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^{119}Sn MÖSSBAUER QUADRUPOLE SPLITTINGS OF LOW SYMMETRY FOUR-COORDINATE TIN ORGANOMETALLIC COMPOUNDS: A SUCCESSFUL APPLICATION OF THE POINT CHARGE MODEL

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SUMMARY

^{119}Sn Mössbauer spectra of Me_3SnZ, Me_2ClSnZ, $MeCl_2SnZ$, Cl_3SnZ [$Z = Mn(CO)_5$] and Ph_3SnY, Ph_2ClSnY, $PhCl_2SnY$, Cl_3SnY [$Y = Fe(CO)_2C_5H_5$-π] are reported. The Point Charge Model is successfully applied.

Although several papers have reported Sn Mössbauer spectra of metal–metal bonded compounds[1-7], little attempt at explaining the Sn quadrupole splittings (*QS*) in these compounds has been made. Point charge parameters[8] partial quadrupole splittings (*PQS*)[9] or partial field gradients[10] have been very useful for rationalizing quadrupole splittings in Fe^{II} low spin compounds[9,11] and Sn^{IV}[8,12,13] compounds. For example, previous results[8,13] have shown that four coordinate Sn^{IV} compounds should generally have smaller quadrupole splittings than five coordinate or *trans*-octahedral Sn^{IV} compounds. In this communication, we show that comparatively large quadrupole splittings (up to 2.8 mm/sec) can be obtained by lowering the molecular symmetry from a $SnAB_3$ or $SnAC_3$ compound by replacing ligands B or C by another ligand having markedly different bonding properties than either B et C, or by distorting the molecule greatly from tetrahedral geometry. These large four coordinate splittings are rationalized using derived self-consistent *PQS* values. The sign of the *QS* and the magnitude of η are also predicted, and bonding properties for the metal moieties $Mn(CO)_5$ and $Fe(CO)_2C_5H_5$ are discussed.

The compounds in Table 1 were prepared as reported previously[14]. X-ray structures of $(CH_3)_3SnMn(CO)_5$[15], $(C_6H_5)_3SnMn(CO)_5$[16], $(C_6H_5)_3SnFe(CO)_2C_5H_5$[17], $Cl_3SnFe(CO)_2C_5H_5$[18] and $(C_6H_5)Cl_2SnFe(CO)_2C_5H_5$[19] clearly show that the Sn atom is four coordinate with no abnormally short non-bonded distances—either inter or intramolecular. The distortion from tetrahedral symmetry about the Sn atom increases in the order given above. Thus in $(CH_3)_3SnMn(CO)_5$, the CH_3–Sn–Mn and CH_3–Sn–CH_3 bond angles vary from 106.9° to 112.2°; in contrast, the corresponding angles in $C_6H_5Cl_2SnFe(CO)_2C_5H_5$ vary from 99.1° to 129.7°.

Mössbauer spectra were taken at 80°K using a $BaSnO_3$ source and an Austin Science Associates spectrometer. All spectra were fitted to two lines using methods described previously[9,20]. Full widths at half height were 1.05±0.10 mm/sec for all compounds. For the $(C_6H_5)_3SnFe(CO)_2C_5H_5$ spectrum, χ^2 decreased by over 50 on fitting two lines instead of one.

TABLE 1

^{119}Sn MÖSSBAUER PARAMETERS AT 80K

	Compound	*QS*		*η*	
		Observed[a]	Predicted[b]	Predicted[b]	*CS*[c]
(I)	$(CH_3)_3SnMn(CO)_5$	0.82	–	0	1.41
(II)	$(CH_3)_2ClSnMn(CO)_5$	2.60	−2.28	0.47	1.52
(III)	$(CH_3)Cl_2SnMn(CO)_5$	2.62	+2.42	0.86	1.62
(IV)	$Cl_3SnMn(CO)_5$	1.60	+	0	1.65
(V)	$(C_6H_5)_3SnFe(CO)_2C_5H_5$	0.32±0.10	–	0	1.39
(VI)	$(C_6H_5)_2ClSnFe(CO)_2C_5H_5$	2.54	−2.06	0.25	1.58
(VII)	$(C_6H_5)Cl_2SnFe(CO)_2C_5H_5$	2.84	+2.30(+2.79)	0.97(0.69)	1.70
(VIII)	$Cl_3SnFe(CO)_2C_5H_5$	1.83	+	0	1.75

[a] The errors in the *QS* are ±0.02, except where noted. [b] All predicted values (except the ones in brackets for compound (VII) were calculated assuming tetrahedral bond angles. The bracketed values were calculated using the known bond angles for compounds (V), (VII) and (VIII). Note that the signs given are those of the *QS*; the signs of V_{zz} and *q* are opposite to these. [c] Relative to $BaSnO_3$; ±0.02 mm/sec.

The observed quadrupole splittings for the compounds $B_{3-n}C_n$ SnA (B=Cl; C=C_6H_5, CH_3; A=$Fe(CO)_2C_5H_5$, $Mn(CO)_5$) are given in Table 1. The order of quadrupole splittings as *n* increases is very unexpected; the *QS* values for $n=1$ and $n=2$ are much larger than for $n=0$ or $n=3$. The same trend is found for other compounds with B=Cl, Br, C_6F_5 and C=C_6H_5 and CH_3. The *QS* value for compound (VII) appears, to be the largest four coordinate *QS* yet known[13]. The agreement with previously published values for compounds (I), (IV), (V), (VII) and (VIII)[2–5] is good, except for compound (V) in which computer processing reveals a *QS* of about 0.3 mm/sec.

The trend in quadrupole splittings for $n=0$ to $n=3$ can be readily rationalized using *PQS* values derived from a point charge approach. The expressions for the *EFG** tensor components for tetrahedral bond angles are given in terms of *PQS* values in Table 2. The *PQS* value for Cl^- (+0.63) is taken from Parish and Platt[8,12]**. The *PQS* values for $Mn(CO)_5$ (−0.17) and $Fe(CO)_2C_5H_5$ (−0.28) are calculated from the *QS* of compounds (IV) and (VIII) respectively, assuming the sign of the *QS* in both compounds to be positive. The sign of the *QS* for $Cl_3SnFe(CO)_2C_5H_5$ has recently been shown to be positive[21]. Then, the *PQS* values for CH_3 (−0.58) and C_6H_5 (−0.44) are calculated from compounds (I) and (V), taking the signs of the *QS* to be negative to obtain reasonable *PQS* values for these ligands[8,12,21]. There will be a large uncertainty in the *PQS* value for C_6H_5 (~0.05 mm/sec) because of the very small *QS* in compound (V). Using the above *PQS* values, and the expressions in Table 2 for $SnABC_2$ compounds, the predicted *QS* and *η* values are calculated. We take $|V_{zz}| \geqslant |V_{yy}| \geqslant |V_{xx}|$ after diagonalizing the *EFG* tensor.

In agreement with the observed trend, the calculated values indicate that the dichlorides should have a larger *QS* than the corresponding monochloride, and that

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* EFG=electric field gradient.

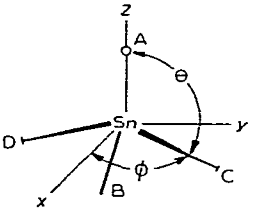
** There is some doubt now whether the sign of the chloride *PQS* is positive or negative (Parish, personal communication). A change in sign will not affect the following calculations.

these two compounds should have larger splittings than either of the two end members. The quantitative agreement between predicted and observed values is excellent for compounds (II) and (III), whereas for compounds (VI) and (VII), the predicted values are considerably smaller than the observed *QS*. However, the crystal structures for compounds (V) (VII) and (VIII)[17-19] all show considerable distortion from tetrahedral bond angles, and this should have a large effect on the predicted value for compound (VII). Using the structural data for compounds (V) and (VIII), we redefined *PQS* values for C_6H_5 (−0.61) and $Fe(CO)_2C_5H_5$ (−0.64), and recalculated the *QS* for compound (VII). This value (2.79 mm/sec) is now in excellent agreement with the observed value of 2.84 mm/sec. Thus, distortions from tetrahedral bond angles can markedly affect both calculated *PQS* values and predicted *QS* values. Even the signs of some of the contributions to the *EFG* components changed from the tetrahedral calculation to the final calculation on compound (VII).

TABLE 2

COMPONENTS OF THE *EFG* TENSOR FOR FOUR CO-ORDINATE "TETRAHEDRAL" Sn COMPOUNDS[a]

[L] are partial field gradients.



Components of *EFG* tensor	SnABCD	$SnABC_2$	SnA_2C_2[b]	$SnAC_3$[b]
V_{xx}	$-[A]+\frac{5}{3}[B]-\frac{1}{3}([C]+[D])$	$-[A]+\frac{5}{3}[B]-\frac{2}{3}[C]$	$\frac{2}{3}[A]-\frac{2}{3}[C]$	$-[A]+[C]$
V_{yy}	$-[A]-[B]+[C]+[D]$	$-[A]-[B]+2[C]$	$-2[A]+2[C]$	$-[A]+[C]$
V_{zz}	$2[A]-\frac{2}{3}([B]+[C]+[D])$	$2[A]-\frac{2}{3}([B]+2[C])$	$\frac{4}{3}([A]-[C])$	$2[A]-2[C]$
$V_{xy}=V_{yx}$	$\frac{2}{\sqrt{3}}([C]-[D])$	0	0	0
$V_{xz}=V_{zx}$	$\frac{\sqrt{2}}{3}(-2[B]+[C]+[D])$	$\frac{\sqrt{2}}{3}(-2[B]+2[C])$	$\frac{\sqrt{2}}{3}(-2[A]+2[C])$	0
$V_{yz}=V_{zy}$	$\sqrt{\frac{2}{3}}([C]-[D]]$	0	0	0

[a] The axes system *x, y, z* as defined above does not in general coincide with the principal directions *X, Y, Z* of the *EFG* tensor. For example, in $SnABC_2$ compounds, *y* coincides with *Y*, but *x* and *z* are rotated to coincide with *X* and *Z* when the *EFG* tensor is diagonalized. [b] See also refernce 8.

The *PQS* values for CH_3 and C_6H_5 are much larger than those calculated previously[8,12], and our predicted splittings for tetrahedral four coordinate compounds such as $(C_6H_5)_3SnCl$ are ~2.4 mm/sec, in agreement with observations cited recently[13].

The *PQS* values for $Mn(CO)_5$ and $Fe(CO)_2C_5H_5$ given above indicate that $Fe(CO)_2C_5H_5$ is an appreciably better σ donor and/or worse π acceptor than $Mn(CO)_5$[9].

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