongation of the Sn–I bond corresponds to the increase in the negative effective charge on the I atom by ca. 0.13 e. Earlier, a σ-electron density increase (assuming $\pi = 0$), that accompanied the similar Sn–Br and Sn–Cl bond elongations in the related adducts, was estimated to be notably weaker (0.1 and 0.08 e, respectively [1]). It is of interest to recall that according to the X-ray diffraction data [9], the Sn–Hal bond elongation, resulting from alkyl substitution, was the same for the adducts of any halogen elements, amounting approximately to 0.1 Å per one alkyl group.

As one can see from Tab. 2, the phenyl substituents also weaken the appropriate Sn–I bonds, although to a lesser extent. The effective charges born by the iodine atoms in diphenyl- and dialkyl-substituted adducts differed, on average, by 0.08 e.

Figure 2 illustrates a typical variation of the σ- and π-electron characteristics of the Sn–Hal bonds in pseudooctahedral $SnHal_4L_2$ adducts due to alkyl/phenyl substitution and/or rearrangement of the adducts to a trigonal-bipyramidal configuration. As one can see from this figure, a monoalkyl substitution results in *cis* lengthening and *trans* shortening of the Sn–Hal bonds. The latter acts mainly through the σ-system of the Hal atoms. The effect is readily detected by an upward NQR frequency shift (Table 1), but it is evidently less pronounced than the *cis* weakening, which results in an increase in the effective negative charges on the corresponding Hal atoms of ca. 0.09 e (14%) and 0.13 e (25%) in the chloro and iodo adducts, respectively, whereas their π-systems remain virtually undisturbed.

When an adduct of pseudooctahedral configuration is compared to that of trigonal-bipyramidal geometry, one can see that the largest negative charge locates at the axial Hal atom of the latter molecule, whereas the charge born by the equatorial Hal atom substantially decreases with respect to that in the hexacoordinate adduct; the π-system of the appropriate Sn–Hal bond seems to contribute also to the bond strengthening.

The π-system of equatorial halogen atoms in pentacoordinate adducts participates in a bond formation, as was concluded earlier based on ^{35}Cl NQR studies [3] of a number of MCl_4L adducts (M = Si, Ge, Sn). The results showed that, first, the average Cl $3P\pi$

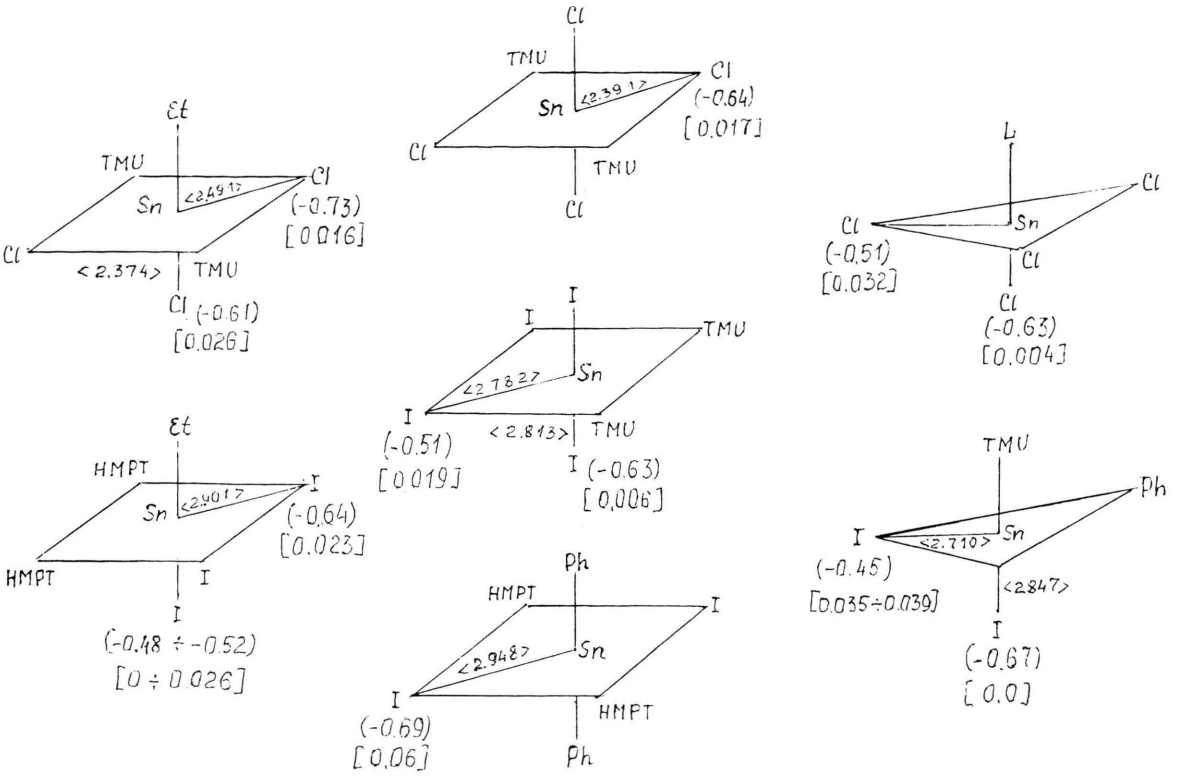

Fig. 2. Effective charges on halogen atms ($-\delta$, e), their $nP\pi$ orbital occupancy differences ($\Delta n\, P\pi$, e) and Sn–Hal interatomic distances $\langle d, A\rangle$ in various adducts of tin(IV) halides.

orbital occupancy difference at equatorial sites decreases in the order Si (0.1) <Ge (0.08) <Sn (0.03), and, second, the adduct formation can be accompanied by an increase in the Cl $3P\pi$ orbital occupancy difference with respect to that in the parent MCl_4 compounds, provided the donor ability of ligands L is small.

In general, as is seem from Table 1, the entire effective negative charge, born by all the Cl atoms in pentacoordinate ($SnCl_4L$) adducts, is lower by c.a. 0.4 e than that in hexacoordinate ($SnCl_4L_2$) adducts. Unfortunately, no structural data are available on any of the spectroscopically examined trigonal-bipyramidal tin(IV) chloro adducts.

As expected, a decrease in the negative effective charge on Hal atoms and a virtual undisturbance of their π-system is observed upon going from chloro to iodo adducts of pseudooctahedral configuration (Figure 2). The maximum Sn–Hal *cis* weakening (lengthening) is observed in dialkyl-substituted iodo adducts. That the weakening influence of the phenyl substituents is also considerable, is demonstrated by Fig. 2: in the diphenyl-substituted adduct of HMPT, the Sn–I bond elongation (0.17 Å) is accompanied by an increase of 0.18 e ($\approx$35%) in the effective charge on the corresponding iodine atom.

Surprisingly, the substitution $SnI_4L_2 \rightarrow Ph_2SnI_2L_2$ was accompanied by an unexpectedly large increase in the EFG asymmetry parameters on the iodine site. The ^{127}I η-value increased from 6% in the unsubstituted adduct to 41.2% in $Ph_2SnI_2(HMPT)_2$ (Table 1), whereas an X-ray examination of the latter compound [7] found no secondary contacts involving the I atoms. Moreover, as seen from Table 2, a considerable increase in η, that accompanies a strong weakening of the presumably terminal Sn–I bonds in disubstituted adducts, is found also in the tin(IV) diethyl- and diphenyldiiodo adducts with DMSO (39.1% and 24.3%, respectively) and diethyldiiodo adduct with Py (25.7%).

Attempts have been made to grow single crystals of $Et_2SnI_2(DMSO)_2$ and $Ph_2SnI_2(TMU)_2$ for their subsequent X-ray study, because the ^{127}I NQR spectrum of the diphenyl-substituted adduct with TMU ($\nu = 112.98$; 171.65; 225.92; > 330 MHz) appeared to be inconsistent with hexacoordinate structure. However, the repeated efforts to prepare $Ph_2SnI_2(TMU)_2$ in different solvents with varied amounts of ligand (TMU) excess yielded only $Ph_2SnI_2(TMU)$. An X-ray diffraction study showed that the adduct has a trigonal-bipyramidal geometry, which is in agreement with its NQR spectrum. The Sn–O bond distance (2.33 Å) shows that the accepting power of diphenyldiiodostannate(IV) is weak, which seems to account for our failure to obtain the adduct of the composition 1:2. The phenyl substituents in the trigonal-bipyramidal adduct show a tendency to enhance the relative weakening of the axial Sn–I bond. This is seen from comparison of the Sn–Hal bond differences in the pairs $SnI_4L_2 \rightarrow Ph_2SnI_2L$ and $SnCl_4L_2 \rightarrow SnCl_4L$ (Figure 2).

Single crystals of $Et_2SnI_2(DMSO)_2$ were obtained successfully, and the structure was found to be pseudooctahedral, with the ethyl groups arranged at *trans* and the DMSO ligands, at *cis* position to each other. The positions of the ligand molecules are disordered, so that the S atoms in both DMSO ligands are located at two unequally occupied (3:1 and 4:1) positions. In both ligands, the sulfur atoms, found at the positions of relatively higher occupancy, are involved in either intra- (4.11 Å) or intermolecular (3.79 Å) nonvalence S...I contacts, so that each iodine atom forms one secondary contact. This might be the reason (at least partially) for the increased η-values in this adduct. The origin of the high asymmetry parameters in the remaining compounds is not clear at the moment.

Conclusions

The measurement of the ^{35}Cl and ^{127}I EFG asymmetry parameters in hexa- and pentacoordinate tin(IV) halo adducts showed that the π-electron contribution is relatively more pronounced in the Sn–Hal equatorial bonds of trigonal-bipyramidal adducts, whereas *cis* weakening and *trans* strengthening of the appropriate Sn–Hal bonds due to monoalkyl/phenyl substitution in pseudooctahedral adducts occurs mainly via the σ-system.

Unexpectedly high ^{127}I EFG asymmetry parameters were found in most dialkyl/phenyl-substituted adducts of tin(IV) iodides. In $Et_2SnI_2(DMSO)_2$, they might originate from the S...I secondary contacts that involve both iodine atoms, whereas no reasonable explanation for the high η-values follows from the results of X-ray examination [7] of the structure of $Ph_2SnI_2(HMPT)_2$.

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