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Isomer Shift and Electronegativity in Compounds of Tin and Group-VI Elements*

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Using the Mössbauer effect in ^{119}Sn we have measured the isomer shift in compounds of divalent and tetravalent tin with elements of Group VI. The isomer shift is linearly dependent on the values of electronegativity in both series of compounds. The coefficient of this dependence is for tetravalent compounds nearly twice that of the divalent ones. This result is discussed in terms of electron structure of the chemical bonds of the compounds.

INTRODUCTION

The nucleus ^{119}Sn is one of the most favorable cases for Mössbauer effect (M.E.) studies, and a great number of experimental results are reported.¹ The isomer shift (i.s.) which measures the electronic charge density at the nucleus, and the quadrupole coupling ($\frac{1}{2}e^2qQ$) which gives the electric field gradient at the nucleus, are used to derive information concerning the electronic structure of molecules and solids.

But although the theoretical expressions are well known,¹ the problem of prediction of these two quantities on the basis of electronic structure calculations is complex. For this reason the M.E. results for ^{119}Sn were initially explained using more chemical concepts and the interpretation of tin tetrahalides² and organo tin compounds³ was given using electronegativity values given by Pauling. A good linear correlation was observed between the values of i.s. and electronegativity of the atoms bonded to tin. This interpretation was later criticized mainly due to the results for divalent tin compounds^{4,5} which have a measurable quadrupole coupling. Lees and Flinn⁵ succeeded in explaining the experimental results using electronic wavefunctions for tin in different configurations.⁶ Noting that for divalent tin compounds the i.s. and $\frac{1}{2}e^2qQ$ are linearly correlated and that the experimental points lie on two straight lines with slopes differing by a factor of 2, they explained that two different hybridization schemes $s(pz)$ or $sp_x(py)$ may be involved, although the total number of $n=5$ electrons is 2.

A different kind of calculations is reported by Unland and Letcher⁷ using localized and equivalent orbitals. One of the important input parameters in this calculation is the σ -bond polarity coefficient $h_{iA,B}$ which described the residual charges on atoms A and B bonded by a σ orbital. Once again this parameter was derived using Pauling electronegativity values through the Hannay-Smith formula.

We have measured the isomer shift and quadrupole coupling constant of tin compounds with elements of the sixth group (O, S, Se, Te) and have found that the results can be interpreted using electronegativity values for the divalent and the tetravalent series.

It is interesting also to note that some of these com-

pounds which are of considerable interest and are relatively simple can be studied with two M.E. nuclei. For example, SnTe may be studied using isotopes of mass number 125, 127, and 129.⁸ Also the selenium compounds offer this possibility, as ^{83}Se was demonstrated to be a valuable source for ^{83}Kr .⁹ $^{83}\text{SnSe}$ when studied with ^{83}Kr revealed a broad line which was assumed to be due to a quadrupole interaction of the Kr(Se) site. And indeed we found that SnSe when studied with ^{119}Sn reveals a well-resolved quadrupole splitting indicating that the asymmetry in the crystal structure is reflected in the electronic structure of the tin atom (see Table I below).

EXPERIMENTAL AND RESULTS

All our compounds were synthesized by vacuum melting of the elements in a quartz tube. The reaction temperature was higher than the melting point of the elements and was maintained for a few hours or, in some cases, days.

The absorbers were then prepared with fine powder of the compounds mixed with small amounts of glass powder to insure homogeneity; they were then encapsulated in plastic.

The experimental apparatus was developed in our laboratory. The source is moved with constant acceleration synchronously with a multichannel analyzer operated in the multiscaler mode forward and backward. This system has a reproducibility of 0.15% using natural Fe. The spectrum of natural Fe was also used for velocity calibration.¹⁰

As M.E. source we used $\text{Ba}^{119}\text{SnO}_3$.¹¹ With this source the i.s. of Sn (β) is 2.51 ± 0.01 mm sec⁻¹ and of SnO_2 is 0.02 ± 0.01 mm sec⁻¹ at room temperature. We then found that the relative i.s. of Sn (β)- SnO_2 is 2.49 ± 0.02 which agrees with the result 2.49 ± 0.03 of Ref. 5. To present the results relative to the standard source Mg_2Sn we have used for the i.s. of SnO_2 the value of -1.93 mm sec⁻¹ as given in the same Ref. 5, and our results have been corrected accordingly.

Measurements were done at room as well as at liquid-nitrogen temperature, but the results are adjusted to 300°K. All the spectra were analyzed by least-squares fitting with a computer, assuming that the resonance had a Lorentz line shape.

TABLE I. Experimental results for Sn compounds with Group VI elements.

Compound	i.s. ^a		$\frac{1}{2}e^2qQ^b$	
	Ref. 5	Present work	Ref. 5	Present work
SnO	0.74 ± 0.01	...	1.33 ± 0.01	...
SnS	1.32 ± 0.03	...	0.86 ± 0.03	...
SnSe	...	1.30 ± 0.02	...	0.75 ± 0.03
SnTe	...	1.44 ± 0.02	...	0
SnO ₂	-1.93 ± 0.02	-1.93	0.64 ± 0.02	0.64 ± 0.03
SnS ₂	...	-0.88 ± 0.02	...	0
SnSe ₂	...	-0.66 ± 0.02	...	0
SnSSe	...	-0.86 ± 0.06	...	0

^a Relative to the standard source of Mg₂Sn in millimeters per second. The value of i.s. for SnO₂ in the present work is taken to coincide with that of Ref. 5 to adjust the experimental values obtained with a Ba¹¹⁹SnO₃

source to the standard source of Mg₂Sn as in Ref. 5.

^b Quadrupole coupling $\frac{1}{2}e^2qQ$ in millimeters per second.

A summary of results is presented in Table I. In Figs. 1 and 2 we present the spectrum of SnSe and SnSe₂. The points are the uncorrected measurements and the solid lines are the computer fittings. In the case of SnSe the dashed lines are the fitting of the two separate absorption peaks due to the quadrupole interaction.

DISCUSSION

In Fig. 3 the i.s. = δ is plotted against the values of Pauling's electronegativities.¹² The left scale refers to Sn(II) compounds and the velocity is positive (millimeters per second). The right scale with negative values

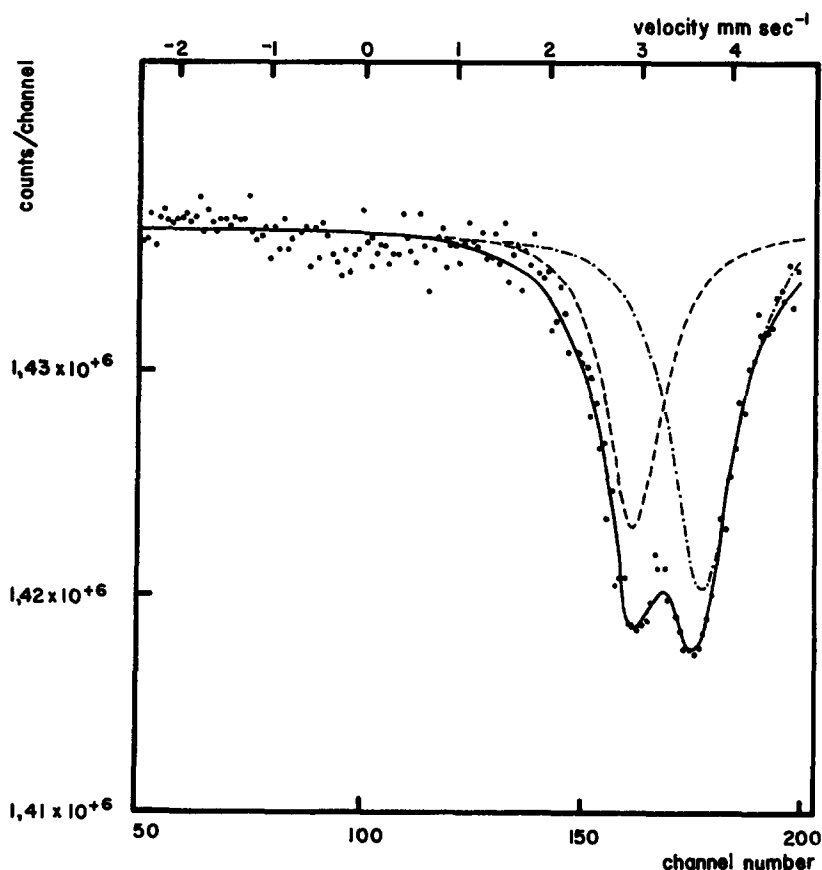


FIG. 1. The Mössbauer effect in SnSe. The source is Ba¹¹⁹SnO₃. Experimental points and computer fitting.

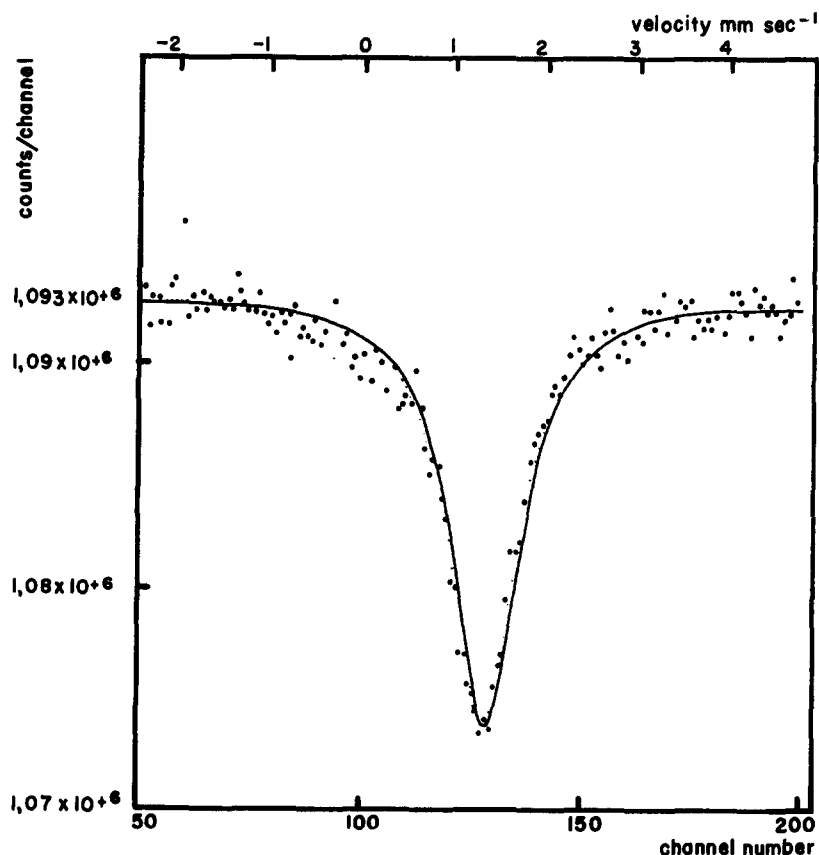


FIG. 2. The Mössbauer effect in SnSe_2 . The source is $\text{Ba}^{119}\text{SnO}_3$. Experimental points and computer fitting.

refers to Sn(IV) compounds; in this case two more points were added to our measurements, one for Sn(α) and the other one for the average value of the i.s. of organic tin compounds $\text{Sn}(\text{R})_4$, where R is a saturated organic radical.¹³

The least-square fitting of the results gives

$$\text{Sn(IV)} \quad \delta = -1.1(\Delta\text{El}) - 0.07, \quad (1)$$

$$\text{Sn(II)} \quad \delta = -0.49(\Delta\text{El}) + 1.62, \quad (1')$$

where ΔEl is the electronegativity difference between tin and the other element bonded to it.

Qualitatively the explanation is simple: The higher the electronegativity of the atoms bonded to Sn the lower is the electron density around the tin atom and hence the i.s. decreases since $\Delta R/R$ is positive.¹⁴ In fact, writing for i.s. = δ the standard expression

$$\delta = \text{const}(\Delta R/R) [|\psi(0)|_A^2 - |\psi(0)|_S^2], \quad (2)$$

the only term which affects the i.s. is $|\psi(0)|_A^2$, the electron density at the Sn nucleus, for the relevant absorber.

$|\psi(0)|^2$ is known to depend mainly on s -electron density. In Ref. 5 the linear term corresponding to the contribution of $5s$ electrons was estimated to be the most important, and higher-order terms corresponding

to screening effect were estimated to be one order of magnitude smaller than the linear term.

The same conclusion was also reached indirectly by the authors of Ref. 7 as in their calculations they computed only the $5s$ -electron density and obtained a reasonable fit to the experimental data (Fig. 3 of Ref. 7).

From the relations (1) and (1') one may see that in the tetravalent compounds twice as many $5s$ electrons participate in the bond as in the divalent compounds, and that the effects due to sp and ss screening slightly reduce the dependence of δ on ΔEl in (1) for the Sn(II) compounds.

All our compounds can be considered as a distortion of a basic NaCl structure (see Table II for details of the structures), where the Sn atom is six coordinated, and in the tetravalent compounds there are twice as many atoms bonded to one Sn as in the divalent. The NaCl structure is perfectly realized in SnTe and this compound has no quadrupole interaction. The bonds may then be considered as sp^2d^2 hybrids. For Sn(α) and SnR_4 , where the Sn is tetrahedrally coordinated, the bonds are sp^3 hybrids.

In both cases of bond hybridization, the ratio of $5s/5p$ electrons is constant = $\frac{1}{3}$, and the i.s. should then depend on the occupation number of different orbitals in

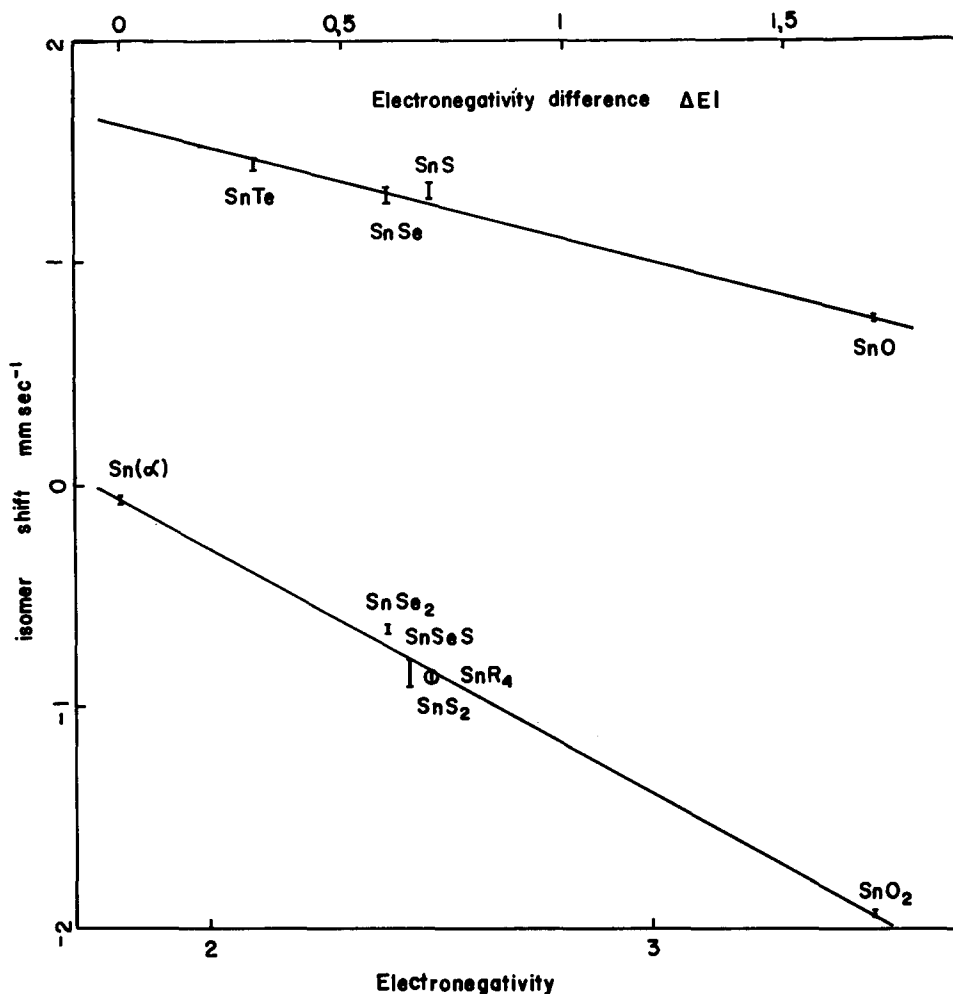


FIG. 3. Linear relationship of isomer shift and electronegativity values, for Sn (II) and Sn(IV) compounds. The point \odot SnR₄ refers to saturated tin compounds (see text).

the various bonds. The exact occupation number may be difficult to estimate. For example, in α Sn it was estimated to be 1.2 for 5s electrons,¹⁵ and not 1, inspite of tetrahedral symmetry. In any case the σ -bond polarity coefficient $h_{iA,B}$, which gives the residual charge on a

tin atom and is determined through the Hannay-Smith formula

$$h_{iA,B} = 1.0 + 0.16(\Delta E|) + 0.035(\Delta E|)^2, \quad (3)$$

is proportional to this occupation number.

If we disregard the quadratic term, the linear relation between the i.s. and electronegativity values is established, and Fig. 3 is justified.

It is worth notice that: (a) in Ref. 7 the electronegativity values for Sn(II) and Sn(IV) were adjusted to fit the data. This is not necessary in the present case, but this adjustment would only shift the points of Fig. 3 without altering their slope; and (b) if we accept the value of 1.2 as the occupation number of 5s electrons in α tin,¹⁵ we have a calibration point and the occupation number for 5s and 5p electrons may be calculated for the other compounds using (3), recalling that for the Group VI compounds their ratio is 1/3, the same constant for all the compounds in both series.

TABLE II. Crystal structure and space groups of tin compounds as from R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1963), Vol. 1.

Structure	Space group
SnO	Tetragonal D_{4h}^{14} ($P4/nmm$)
SnS	Orthorhombic V_n^{16} ($Pb\ nm$)
SnSe	Orthorhombic V_n^{16} ($Pb\ nm$)
SnTe	NaCl
SnO ₂	Tetragonal D_{4h}^{14} ($P4/nmm$)
SnS ₂	Hexagonal Cd(OH) ₂ D_{3d}^3 ($C\bar{3}m$)
SnSe ₂	Hexagonal Cd(OH) ₂ D_{3d}^3 ($C\bar{3}m$)

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¹³ This value equal to 0.89 mm sec⁻¹ is an average of 23 compounds taken from Table 6.2, p. 339 of Ref. 1.

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Molecular and Crystal Structure of Hexamethylenetetramine Triphenol

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The crystal structure of a 1:3 adduct of hexamethylenetetramine (HMT) and phenol has been determined using three-dimensional x-ray data. The crystals are trigonal, with $a = 14.88$ Å, $c = 6.007$ Å, and space group $P\bar{3}$. Three phenol molecules are linked to each HMT molecule through O-H...N hydrogen bonds in the form of a three-leaved propeller, and the crystal structure is based on a packing of such HMT triphenol units. A notable structural feature is the hollow channel parallel to c through the origin and surrounded by the free ends of the phenyl rings. Although the channel is too narrow in places for the enclosure of guest molecules, reorientation of the phenol groups might allow sufficient expansion for the accommodation of normal aliphatic hydrocarbons and their straight-chain derivatives.

INTRODUCTION

Hexamethylenetetramine (hereafter abbreviated to HMT), $(\text{CH}_2)_6\text{N}_4$, forms addition compounds with phenol containing either one^{1,2} or three³ molecules of phenol to one molecule of HMT. The triphenol adduct is of particular interest since it raises the question as to whether the crystal structure is determined by O...H-O or by N...H-O hydrogen bonds. Thus in the former case the phenol molecules might be expected to link to one another in a manner similar to that found in the phenol clathrates,⁴ relegating the HMT molecules to a space-filling role in the crystal lattice. Alternatively, hydrogen bonding may occur between the HMT and phenol molecules such that only three of the four nitrogen atoms in each HMT molecule are involved, as is the case in $\text{HMT} \cdot 6\text{H}_2\text{O}$.⁵

The present work concerns the determination of the crystal structure of HMT triphenol from single-crystal x-ray data. As will be shown below, the formulation $(\text{CH}_2)_6\text{N}_4 \cdot 3\text{C}_6\text{H}_5\text{OH}$ correctly describes the structure of this molecular compound.

EXPERIMENTAL

HMT triphenol was readily prepared by mixing saturated aqueous solutions of its two components in stoichiometric proportions at room temperature. Recrystallization of the adduct from water gave colorless prisms elongated along the c axis. The crystals slowly crumbled into a white powder on exposure to air, and it was necessary to seal them in thin-walled glass capillaries to prevent decomposition. The density of the crystal was measured by the flotation method in a hexane-carbon-tetrachloride mixture. Unit-cell dimensions were determined from high-angle reflections on a $h0l$ Weissenberg photograph calibrated with sodium chloride powder lines and refined by a least-squares procedure.

The crystal data are as follows: Hexamethylenetetramine triphenol, $(\text{CH}_2)_6\text{N}_4 \cdot 3\text{C}_6\text{H}_5\text{OH}$, M.P. ≈ 122 , F.W. = 422.52. Trigonal, $a = 14.88(1)$, $c = 6.007(5)$ Å; $U = 1152$ Å³, $D_m = 1.214$ g cm⁻³, $Z = 2$, $D_x = 1.218$ g cm⁻³ (throughout this paper the estimated standard deviations given in parentheses correspond to the last