

The value of Wiberg bond order must be not lesser than 0.3. The donor-acceptor interactions of main-group elements such as Sb and Sn described in terms of the sp hybridization just as these interactions of transition metal elements mean sd hybridization.

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INVESTIGATION OF TIN AND ANTIMONY COMPOUNDS USING NQR, X-RAY ELECTRON AND QUANTUM-CHEMICAL CALCULATIONS

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This paper is a part of the systematic studies performed by us for understanding the electronic structure of organic compounds of tin and antimony. It was shown in our previous papers that the NQR, X-Ray electron and fluorescence spectroscopies provides a simple way to characterise the electronic properties for qualitative interpretations of the structure, chemical reactivity and aspects of bonding [1–5]. In this paper we try to explain the relations between ³⁵Cl-NQR frequency and the energies of the internal levels in the tin and antimony compounds.

It is well known, from Townes-Dailey approximation [6], that the ³⁵Cl-NQR frequencies are proportional to the degree of ionic character of the bonds. The latest one is dependent on the effective charge on the atoms and therefore is proportional to the energies of the internal levels.

We report analogous relations for Sn and Sb compounds with organic ligands. The calculations were performed by the NDDO method in PM3 modifica-

tion in the basis of sp valent orbitals using MOPAC program [7]. The geometry of the studied compounds optimized by quantum-chemical methods is consistent with that determined in experiment for the same compound in gas phase [8].

The calculated by Koopmans ionization potentials of the valent orbitals were compared with energy orbitals from photoelectron spectra [9]. A good correlation was found between the ionization potentials calculated by PM3 method and experimental values following from the photoelectron spectra. Analysis of this correlation leads to the following relation:

$$IP^{\text{exp}} = 1.06IP^{\text{cal}} - 0.88 \quad (r=0.997, s=0.09). \quad (1)$$

Table 1 presents the effective charge calculated by PM3 method, the experimental X-Ray electron spectroscopy (ESCA) levels [8] and the experimentally found [5] and calculated ³⁵Cl-NQR frequencies. The following relations between the energy of ESCA levels of Cl and Sn atoms and the effective charge were derived:

$$ECl2p_{3/2} = -11.45(-q_{Cl}) + 208.98 \quad (r=0.986, s=0.01), \quad (2)$$

$$ESn3d_{5/2} = 18.0(-q_{Sn}) + 476.82 \quad (r=0.984, s=0.01). \quad (3)$$

A good correlation was also found between the experimental and calculated ^{35}Cl -NQR frequencies: $\nu_{exp}^{35Cl} = 1.49\nu_{cal}^{35Cl} - 29.46$ ($r=0.990, s=0.1$). (4)

The obtained relations (2) and (3) indicate additivity of the internal energy levels as a consequence of the interaction between different ligands. In the studied compounds the ligands complete about the electron density of the central atom. The replacement of Cl by CH_3 groups brings about increase in the ionic character of the Sn-Cl bond which leads to elongation of these bond and to an increase in the binding orbital energy $Cl2p_{3/2}$. The binding orbital energies in the first approximation are a linear function of the effective charge of the studied atom while the values of $Cl2p_{3/2}$ and $Sn3d_{5/2}$ prove to be an additive function of the number of substituents.

Since the ^{35}Cl -NQR frequencies are proportional to the effective charge on Cl atoms, they are correlated with the ESCA energy levels:

$$ECl2p_{3/2} = 0.136\nu_{exp}^{35Cl} \quad (r=0.996, s=0.03), \quad (5)$$

$$ESn3d_{5/2} = 0.121\nu_{exp}^{35Cl} \quad (r=0.996, s=0.03). \quad (6)$$

The obtained dependencies can be applied in analysis of the electronic structure of other tin compounds, in particular $SnCl_4L_2$ complexes with L being an organic ligand. For these compounds ESCA could not have been recorded so far. On the other hand their ^{35}Cl -NQR spectra are well known. Table 2 presents the ^{35}Cl -NQR frequencies and energies of the ESCA levels calculated from (4) and (5) as well as the $ClK\alpha$ shifts obtained from X-Ray fluorescence spectra [5].

The difference between the energies of Cl and Sn atoms as well as the $ClK\alpha$ shifts characterises the donor properties of the ligands. The following correlation was found between $\Delta(Sn3d_{5/2}-Cl2p_{3/2})$ and $ClK\alpha$ values:

$$\Delta(Sn3d_{5/2}-Cl2p_{3/2}) = -1.45(-\Delta ClK\alpha) + 288.6 \quad (r=0.959, s=0.02). \quad (7)$$

On the other hand we found that the analogous correlation between Moessbauer chemical shifts and energy of the $Sn3d_{5/2}$ levels for $SnCl_4L_2$ and

$SnBr_4L_2$ (experimental data were taken from the reference [6]):

$$\delta = -0.54ESn3d_{5/2} + 262.3 \quad (r=0.959, s=0.02) \quad (8)$$

and between Moessbauer chemical shifts and $\Delta ClK\alpha$:

$$\delta = 1.7(-\Delta ClK\alpha) + 0.212 \quad (r=0.970, s=0.02). \quad (9)$$

On the basis of these above-mentioned equations we found the correlation dependence between $ESn3d_{5/2}$ and $\Delta ClK\alpha$:

$$ESn3d_{5/2} = -3.2(-\Delta ClK\alpha) + 486.5. \quad (10)$$

Which is very similar to those (7) obtained for the $SnCl_4L_2$.

The analogous correlation dependencies we obtained for the $SbCl_5L$ complexes. We have also found good correlations between the ΔE [11] and $n^{35}Cl$ as well as between $\Delta ClK\alpha$ and inner levels from photoelectron spectra. The dependence between the ΔE and $\nu^{35}Cl$ is described by the equation:

$$\Delta E(Sb3d_{5/2}-Cl2p_{3/2}) = -0.427 \nu^{35}Cl + 333.58 \quad (r=0.948, s=0.03), \quad (11)$$

what means that the ΔE decrease with $\nu^{35}Cl$ increasing and ionicity of the Sb-Cl bond decreasing.

The dependence between the ΔE and $\Delta ClK\alpha$ was described by the equation:

$$\Delta E(Sb3d_{5/2}-Cl2p_{3/2}) = 12.1(-\Delta ClK\alpha) + 320.9 \quad (r=0.926, s=0.04), \quad (12)$$

what means that q_{Sb} increase with the DN ligand properties increase. If the ligand gives more and more the electron density to the central atom, than more and more the electron density from central atom is transferred. The dependencies (7) and (12) are completely different for $SbCl_5L$ and $SnCl_4L_2$ complexes. It could be explain by the difference between Sn and Sb atoms. It is well known [12], that the change of the trans-shortening of the central atom - ligand bond length to trans-influence of ligand upon exchange from Sn to Sb can be observed.

These relations order the ligand in the following sequence with respect to their donor properties. This sequence is in the agreement with the ordering given by Gutman [13]:

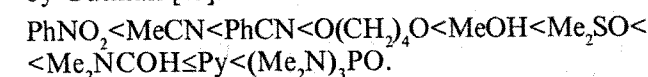


Table 1
The energies of ESCA levels for Sn(IV) compounds studied

Compound	$ECl2p_{3/2}$ [eV]	$-q_{Cl}^{PM3}$ [e]	$ESn3d_{5/2}$ [eV]	q_{Sn}^{PM3} [e]	ν_{Cl}^{exp} [MHz]	ν_{Cl}^{cal} [MHz]
$SnCl_4$	206.19	0.253	494.92	1.011	24.10	36.22
$MeSnCl_3$	205.52	0.294	494.06	0.957	20.24	32.77
Me_2SnCl_2	204.96	0.340	493.21	0.901	15.46	29.71
Me_3SnCl	204.49	0.400	492.27	0.843	11.73	28.08
Me_4Sn	-	-	491.38	0.829	-	-

Table 2
The ^{35}Cl -NQR frequencies and the energies of ESCA levels calculated by (5) and (6) equations as well as the $\text{ClK}\alpha$ shifts obtained from X-Ray fluorescence spectra for SnCl_2L_2 complexes

L	$\nu_{\text{Cl}}^{\text{exp}}$ [MHz]	$\text{ECl}2\text{p}_{3/2}$ [eV]	$\text{ESn}3\text{d}_{5/2}$ [eV]	$\Delta(\text{Sn}3\text{d}_{5/2}-\text{Cl}2\text{p}_{3/2})$ [eV]	$-\Delta\text{ClK}\alpha$ [eV]
$(\text{Me}_2\text{N})_3\text{PO}$	17.91	205.32	493.61	288.29	0.215
Bz_2S	18.33	205.37	493.70	288.33	0.155
$(\text{CH}_2)_4\text{O}$	19.02	205.47	493.84	288.37	0.141
Me_2NCOH	17.71	205.27	493.59	288.32	0.162
$\text{O}(\text{CH}_2)_4\text{O}$	19.46	205.51	493.96	288.45	0.079
Py	17.73	205.27	493.59	288.32	0.165
Me_2SO	18.32	205.35	493.72	288.37	0.119
MeOH	18.89	205.43	493.84	288.41	0.108
MeCN	20.12	205.60	494.10	288.50	0.075
PhCN	19.79	205.55	494.03	288.48	0.062

Table 3
The ^{35}Cl -NQR frequencies and the energies of the photoelectron levels as well as the $\text{ClK}\alpha$ shifts obtained from X-Ray fluorescence spectra for SbCl_2L complexes

L	$\nu^{35}\text{Cl}$ [MHz]	$\Delta\text{E}(\text{Sb}3\text{d}_{5/2}-\text{Cl}2\text{p}_{3/2})$ [eV]	$-\Delta\text{ClK}\alpha$ [eV]
$(\text{Me}_2\text{N})_3\text{PO}$	24.54	323.10	0.189
Py	25.30	322.78	0.148
Me_2NCOH	24.90	322.95	0.156
$\text{O}(\text{CH}_2)_4\text{O}$	25.65	322.63	0.133
MeCN	25.93	322.51	0.140
PhCN	26.21	322.39	0.136
PhNO_2	26.68	322.19	0.110

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CONCEPT OF TECHOGENESIS DEPENDENT FOOD CHAINS

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At the normal conditions of life activity, the organism of a human being needs 22 biogenous elements which source is water and food of vegetal and animal origin. A state of environment is a major factor of human existence, since it is environment that determines the quality of nutritive [1].

The content of chemical elements in alive organisms is not a direct function of their abundance in nature [2]. At the same time it is known that the passage of chemical elements along a food chain can lead to both their dissipation and their accumulation, biological concentration [3].