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Relationship between XPS Core Binding Energies and Atomic Charge in Adducts of Sn^{IV} Derivatives with Pyrazine, and Comparison with Mössbauer Isomer Shift Data

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Adducts Snhal·pyz (hal = Cl, Br, I; pyz = pyrazine), $RnSnCl_{4-n}$·pyz (n = 1, R = Me, Bu^n, Oct^n, Ph; n = 2, R = Ph) and $SnCl_4$·$(pyz)_2$ have been investigated by X-ray photoelectron spectroscopy. Binding energy (b.e.) values are discussed in the light of structural characteristics of the adducts as well as of valence state electronegativities of atoms and groups bound to tin. Sn $3d_{5/2}$ b.e.s, corrected for the Madelung potential at the metal atom, linearly correlate with both partial atomic charges on tin, accounting for relaxation upon ionization, and ^{119}Sn Mössbauer isomer shifts.

The results are interpreted in terms of six-coordinated, octahedral type, configurations of the environment of tin throughout all terms of the homologous series.

Introduction

The purpose of the present work is the investigation of the contribution by X-ray photoelectron spectroscopy (XPS) to the structural characterization of the title compounds, and the comparison between the information provided by XPS and by Mössbauer isomer shift spectral data. Structural effects, whose elucidation can be aided by core binding energy data from XPS, include the influence of the number and nature of atoms and groups bound to Sn on its b.e. values, and the consequent correlation between Sn core b.e.s and the atomic charge q_{Sn}. Since also ^{119}Sn Mössbauer isomer shifts, δ, depend on the atomic charges (although only through their s-fractions), it appears interesting to determine the type of dependence of both δ and b.e. on q_{Sn}, and the cross-correlation between δ and b.e.

Previous work established parabolic or linear correlations of δ of a coordinated atom with the overall ligand electronegativity, $\Sigma\chi$, or more correctly with the s electron density at the Mössbauer nucleus [1]. For the pyrazine adducts here investigated, a good linearity of δ with computed q_{Sn} values has been observed on the hypothesis of six-coordination of tin [2]. It turns out however that a relation between δ and $\Sigma\chi$ or q_{Sn} holds usually within homologous series of compounds, and different functions are found for any individual series (*e.g.*, $Snhal_4$, $Snhal_6^{2-}$, $RSnhal_3$, *etc.*) [1]. On the other hand, the relation b.e./q_{Sn} is expected to generally hold and literature work supports this view on the ground of XPS b.e. data on a number of tin compounds both in gas and solid state [3, 4]; a better correlation is achieved for solids if tin XPS b.e.s are corrected for the Madelung potential generated by the atomic charge distributions in the neighbourhood of the tin atom, and by accounting for relaxation energy on ionization [3, 4]. The cross correlation between Mössbauer isomer shifts and XPS b.e. data has been investigated for several tin(IV) derivatives [5–10], and distinct correlation functions have been observed to occur for any homologous series.

Experimental, and Methods of Data Treatment

The adducts SnX_4·pyz (X = Cl, Br, I; pyz = pyrazine), $SnCl_4$·$(pyz)_2$, $RSnCl_3$·pyz (R = CH_3, n-C_4H_9, n-C_8H_{17} and C_6H_5) and $(C_6H_5)_2SnCl_2$·pyz were prepared and purified according to previous literature [2, 11, 12], and their purity checked by physical methods.

XP spectra were taken on solid samples deposited as thin films on gold probes, and cooled to liquid N_2 temperature to avoid possible sublimation or loss of ligands. The spectrometer used was the VG ESCA-3 model, operated with AlKα (1486.6 eV) source. Calibration by the gold $4f_{7/2}$ signal at 84.0 eV and the

TABLE I. XPS Data, Mössbauer Isomer Shifts, Partial Atomic Charges, and Potential Energies at Tin Sites, for Pyrazine Adducts of Tin(IV) and Organotin(IV) Halides.

Code No.	Compound[a]	b.e. Sn $3d_{5/2}$[b]	b.e. N1s[b]	b.e. halnp[b]	δ[c]	Q_R[e]	$q_N(Sn)$[f] ($q_N(Sb^+)$)	$q_c(Sn)$[f] ($q_c(Sb^+)$)	$q_{hal}(Sn)$[f] ($q_{hal}(Sb^+)$)	V_R
1	$SnCl_4 \cdot pyz$	488.0	401.1	199.8	0.52	+0.016	+0.029 (+0.153)	– –	−0.339 (−0.220)	−1.5(5)
2	$SnBr_4 \cdot pyz$	487.6	401.1	183.2	0.83[d]	−0.039	+0.028 (+0.151)	– –	−0.328 (−0.202)	−0.8
3	$SnI_4 \cdot pyz$	487.8	401.2	632.5	1.29[d]	−0.103	+0.026 (+0.149)	– –	−0.309 (−0.186)	−0.0(6)
4	$SnCl_4 \cdot (pyz)_2$	488.3	401.3	200.0	0.50	+0.016	+0.027 (+0.151)	– –	−0.339 (−0.220)	−1.8
5	$MeSnCl_3 \cdot pyz$	487.7	401.5	200.1	0.99	−0.066	+0.004 (+0.119)	−0.001 (+0.124)	−0.405 (−0.296)	−0.9
6	$Bu^nSnCl_3 \cdot pyz$	487.8	401.4	200.2	1.13	−0.065	+0.005 (+0.119)	+0.012 (+0.137)	−0.405 (−0.296)	−1.1
7	$Oct^nSnCl_3 \cdot pyz$	487.8	401.4	199.8	1.03	−0.065	+0.005 (+0.119)	+0.012 (+0.137)	−0.405 (−0.296)	−1.1
8	$PhSnCl_3 \cdot pyz$	488.1	401.4	200.1	0.91	−0.045	+0.005 (+0.119)	+0.019 (+0.149)	−0.404 (−0.295)	−1.0(5)
9	$Ph_2SnCl_2 \cdot pyz$	487.7	400.9	200.2	1.36	−0.101	−0.032 (+0.067)	+0.016 (+0.146)	−0.505 (−0.411)	−0.3(5)

[a] pyz = pyrazine (1,4-diazine). [b] Experimental XPS binding energies, eV. [c] Mössbauer isomer shift with respect to R.T. $Ca^{119}SnO_3$, mm s^{-1}; data from Ref. [2] unless otherwise stated. [d] This work. Ref. [11]: $SnBr_4 \cdot pyz$, δ = 0.85; $SnI_4 \cdot pyz$, δ = 1.48, mm s^{-1}. [e–g] Parameters calculated by the CHELEQ program, referred to the input structures of Fig. 1. See text. [e] Partial charges on tin atoms obtained through valence state electronegativity equalization upon bond formation and relaxation on ionization. [f] Examples of partial atomic charges on atoms in the tin environment, concerning unionized, $q_i(Sn)$, and core-ionized ($q_i(Sb^+)$) molecules, to be employed in the calculation of V_R (in conjunction with Sn–i distances of Table II). Data in this Table refer only atoms directly bound to tin. The full list of q_i values here used in estimating V_R is available on request. [g] The potential energy at tin sites, corrected for relaxation, eV.

b.e. values referred to C1s (from contamination) taken as 285.0 eV proved the absence of significant charging effects. Measured signals include Sn $3d_{5/2,3/2}$, N1s, Hal $np_{3/2;1/2}$ and C1s. Other Sn signals (3s, 3p) were measured too, but proved less sensitive and less well resolved than Sn 3d; the C1s band was composite due to the presence of partly distinguishable signals from carbon atoms of pyrazine, of alkyl- and phenyl-groups, and of contamination. Accuracy of b.e. data can be estimated as better than ∓0.2 eV throughout the work. Results are partly reported in Table I.

Mössbauer data have been determined previously [2]; additional δ values have been obtained under the same experimental conditions of ref. [2]. In particular, the value δ = 1.29 mm s^{-1} (Table I) of the SnI_4 adduct, which differs from the literature report [11], has been obtained through repeated spectra on samples from different synthetic batches, all having the correct elemental composition.

Partial atomic charges originated upon bond formation have been calculated through the valence state electronegativity equalization procedure proposed by Jolly and Perry [13]. To this purpose, the CHELEQ program [13] has been employed, which

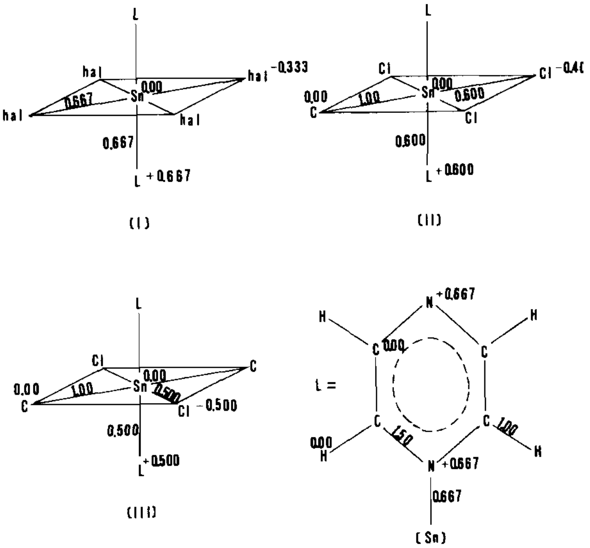


Fig. 1. Valence bond formulas and input parameters used in CHELEQ charge calculations. In the case of $SnCl_4 \cdot (pyz)_2$, considered as a monomeric unit, formal charge = 0.00 was assigned to the pyrazine nitrogen not linked to tin. In alkyl radicals, formal charges were 0.00 and bond orders 1.00; analogously in phenyl substituents, except for the C$\overset{...}{-}$C bond order in phenyl rings, which was assumed as 1.500.

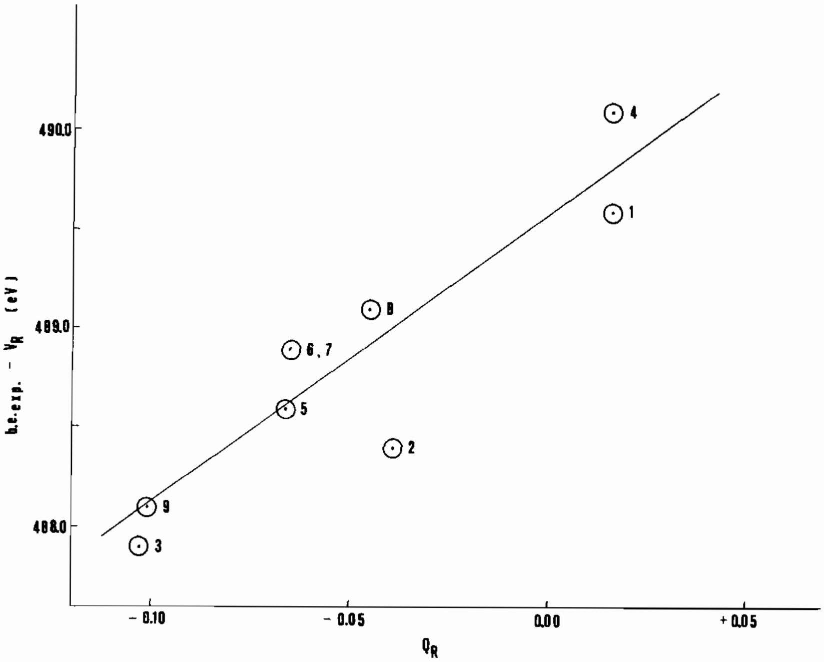


Fig. 2. Sn $3d_{5/2}$ b.e. values, corrected for the Madelung potential V_R, *vs.* the relaxation-corrected partial atomic charges (CHELEQ) on Sn, Q_R. Full line is the least squares fit of data points, from the eqn. $(\text{b.e.}_{\text{exp}} - V_R) = 14.65\,Q_R + 489.58$, the correlation coefficient being $r = 0.909$.

has been partly modified in order to suit our purposes (the empirical constants $C_n = C_m = 2.7$ [13] have been used throughout). Input data, *i.e.*, bond orders and formal charges in the studied molecules, are shown in Fig. 1; a bond order = 1.00 has been attributed to tin–carbon bonds in (II) and (III) in view of experimental evidence as well as of their interpretation (see *e.g.* Ref. [14]), while (I) implies equal participation of tin s and p orbitals on bonding. Partial charges have been correlated to binding energies through the potential model equation [13] in the form:

$$\text{b.e.} = KQ_R + V_R + l \qquad (1)$$

The parameters Q_R have been obtained from Eqn. (2):

$$Q_R = q_{Sn} + \Delta Q = q_{Sn} + (q_{Sb^+} - 1 - q_{Sn})/2 \qquad (2)$$

in which q_{Sn} and q_{Sb^+} are the partial charges on the Sn atom of a given adduct before and after ionization, respectively, according to the principle of equivalent cores. It follows that Q_R is the charge on Sn in a molecule in the 'transition state' [13]. Analogously, the potential term V_R is defined as:

$$V_R = V_{Sn} + \Delta V = V_{Sn} + (V_{Sb^+} - V_{Sn})/2 \qquad (3)$$

where V_{Sn} and V_{Sb^+} are the Coulomb potentials created at the unionized and ionized tin sites, respectively [13] The values of V $(= 14.4 \sum_i (q_i/d_i))$ have been obtained by using the tin–neighbor atom distances, d_i, listed in Table II, as well as $q_i(\text{Sn})$, $q_i(\text{Sb}^+)$ charges such as those in Table I. The empirical constants K and l have been determined by least-squares fit of $(\text{b.e.}_{\text{exp}} - V_R)$ *vs.* Q_R data points, Fig. 2 and legend. All calculations have been performed by the aid of the CHELEQ program and its

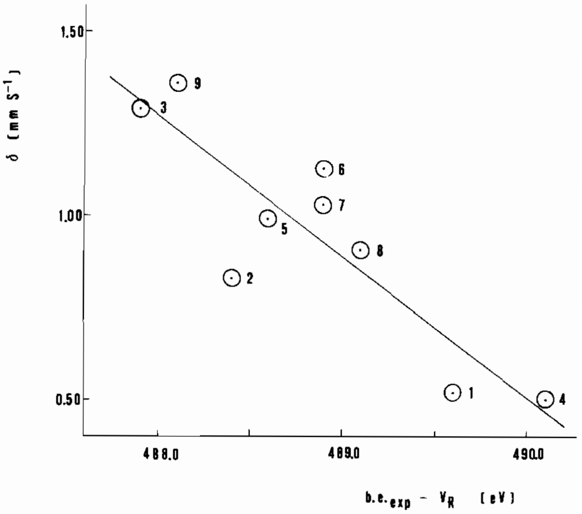
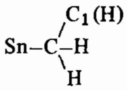
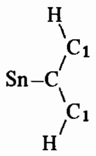
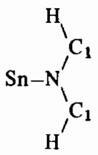


Fig. 3. ^{119}Sn Mössbauer isomer shifts *vs.* Sn $3d_{5/2}$ b.e. values corrected as in Fig. 2. Full line is the least squares fit of data points, the correlation coefficient being $r = 0.873$.

TABLE II. Interatomic Distances Employed in the Calculation of Potentials at the Ionizing Atom[a].

Pyz adduct	Distance from tin of atom	d (Å)
A) Bonds at tin		
$SnCl_4$	Cl	2.383
$SnBr_4$	Br	2.358
SnI_4	I	2.729
AlK- and $PhSnCl_3$	Cl	2.399
AlK- and $PhSnCl_3$	C	2.136
Ph_2SnCl_2	Cl	2.493
Ph_2SnCl_2	C	2.134
All compounds	N	2.362
B) Atoms of alkyl groups:		
$AlKSnCl_3$	C_1	3.079
$AlKSnCl_3^3$	H	2.720
C) Atoms of phenyl groups:		
$PhSnCl_3$ and Ph_2SnCl_2	C_1	3.079
$PhSnCl_3$ and Ph_2SnCl_2	H	3.139
D) Atoms of pyrazine rings:		
All compounds	C_1	3.252
All compounds	H	3.247

[a] The data tabulated here derive from published crystal and molecular structures of pertinent compounds. For example, the value d(SnCl) for $SnCl_4 \cdot Pyz$ is the average of 24 data from six references concerning adducts $SnCl_4 \cdot 2L$.

Distances pertaining to atoms not directly bound to Sn have been calculated trigonometrically through published bond lengths and angles. As an example, the value $Sn\widehat{-N-}C = 119.7°$ is the average of 18 data from four references, and it has been used in calculating $d(SnC_1)$, (see D). In some cases (d(CH), d(CC)AlK *etc.*) values from L. E. Sutton (Ed.), 'Tables of Interatomic Distances and Configurations in Molecules and Ions', Special Publ. No 11 and No 18, London (Chem. Soc.), have been used, also in order to get estimates of apparently not reported data (*e.g.*, $Sn-C_{AlK}-C_{AlK}$ has been taken as $C_{AlK}\widehat{-C_{AlK}-}C_{AlK} = 112.9°$ in n-pentane). Lists of references here employed are available on request.

subroutines [13], and some resulting parameters are in Table I. Lastly, the correlation between ^{119}Sn Mössbauer isomer shifts and the Madelung corrected Sn $3d_{5/2}$ b.e. parameters, (b.e.$_{exp}$ – V_R), is reported in Fig. 3.

Discussion

The N1s b.e. values of Table I are almost constant around 400.3 eV; the signals are fairly narrow (~2.0 eV FWHM), which suggests under our experimental conditions the occurrence of a single type of nitrogen atom in all compounds here investigated. This is consistent with the polymeric six-coordinated structures previously advanced (on the basis of vibrational and Mössbauer spectroscopic studies) for the adducts $Snhal_4 \cdot pyz$ and $R_nSnCl_{4-n} \cdot pyz$, where the ligand acts as bridging bis-monodentate [11, 2]. The latter would then occur also in $SnCl_4 \cdot (pyz)_2$ according to the uniqueness of its N1s signal (Table I), which would favour the polymeric structure inferred from the lattice dynamics parameters of this compound [2] rather than the monomeric six-coordinated configuration, with monodentate pyz, extracted from infrared and Mössbauer studies [2, 11]. On the other hand, inequivalent nitrogen atoms (*i.e.*, free and coordinated) in the pyrazine molecule are expected to yield either two N1s b.e. signals differing by about 1 eV or a broadened band, in consonance with findings for analogous cases. In our pyrazine adducts, the full widths at half maximum of the N1s signals constantly lie around 2 eV, and this may forbid the detection of peaks from inequivalent N sites.

Tin $3d_{5/2,3/2}$ experimental uncorrected b.e. values do not consistently vary along the investigated series of compounds (for example, $3d_{5/2}$ for $Snhal_4 \cdot pyz$ and $R_nSnCl_{4-n} \cdot pyz$ lie within 0.5 eV, Table I). Besides, they do not show the expected relationship with electronegativity-dependent parameters. In fact, uncorrected Sn b.e. data of Table I are not sequantially related to, *e.g.*, the sum of the valence state 'inherent electronegativities' [15], $\Sigma\chi$, of the halogen atoms and organic groups bound to Sn in each compound. Moreover, they do not correlate to partial charges q_{Sn} (*vide supra*), whatever coordination number of Sn is assumed in our adducts. It is instead determined, in consonance with previous literature reports [4], that experimental b.e.s. have to be corrected for the Madelung potential at tin sites V_R, due to neighbour atoms, in order to satisfactorily correlate to both $\Sigma\chi$ and q_{Sn}. To some approximation tin $3d_{5/2,3/2}$ b.e. values vary quite considerably along the investigated series of compounds, roughly depending on the overall electronegativity of the groups bonded to Sn, and spread over an interval of about 1 eV throughout the investigated series.

Inspection of the b.e. values of Sn, after correction for intramolecular Madelung effects and relaxation processes, Table I, allows rationalization of some structural trends within the investigated series. A first effect is the halogen replacement X = Cl, Br, I in $SnX_4 \cdot pyz$: corrected Sn $3d_{5/2}$ b.e. values decrease steadily in the order Cl > Br > I, according to the steady decrease of computed q_{Sn} value [1]. It is however to be recalled that such regular trend is verified only within the Madelung relaxation corrected, and not with the experimental uncorrected b.e. values. It is interesting to mention here the XPS data measured for $SnCl_4 \cdot 2pyz$ which shows a slightly higher measured b.e. value for Sn $3d_{5/2}$.

Another structural effect which can be followed in our series is the replacement of Cl through a carbon radical in $RSnCl_3 \cdot pyz$ (R = C_6H_5, CH_3, higher alkyl) as compared with $SnCl_4 \cdot pyz$. For all R, Sn 3d b.e. is lowered by an average of 0.7 eV; no significant difference occurs in XPS data between alkyl R substituents of different chain length (methyl, n-butyl, n-octyl), differently from the observed variations in the Mössbauer parameter δ (see Table I). The overall electron-releasing effect appears to be somewhat smaller for R = phenyl in $PhSnCl_3 \cdot pyz$; this is certainly due to the electronic structure of the phenyl group, although the actual mechanism of phenyl substituent effect is still subject to controversial estimates. To a further approximation in particular, the function (b.e. $-V_R$) *vs.* Q_R is nearly linear when the six-coordinated structures of Fig. 1 are assumed as actual, its intercept and slope corresponding to literature data [3, 4] reported for a series of tin(IV) derivatives (see Table I, Fig. 2, and Method of Treatment of Data). The b.e. value for $Q_R = 0$ is 489.6 eV, in substantial agreement with the values reported by previous authors [3, 4]. The slope of the line (b.e.$_{exp}$ $- V_R$) *vs.* Q_R turns in our case close to 14.7 eV, again of the same order as given by other authors: 14.77 [3], 9.72 [4] and close to $I_2(Sb) - I_1(Sn) \cong 11.7$ eV. It then may be concluded that the present XPS data and their rationalization support the octahedral type structures already proposed for our adducts on the basis of infrared and Mössbauer spectroscopic studies [2, 11], including the linear dependence of isomer shifts, δ, on partial atomic charges on tin [2].

At this point, the correlation between δ and (b.e. $- V_R$) shown in Fig. 3 follows in a straightforward way from the foregoing discussion together with the general consideration, already discussed in the literature, that the two quantities δ and b.e. depend in different ways on the steric and bond structure of the tin atom. In fact, δ depends directly only on intraatomic effects, *i.e.*, the s electron density at the nucleus and by extension, in the present homologous series, on the net atomic charge q_{Sn}, whereas b.e. values have to be corrected previously for interatomic Madelung effects and relaxation, in order to allow significant correlations; the latter depend therefore directly on the charge and distances of the atoms in the enviroment around the tin atoms, as well as on the valence state electronegativities of Sn and Sb. These facts imply a different sensitivity of δ and of b.e. on structural effects.

Our data reflect previous findings on δ/b.e. correlations, as reported for tin oxinates [6], hexahalostannates [7], acetyl-, benzoyl-acetonates and dibenzoylmethanates [9]. Besides, it is easily seen that the compounds treated by Grutsch *et al.* [8] (No. 8–19 in their Table II) practically constitute two homologous series, $SnCl_4 \cdot L_2$ and $SnBr_4 \cdot L_2$, since couples of data points δ/Sn $3d_{5/2}$ b.e. practically describe two distinct lines, one per series (the $Ph_2Sn(oxinate)_2$ point belonging to the $SnCl_4 \cdot L_2$ line). In all these correlations there appears a general decrease of δ with increasing b.e. (as in the pyz adducts, Fig. 3) which is just the effect expected on the basis of a steady concurrent depletion of charge on the Mössbauer, and ionizing, atom. In any event, this type of correlation may fail, due to peculiar bonding characteristics, even in homologous series [9]. We intend to continue our investigations in this field, in order to better understand the significance and potentiality of these relationships.

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