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Comments on the Structure, Bonding and ^{119}Sn Mössbauer Parameters of Tin(II) Derivatives of the Type $MSnX_3$

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In this letter we present a simple rationale of the structures of, and the trends in the ^{119}Sn Mössbauer parameters, of some tin(II) derivatives based on the concept of orbital energy matching. The concept is found to be useful in a similar context for series of other compounds containing ions isoelectronic to Sn(II) but here discussion is confined to the structure and bonding in $MSnX_3$ (M = alkali metal, X = halogen) derivatives.

It is now clear, from ^{119}Sn Mössbauer and X-ray diffraction studies that the stereochemistry of the environment of tin(II) in Solid $MSnX_3$ compounds is a strong function of the ligand X [1]. If these compounds contained perfectly spherical stannous ions their structures would be based on the postulates of close packing of large anions with metal ions occupying suitable high symmetry intertices with little or no distortion of the anion lattice. Many of the $MSnX_3$ compounds, however, in common with the majority of tin(II) compounds [2], have distorted tin(II) environments because of the presence of a stereochemically active lone-pair of electron on tin(II). One of the simplest distortions to envisage is a trigonal distortion of an octahedral ligand environment around a central tin(II) ion brought about the presence of a lone pair of electrons directed along a three-fold axis thus, in effect, preventing the close approach of three ligands. In this way the formation of 'isolated' SnX_3^- complex ions may be envisaged. Other types of distortion can lead to tin ligand moieties with for example, C_{4v}, C_{2v}, or C_s symmetry. In practice it is found that electronegative ligands such as fluorine give rise to the more distorted tin environments and less electronegative ligands such as iodine to more regular environments. The electronic implication is that the lone-pair in the $MSnX_3$ fluorides is highly directional and therefore stereochemically active and contains high tin 5*p* character but that the lone-pair in, for example, the iodides contains high tin 5*s* character and therefore has less directional character.

These structural observations are paralleled by YX_6E^{n-} complex anions (Y = Pb^{2+}, Sb^{3+}, Bi^{3+}, Se^{4+}, Te^{4+} or Po^{4+}) where Y is isoelectronic with Sn^{2+}. Wynne has noted [3] that complex anions containing these cations are octahedral where X is a Pearson soft base but are distorted when X is a hard base.

For the formation of a strong bond in the LCAO approximation the atomic orbitals involved should, a) be of the correct symmetry, and b) be of similar energy. This second factor has not often been discussed but its importance *vis à vis* overlap criteria has been emphasised by Coulson [4]. All other things being equal the strongest bond should be formed when the energies of the component atomic orbitals are equal. In the following it is shown that the general structural observations together with the trends in the ^{119}Sn Mössbauer parameters of $MSnX_3$ compounds may be rationalized by the simple concept of 'orbital energy matching' arising from criteria (b) above. The related bond electronegativity equalisation method, in which the orbital electronegativities as function of their own occupancy and the occupancy of other orbitals on the same atom are equal in a two centre bond, has been used by Whitehead in interpretation of nqr data and would lead to a similar pattern of results [5].

It is convenient to discuss an isolated $(SnX_3)^-$ species of C_{3v} symmetry although the arguments can be extended to other geometries and metal ions. In a σ-bonding only scheme and assuming that ligand group orbital transforming as A_1 in C_{3v} mixes preferentially with tin A_1 hydrid orbital, directed towards the ligands, the occupied molecular orbitals may be written as

$(\cos\alpha)(5s) - (\sin\alpha)(5p_z)$ non-bonding a_1

$(c_2\,\phi_L + c_1\,[(\sin\alpha)(5s) + (\cos\alpha)(5p_z)]$ bonding a_1

$c_3\,(5p_x) + c_4\,\phi_{Le}$ bonding e

$c_3\,(5p_y) + c_4\,\phi_{Le}$ bonding e

where c_n are proper coefficients and ϕ_L are correctly chosen ligand group orbitals which are in this example mainly halogen *np* in character. The stereochemical activity of the tin lone-pair will depend on the directional tin $5p_z$ orbital character in the non-bonding orbital (lone-pair orbital) and the Mössbauer parameters, in the Townes-Dailey approximation, on the fractional 5*s* and 5*p* character of the molecular orbitals [6]. We suggest that in order to form a strong a_1 bond tin 5*s* and $5p_z$ orbitals will premix such that the energy of the hybrid orbital so formed will match that of the halogen *np* orbital. The binding energies of the tin 5*s* and 5*p* and halogen *np* orbitals are shown in the Figure and can be seen that in order

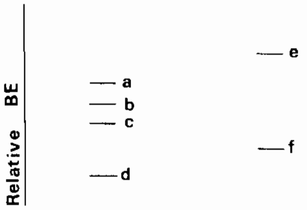

Figure. Relative binding energies (BE) of a) I-5*p*, b) Br-4*p*, c) Cl-3*p*, d) F-2*p*, e) Sn-5*p*, and f) Sn-5*s*.

TABLE. ^{119}Sn Mössbauer Isomer Shifts (δ), Quadrupole Splitting (Δ) and Line Widths (Γ) (in mm s^{-1}) for $MSnX_3$ Compounds. These data are taken from the more extensive tabulation in reference 7.

	δ	Δ	Γ
$KSnF_3$	1.02	1.92	–
$KSnCl_3$	1.71	0.77	1.97
$KSnBr_3$	1.72	0	1.96
$KSnI_3$	1.96	0	1.39
$NaSnF_3$	1.07	1.84	–
$KSnF_3$	1.02	1.92	–
$RbSnF_3$	0.97	1.96	–
$CsSnF_3$	0.93	2.00	–

to obtain a good energy match with the appropriate halogen group orbital the tin a_1 bonding orbital should contain high 5*s* character when bound to fluorine but high $5p_z$ character where bound to iodine. The non-bonding orbital (because of orthogonality requirements) thus contains high tin $5p_z$ and low 5*s* character in SnF_3^-. This orbital occupancy would lead to a highly directional lone-pairs containing high tin $5p_z$ character and hence distorted tin(II) environments, large negative quadrupole coupling constants and small isomer shifts for SnX_3^- ions containing electronegative ligands such as fluorine. In contrast for SnX_3^- ions containing less electronegative ligands such as iodine the lone-pair would contain high tin 5*s* character and would therefore be much less stereochemically active, the isomer shifts would be large and the quadrupole coupling constants small. These predictions concur with the general observations on the structure of tin(II) derivatives and the observed trends in the experimental Mössbauer data (see Table) [7].

The smaller observed variations of the Mössbauer parameters (see Table) within a series of $MSnX_3$ compounds as M changes for fixed X presumably arises from varying polarization and charge transfer between M and X, which causes a further modification of ligand atomic orbital energies. In terms of the above model the implication from the experimental trends is that halogen *np* orbitals move to higher energies as the polarising power of the cation increases.

A simple molecular orbital picutre which postulates that the tin 5*s*, $5p_z$ mixing varies in order to equalise the energy of the resulting hydrid orbital with that of the appropriate ligand combinations has been shown to provide a qualitative explanation of the observed structural trends and Mössbauer parameters of $MSnX_3$ compounds. Although 'isolated' ions and hence discreet molecular orbitals have been considered it is recognised that in the solid state extended interactions between molecular orbitals will not be greatly influenced by this phenomenon. It should be further noted that the approach is applicable to related systems and further details will appear elsewhere.

References

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