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XPS Structural Data, and Correlation with Mössbauer Spectra for Tin-organic Compounds: Adducts of R_nSnCl_{4-n} with 1,2-bis(diphenylphosphino)ethane

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Core level X-ray photoelectron spectra of 1:1 adducts of $SnCl_4$ and $RSnCl_3$ with DPE [$R_nSnCl_{4-n}\cdot$ DPE ($n = 1$, R = Me, Bu^n, Oct^n, Ph^n; $n = 2$, R = Ph; DPE = 1,2-bis(diphenylphosphino)ethane], have been measured in solid phase. The $Sn3d_{5/2}$ binding energies, corrected for the Madelung potential at the metal atom, are well correlated with both partial atomic charge on tin, accounting for relaxation upon ionization, and ^{119}Sn Mössbauer isomer shifts. The results are discussed in terms of these molecular parameters.

Introduction

Of the many synergic combinations of different investigation techniques employed in the elucidation of electronic molecular structure, X-ray photoelectron spectroscopy (XPS) and Mössbauer spectroscopy have proved a valuable combination, particularly for tin compounds [1–7]. Satisfactorily linear correlations have been found previously [7] between computed atomic charge of tin on the one hand and Mössbauer isomer shifts δ and Sn inner core ($3d_{5/2}$) binding energies on the other, for a series of adducts of metal-organic tin(IV) halides with pyrazine (pyz). The present extension is a further check on the limits of validity and applicability of the above correlations, which until now [7] were only tested in compounds of the same (or strictly related) structural types. The same type of correlation is investigated here for another class of metal-organic tin complexes of different bonding characteristics, namely 1:1 adducts of $SnCl_4$ and $RSnCl_3$ with the bidentate ligand DPE (= 1,2-bis(diphenylphosphino)-ethane). While formally analogous to the previously investigated series of pyrazine complexes [7], the series of DPE adducts differs in minor changes in coordination geometry, as well as in the lower electronegativity of the P *versus* the N donors, resulting in a lower range of positive tin charges in the DPE series. In addition, the different σ and π bonding ability of both ligand systems results in a different hybridization of the atoms present in the coordination spheres, and therefore in a different participation of 's' in the valence structure of tin.

Experimental

The investigated compounds were of minimum formula $RSnCl_3\cdot DPE$ (R = Cl, CH_3, C_6H_5, n-Bu, n-Oct) and $(C_6H_5)_2SnCl_2\cdot DPE$; they were prepared according to known literature methods [8–11] and characterized by their physical properties. Experimental XPS measurements were run on a VG-ESCA 3 spectrometer equipped with AlKα (1486.6 eV) source. Calibration by the gold $4f_{7/2}$ signal at 84.0 eV, and b.e. values referred to C1s (from carbon contamination) taken as 285. 0 eV, proved the absence of significant charging effects. Measured b.e. values include Sn $3d_{5/2,\ 3/2}$, P 2p, Cl 2p and C1s. Further Sn signals such as 3s and 3p were also measured but proved less sensitive and less well resolved than Sn 3d. Accuracy of b.e. data can be estimated as better than ±0.2 eV throughout this work. Relevant results are listed in Table I.

Mössbauer data have been described at length elsewhere [9]; in particular, the values of δ = 0.72 and 1.35 mm s^{-1} for $SnCl_4\cdot DPE$, and $(C_6H_5)_2$-$SnCl_2\cdot DPE$ respectively are in good agreement with previous literature reports [8, 10].

Computed atomic charges were obtained by the valence state electronegativity equalization procedure

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TABLE I. XPS Data, Mössbauer Isomer Shifts, Partial Atomic Charges, for DPE Adducts of Tin(IV) and Organotin(IV) Halide.

Code	Compound[a]	b.e. calc.[b]	b.e. exp.[c]	b.e. exp − V_R[d]	Q_R[e]	δ[f]
No.		Sn $3d_{5/2}$	Sn $3d_{5/2}$	Sn $3d_{5/2}$		
1	$SnCl_4$•DPE	487.7	487.7	489.0	−0.093	0.72
2	$MeSnCl_3$•DPE	487.2	487.3	488.0	−0.164	1.18
3	Bu^nSnCl_3•DPE	487.0	487.3	488.1	−0.163	1.19
4	Oct^nSnCl_3•DPE	487.0	487.2	488.0	−0.163	1.20
5	$PhSnCl_3$•DPE	487.4	487.3	488.1	−0.143	1.06
6	Ph_2SnCl_2•DPE	487.5	487.2	487.3	−0.185	1.35

[a] DPE = 1,2-bis(diphenylphosphino)ethane. [b] According to the equation: b.e. calc = $K \cdot Q_R + V_R + 1 + E_R$. Standard deviation = 0.2. [c] Experimental XPS binding energies, eV. [d] V_R is the potential at the ionizing atom accounting for the relaxation process. [e] Partial charges on tin atoms obtained through valence state electronegativity equalization upon bond formation and relaxation on ionization. [f] Mössbauer isomer shift with respect to R.T. Ca $^{119}SnO_3$.

(CHELEQ) [7], adopting the set of bond lengths and angles reported in ref. 14.

Table I lists the relevant experimental XPS b.e. data, together with corrections for intramolecular Madelung effects V_R, (b.e.$_{exp}$ − V_R), Mössbauer data, and atomic charges (CHELEQ), as computed taking into account relaxation effects occurring upon ionization.

Discussion

As in our previous investigation of a related series of tin(IV) halides and tin(IV)-organic halides with the pyrazine ligand [7], Sn $3d_{5/2}$ b.e. values vary to some extent according to the nature of the groups bonded to Sn. There is however no strict correlation between computed values of atomic charge on the tin atom and the experimentally measured b.e.s of Sn core orbitals, and the total spread of experimental b.e.s is relatively small. Only if corrections for intramolecular Madelung potentials V_R are applied to measured b.e.s, does the correlation with relaxation-corrected Q_R values become more regular. As in the previously investigated series of pyrazine adducts [7], the size of Madelung correction depends on the geometry of coordination around the tin atom, so the fitness of correlation between corrected Sn $3d_{5/2}$ b.e.s and computed Q_R depends ultimately on the stereochemistry of the investigated metal-organic complexes, for which no less than three alternatives can be considered, *viz.* monomeric pentacoordination with monodentate DPE, discrete hexacoordination with *cis*-bidentate DPE, and polymeric hexacoordination with bridging DPE. In the latter case both *cis*- and *trans*-coordination of the diphosphine can be considered [10].

Unlike the pyrazine series of tin-organic adducts [7], XPS data for the series of DPE adducts do not lend themselves to unambiguous structure determination. This is a general aspect of XPS which is as a rule scarcely capable of distinguishing between geometric isomers of the same coordination numbers (in the present case, between *cis*- and *trans*-octahedral arrangements), rather than a specific consequence of the potential bidentate *cis*-chelating behaviour of DPE, obviously not possible for the pyrazine ligand. Indeed, the relationship between corrected b.e. values and computed charges Q_R turns out in the present case to be accidentally quite close for the two types of assumed geometry. Only a more reasonable slope in the (b.e.$_{exp}$ − V_R) *vs.* VQ_R correlation represents an indication in favor of 6-coordination (*ca.* 16 eV against 11 eV for 5-coordination), since it is closer to previously reported slope values around 14–15 eV [12, 13], as well as to the 14.7 eV value found in our previous investigation of tin-organic adducts with pyrazine [7]. No further distinction can be deduced from XPS data as to monomeric or polymeric, *cis*- or *trans*-hexacoordination in the investigated adducts; besides, exact correlation to XPS data previously obtained for the analogous series of pyrazine adducts [7] is impaired by inherently different calibration procedures, as discussed below in more detail. Our conclusion in favor of a hexacoordinated polymeric structure for the tin-organic DPE adducts is therefore based largely on considerations of analogy with the series of pyrazine adducts, and of evidence from other investigation techniques, and is only indirectly supported by XPS evidence. Structural evidence from XPS data obtained in the pyrazine series is lacking, namely the inner core photoionization patterns of the donor atom of the coordinated base. The N1s peaks of nitrogen in the pyrazine adducts are sharp and narrow, and are thus indicative of a single species of nitrogen atoms (necessarily involved in a bridged coordinated structure), in the DPE series P2p signals

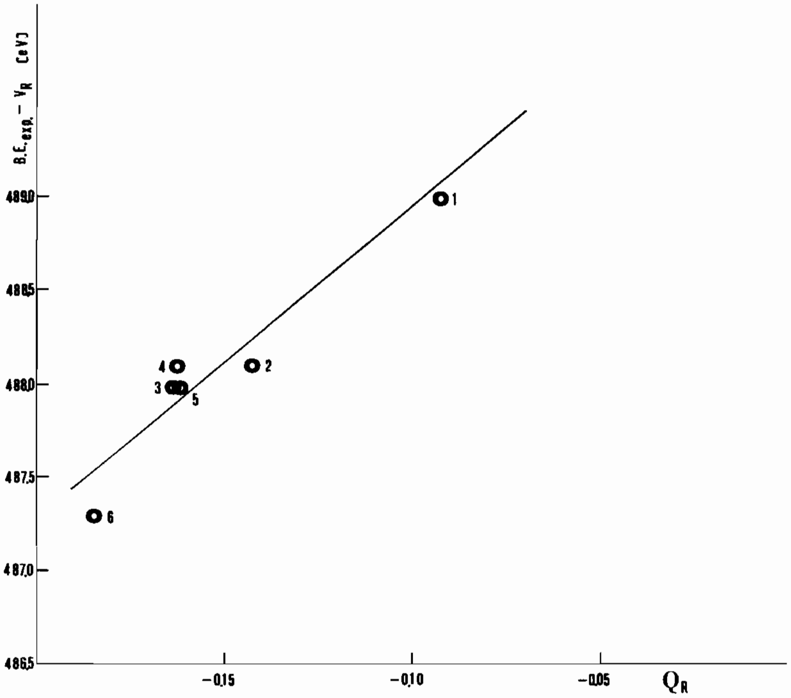

Fig. 1. Sn $3d_{5/2}$ b.e. values, corrected for the Madelung potential V_R, *vs.* the relaxation-corrected partial atomic charges (CHELEQ) on Sn, Q_R. Full line is the least squares fit of data points from the eqn. $(b.e._{exp} - V_R) = 16.60\ Q_R + 490.61$, the correlation coefficient being r = 0.936.

appear broader because of their only partially resolved spin doublet structure, and are not strictly constant in b.e. throughout the investigate series. Substituent effects and general trends of b.e. data in the series of DPE adducts closely resemble (apart from minor differences) the situation found previously in a series of pyrazine adducts [7]. Thus, an increasing trend of Sn $3d_{5/2}$ b.e. values is observed with increasing ligand electronegativity; apparently, the small spread of b.e. values for the investigated series is quite small if we take the uncorrected b.e. values into consideration, but becomes considerable (as expected) and of the correct order of magnitude (*ca.* 2 eV) as the Madelung-corrected b.e. values $(b.e._{exp} - V_R)$. The correction term is computed assuming point-charge distributions, and atomic charges as supplied by CHELEQ calculations); only in the latter case is a satisfactorily linear relationship obtained between b.e. values and computed Q_R (accounting for relaxation), as shown in Fig. 1. The V_R corrections on the tin atom are due mainly to the effect of negatively charged Cl ligands and are, as expected, increasing in absolute value with the number of Cl neighbours. The slope of the correlation straightline $(b.e._{exp} - V_R)$ *vs.* Q_R in Fig. 1 is 16.6 eV, and the intercept at $Q_R = 0$ is 490.6 eV for Sn $3d_{5/2}$, hence both are in good agreement with previous findings for other series of Sn compounds [12, 13], as well as with our data for the analogous series of pyrazine adducts [7]. The agreement between our data for the two series of adducts, those with pyrazine and with DPE, is to be regarded as satisfactory despite a relatively large quantitative uncertainty due to an inherent difficulty in the calibration procedures. In fact, XPS calibration was performed in both series of adducts using the Cls signal from contamination carbon, taken as 285.0 eV as the reference.

Further structural effects in XP spectra of DPE adducts, again similar to the ones found in the corresponding series of pyrazine adducts, include replacement of Cl through an alkyl or phenyl group in $RSnCl_3 \cdot DPE$ (R = Cl, CH_3, n-C_4H_9, n-C_8H_{17} or C_6H_5). Such replacement produces (as expected and as known from previous analogous cases) a decreasing shift of Sn $3d_{5/2}$ b.e. by 0.8 ∓ 0.1 eV; the variation is here more regular, almost constant and somewhat larger than observed in the pyrazine analogs [7]. Also in the series $(C_6H_5)_nSnCl_{4-n} \cdot DPE$ the decreasing trend of Sn $3d_{5/2}$ b.e. on going from n = 0 to n = 1 and to n = 2 is more regular and slightly more pronounced than in the pyrazine analogs, and amounts to 1.7 eV between n = 0 and n = 2. Thus, the expected qualitative similarity of substituent effects in the pyrazine and in the DPE series contrasts with some slight but significant quantitative differ-

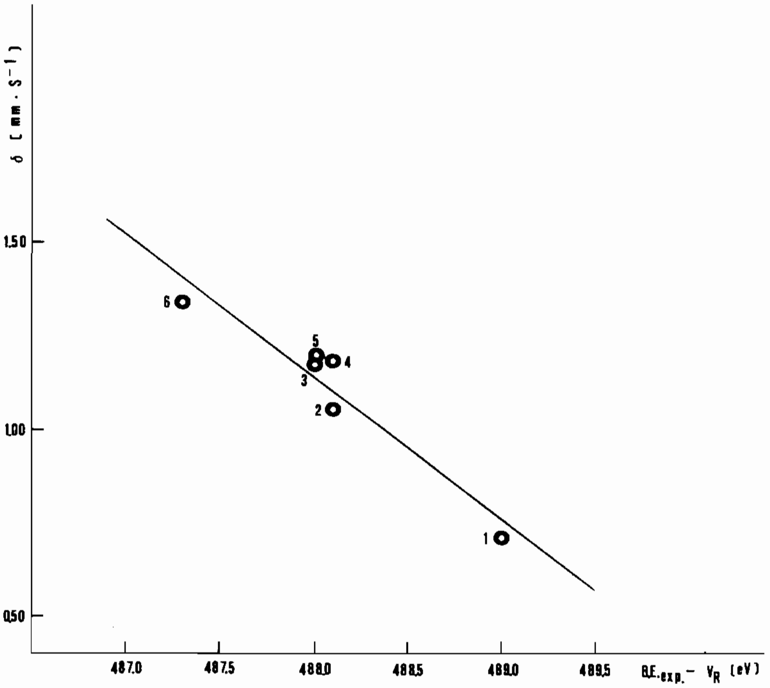

Fig. 2. ^{113}Sn Mössbauer isomer shift *vs.* Sn $3d_{5/2}$ b.e. values (corrected for intramolecular Madelung effects and relaxation). Full line is least squares fit, r = 0.958.

ences; it is tempting to speculate about the possible reasons for such differences in the two series of adducts, but such a self-evident structural difference is present to justify the above differences. The only possible, even if indirect, explanation lies probably in the different structure of the conjugated systems in both kinds of ligands, and in a more regular and less specific mode and intensity of long range interactions between the tin-bonded phenyl groups and the adduct bases.

Correlation between the Mössbauer isomer shift δ and (b.e.$_{exp}$ – V_R) XPS values is, as expected, linear for the present series of DPE adducts (see Fig. 2). The correlation straightlines are however, as expected and as discussed previously [1–7], valid only within a limited series of strictly analogous compounds, and do not match *e.g.* the correlation straightlines obtained for other series of tin-organic adducts with different bases [7]. The (b.e.$_{exp}$ – V_R) *vs.* Q_R straightline is verified to be, as expected, a universal function for all Sn compounds, within experimental errors.

In summary, XPS b.e. data and isomer shift δ values are potentially informative on different and in part complementary aspects of the electronic and steric structure of molecular systems such as tin-organic coordination compounds. The common dependence on atomic charge represents a mutual check of the validity of general structural correlations concerned with either technique.

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