An Interpretation of the Mössbauer Spectra of Mixed-Hexahalo Complexes of Tin(IV)[1]

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The series of hexahalotin(IV) compounds of the types $[(C_2H_5)_4N]_2[SnX_4Y_2]$, where X = Cl, Br, or I and Y = F, Cl, Br, or I, has been studied by Mössbauer spectroscopy. The chemical shifts observed have been related to the Mulliken electronegativities of the halide ligands and to the metal–ligand bonds involved. The line broadening observed in some of the complexes has been related to the geometry of the complex under consideration.

Introduction

There have been several papers published in the recent past concerned with the Mössbauer parameters of hexacoordinate tin(IV).[2-4] Most of these studies have involved hexacoordinate tin(IV) adducts of the type $SnX_4 \cdot 2L$, where X = Cl, Br, or I and L is an organic ligand containing a donor atom such as N, O, P, or S. Many of the compounds studied exhibited no quadrupole splitting, even though the ligand arrangement about the tin ion was not symmetrical. On the basis of these results Greenwood, *et al.*,[2b] postulated a rule as follows: no quadrupole splitting will be observed in tin(IV) compounds if the donor atoms about the central tin atom all have nonbonding p_π electrons. However, Curran and coworkers[2a] have observed quadrupole splitting in hexacoordinate tin(IV) compounds where all of the donor atoms have lone pairs of electrons; thus the Greenwood rule is not universally valid. Herber and Cheng[4] reported the Mössbauer spectroscopic data for the tetramethylammonium salts of $SnCl_6^{2-}$, $SnBr_6^{2-}$, SnI_6^{2-}, $SnCl_4Br_2^{2-}$, $SnCl_2Br_4^{2-}$, $SnCl_2I_4^{2-}$, and $SnBr_2I_4^{2-}$ and related the observed isomer shift values to the average Pauling electronegativities of the halide ligands. Their results for the hexahalides agree quite well with those reported by Greenwood, *et al.*,[2b] except for the SnI_6^{2-} where IS = 1.25 mm/sec is reported by Greenwood and IS = 1.43 mm/sec is reported by Herber.

In view of these discrepancies in the literature, it appeared desirable to underake an investigation of the isomer shift values and to determine the dependence of the quadrupole splitting in a series of tin(IV) complexes on (1) the dissymmetry in the electric field about the tin ion produced by differences in the metal–ligand bond and (2) the dissymmetry in the electric field produced by differences in size and configuration of the ligands. This investigation was initiated by the study reported herein on the homologous series of mixed hexahalotin(IV) complexes of the type $SnX_4Y_2^{2-}$

where X = Cl, Br, or I and Y = F, Cl, Br, or I. This series of compounds allows the effect of systematic changes in the metal–ligand bonds to be observed within a series of geometrically similar ligands. This paper reports an interpretation of the Mössbauer parameters of these hexahalotin(IV) complexes in terms of the metal–ligand bonding.

Experimental Section

The tin salts were prepared by adding dropwise a stoichiometric amount of the appropriate tetraethylammonium halide dissolved in a 50:50 mixture of chloroform and methanol to the appropriate tetrahalotin compound dissolved in chloroform. The compounds precipitated immediately, were filtered, washed with a 50:50 mixture of chloroform–methanol followed by anhydrous ether, and dried under vaccuum. All manipulations involved in the preparation of these complexes were performed in a drybox. The pertinent analytical data are given in Table I. Tin was determined as SnO_2 after careful evaporation with concentrated nitric acid and ignition at 800°. The halide content was determined volumetrically by the Volhard method. X-Ray diffraction data for all the mixed-halo complexes confirmed the existence of pure single phases.

During the course of this work, Clark and coworkers[5] reported the preparation and vibrational spectra of the mixed-halo species of the type $SnX_4Y_2^{2-}$, where X and Y = Cl, Br, or I. Based upon the appearance of several well-resolved bands in the Sn–Cl stretching frequency region, these authors assigned the *cis* configuration (C_{2v} symmetry) to the $SnCl_4Br_2^{2-}$, $SnCl_4I_2^{2-}$, $SnCl_2Br_4^{2-}$, and $SnCl_2I_4^{2-}$ anions. The $SnCl_4F_2^{2-}$ and $SnBr_4F_2^{2-}$ complexes prepared in the present study appear to be new compounds.

The Mössbauer measurements reported herein were obtained using the recoilless radiation from the first excited state (23.8 keV) of ^{119m}Sn in a barium stannate matrix. The mounted source was purchased from New England Nuclear Corp. and contained 2.5-mCi of ^{119m}Sn. The spectra were taken with an Austin Science Associates constant-acceleration electromagnetic drive. A Nuclear Data Model 2200 1024-channel analyzer operated in the time mode and using 512 channels was used for data accumulation. The 23.8-keV X-ray was detected with a Reuter–Stokes Kr–CH₄ proportional counter in combination with a fast, low-noise preamplifier system from Austin Science Associates. The samples were contained in a 2-cm diameter thin plastic holder in thermal contact with the copper cold finger of a liquid nitrogen dewar. All absorbers were maintained at the same thickness of 8–9 mg of Sn/cm². With the source and instrumentation described above, the narrowest lines thus far reported in the literature for hexacoordinate tin(IV) compounds were obtained.[2a] A representative spectrum is shown in Figure 1. The data points are shown together with the calculated line shape obtained by a

(1) Taken in part from the thesis presented by C. A. Clausen, III, for the Ph.D. degree from Louisiana State University in New Orleans, Aug 1969.

(2) (a) J. Phillip, M. A. Mullins, and C. Curran, *Inorg. Chem.*, **7**, 1895 (1968); (b) N. N. Greenwood and J. N. R. Ruddick, *J. Chem. Soc., A*, 1679 (1967).

(3) S. Ichiba, M. Mishima, H. Sahai, and H. Negita, *Bull. Chem. Soc. Japan*, **41**, 49 (1968).

(4) R. H. Herber and H. S. Cheng, *Inorg. Chem.*, **8**, 2145 (1969).

(5) R. J. Clark, L. Maresca, and R. J. Puddephatt, *ibid.*, **7**, 1603 (1968).

Table I

Analytical Data for the Hexahalide Complexes of Tin(IV)

| Complex | % Sn | | Wt of compd, mg | Equiv of halide | |
	Calcd	Found		Calcd	Found
[(C₂H₅)₄N]₂[SnCl₆]	20.1	19.9	150.2	1.525	1.517
[(C₂H₅)₄N]₂[SnBr₆]	13.9	14.1	160.1	1.120	1.111
[(C₂H₅)₄N]₂[SnI₆]	10.4	10.7	180.1	0.947	0.935
[(C₂H₅)₄N]₂[SnCl₄F₂]	21.3	21.0	124.1	0.890	0.901
[(C₂H₅)₄N]₂[SnCl₄Br₂]	17.5	17.6	155.2	1.368	1.377
[(C₂H₅)₄N]₂[SnCl₄I₂]	15.4	15.6	130.9	1.012	1.001
[(C₂H₅)₄N]₂[SnBr₄F₂]	16.1	16.0	135.2	0.735	0.750
[(C₂H₅)₄N]₂[SnBr₄Cl₂]	15.5	15.5	141.2	1.100	1.106
[(C₂H₅)₄N]₂[SnBr₄I₂]	12.5	12.9	140.1	0.883	0.870
[(C₂H₅)₄N]₂[SnI₄Cl₂]	12.4	12.2	154.3	0.968	0.981
[(C₂H₅)₄N]₂[SnI₄Br₂]	11.4	11.1	169.1	0.974	0.987
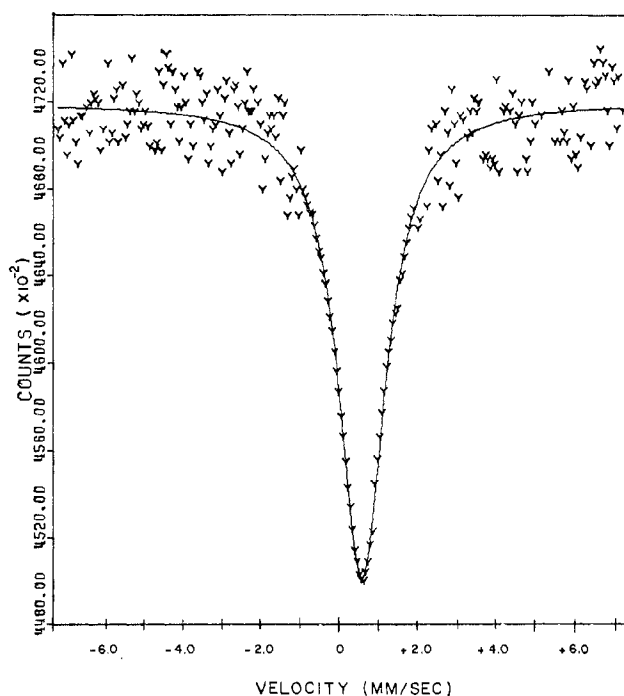
Figure 1.—Mössbauer spectrum for [(C₂H₅)₄N]₂[SnCl₄I₂]. Data points and computed least-squares line shape are shown.

least-squares fit to a Lorentzian line shape computed on an IBM 7040 computer.

Results and Discussion

The Mössbauer parameters for the hexahalides of tin(IV) are presented in Table II. Greenwood, *et al.*,[2b] recorded the Mössbauer spectra of [(CH₃)₄N]₂[SnCl₆], [(CH₃)₄N]₂[SnBr₆], and [(CH₃)₄N]₂[SnI₆] and reported the respective values for the isomer shifts (δ) to be +0.50, +0.87, and +1.25 mm/sec. These values are in excellent agreement with those obtained for these same anions with the tetraethylammonium cation. A comparison with the data presented by Herber and Cheng[4] shows good agreement for the SnCl₆²⁻, SnBr₆²⁻, SnCl₄Br₂²⁻, and SnBr₄Cl₂²⁻ anions but not for the iodide-containing anions.

The values of δ in Table II show an interesting trend. In the series SnX₄Y₂²⁻, there is a decrease in δ with an increase in electronegativity of Y. Early in the study of tin compounds, relationships were noted between values of δ for stannic halides and the electronegativity of the halide. Greenwood, *et al.*,[2b] plotted

Table II

Mössbauer Data for Complexes of the Types
[(C₂H₅)₄N]₂[SnX₆] and [(C₂H₅)₄N]₂[SnX₄Y₂]

No.	Compound	Isomer shift,[a] δ, mm/sec	Line width,[b] Γ, mm/sec
1	K₂SnF₆	−0.36	0.80
2	SnCl₄F₂²⁻	+0.29	1.09
3	SnCl₆²⁻	+0.52	0.74
4	SnCl₄Br₂²⁻	+0.67	0.94
5	SnCl₄I₂²⁻	+0.78	1.10
6	SnBr₄F₂²⁻	+0.53	1.43
7	SnBr₄Cl₂²⁻	+0.77	1.00
8	SnBr₆²⁻	+0.84	1.03
9	SnBr₄I₂²⁻	+0.96	1.17
10	SnI₄Cl₂²⁻	+0.99	1.19
11	SnI₄Br₂²⁻	+1.09	1.15
12	SnI₆²⁻	+1.23	1.12

[a] Relative to a SnO₂ absorber at room temperature with a precision of ±0.03 mm/sec.   [b] Precision of ±0.03 mm/sec.

δ against Pauling's electronegativity values for the halides in the series of compounds SnX₆²⁻ (X = F, Cl, Br, I) and obtained a smooth curve through the hexahalides except for SnF₆²⁻. Herber and Cheng[4] obtained a linear relationship between the δ values and the average Pauling electronegativities for all of their tin(IV) hexahalides except Br₄I₂²⁻, Cl₄I₂²⁻, and SnF₆²⁻. Plots of isomer shifts against Pauling's electronegativity values for the halides in the series of tin tetrahalides have also given smooth curves through the compounds, except for SnF₄.[6,7] It was of interest to see if a smooth curve could be obtained for the homologous series of mixed halides when isomer shifts are plotted against the average electronegativity of the halides in the coordination sphere of the tin atom. Pauling's electronegativity values were not used, because Pauling's equation[8] gives excessively large values for the bond energy of highly polar bonds (*i.e.*, the Sn–F bond) as a result of the overestimation of the covalent bond energy. Pauling's electronegativities also give a value for the fluorine atom which appears to be too high. This is caused by the failure of his method to account fully for the anomalous destabilization energy inherent in the formation of the fluoride ion.[9] An electronega-

(6) V. I. Goldanskii, "The Mössbauer Effect and Its Applications in Chemistry," Consultants Bureau, New York, N. Y., 1964.

(7) M. Cordey-Hayes, *J. Inorg. Nucl. Chem.*, **26**, 915 (1964).

(8) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 92.

(9) P. Politzer, *J. Am. Chem. Soc.*, in press.

tivity scale which would be consistent over the entire range of bond polarities covered in these mixed tin halides is that proposed by Mulliken.[10] Mulliken's electronegativity values are calculated from the sum of the average ionization energy and the electron affinity of an atom. Since Mulliken electronegativity values could not be found in the literature for the halides utilizing the most recent ionization potential and electron affinity data, it was necessary to recalculate these values as shown in Table III.

TABLE III

MULLIKEN ELECTRONEGATIVITY VALUES

Element	Ionization potential,[a] eV	Electron affinity,[b] eV	Mulliken electronegativity[c]
F	17.418	3.448	10.43
Cl	12.96	3.613	8.29
Br	11.811	3.363	7.59
I	10.448	3.063	6.75

[a] C. M. Sitterly, *Atomic Energy Levels Program*, National Bureau of Standards, Washington, D. C., Oct 1966. [b] B. L. Moiserwitsch, *Advan. Atom. Mol. Phys.*, 1, 61 (1965). [c] Calculated by: Mulliken electronegativity = (IP + EA)/2.

The largest difference between the electronegativity values in Table III and those given by Pritchard and Skinner[11] occurs for the fluorine atom where a value of 12.32 was reported. Using the electronegativity values listed in Table III, average electronegativities were calculated for the particular halide arrangement about the tin ion in the mixed tin halides. These average electronegativity values were plotted against the corresponding isomer shift values reported in Table II. As can be seen from Figure 2, there is a linear decrease in isomer shift with an increase in electronegativity of the halides bonded to the tin atom. It is also significant to note that the data points corresponding to $SnF_6{}^{2-}$, $SnCl_4F_2{}^{2-}$, and $SnBr_4F_2{}^{2-}$ and to the iodide-containing anions all fall on the line.

The σ-bonding framework in these hexahalo compounds involve the $5s5p^35d^2$ orbitals of tin. Any π bonding involves the donation of lone-pair p_π-electron density from the halides back to the empty $5d_{xy}$, d_{xz}, and d_{yz} orbitals of tin. Only the contribution of the s electrons to δ is *via* the electrostatic interaction between the Sn nucleus and the s-electron density at the nucleus; the contribution of the p and d electrons is *via* shielding of the s electrons and hence has the opposite sign although comparable magnitude. A possible implication of the present data is that the separate contributions of the s, p, and d electrons (whether or not the last are involved in π bonds) are independently linear with the electronegativity of the halide ligands.

A change in the type of bonding between the tin atom and the halide groups should affect the slope of the relationship between δ and the electronegativity of the halide. This effect is illustrated by a comparison of the two curves in Figure 2, where the isomer shift

(10) R. S. Mulliken, *J. Chem. Phys.*, 2, 782 (1934); 3, 573 (1935).
(11) H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, 55, 745 (1955).
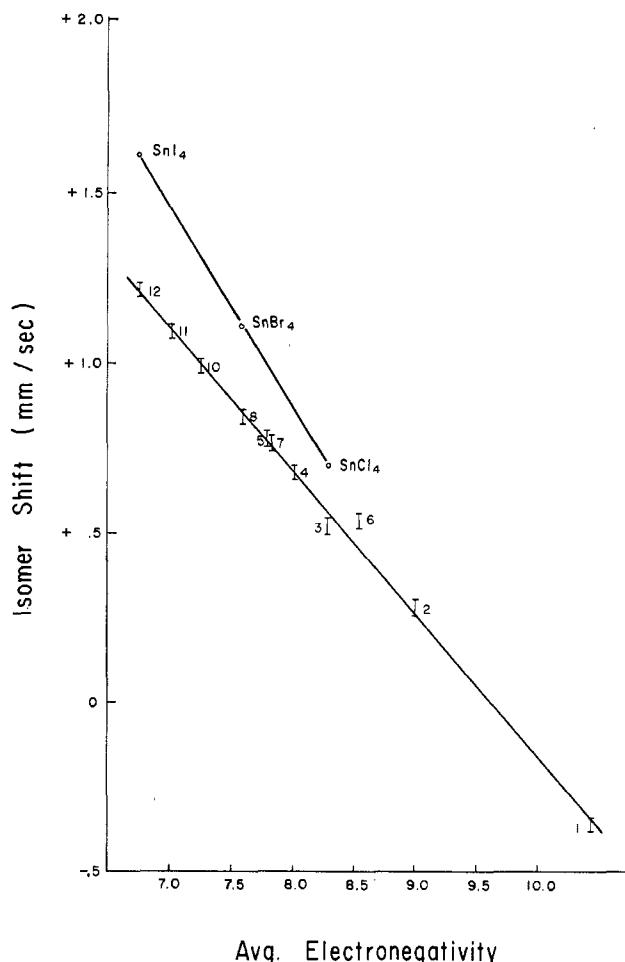

Avg. Electronegativity

Figure 2.—Isomer shift *vs.* average halide electronegativity for tin hexahalides and tetrahalides. (Data points for the hexahalides are numbered according to the listing of compounds in Table II and the line is a least-squares fit to all of the data points presented. The isomer shift data for the tin tetrahalides are from ref 12.)

values of Goldanskii, *et al.*,[12] for the tin tetrahalides are also plotted against the Mulliken electronegativity for the respective halide. SnF_4 was not included in this plot, because it has been shown[13] that the tin atom is at the center of a distorted octahedron, rather than in the tetrahedral configuration characteristic of the other tin tetrahalides. The absolute value for the slope of the curve in the tin tetrahalide plot is 0.65 compared to 0.43 for the slope of the tin hexahalides. The change in slope in going from the tetrahalides to the hexahalides is probably a result of differences in the magnitude of d-electron shielding brought about by differences in hybridization. In going from sp^3 hybridization in the tetrahalides to sp^3d^2 hybridization in the hexahalides, effective s-electron density at the tin nucleus would be expected to be reduced by the screening effect of the d electrons.

As was expected, resolved quadrupole splitting was not observed in any of the mixed-halide complexes, but line broadening was observed in all complexes where

(12) V. I. Goldanskii, E. F. Makarov, R. A. Stukan, T. N. Sumarokova, V. A. Trukhtanov, and V. V. Khrapov, *Dokl Akad. Nauk SSSR* 156, 400 (1964).
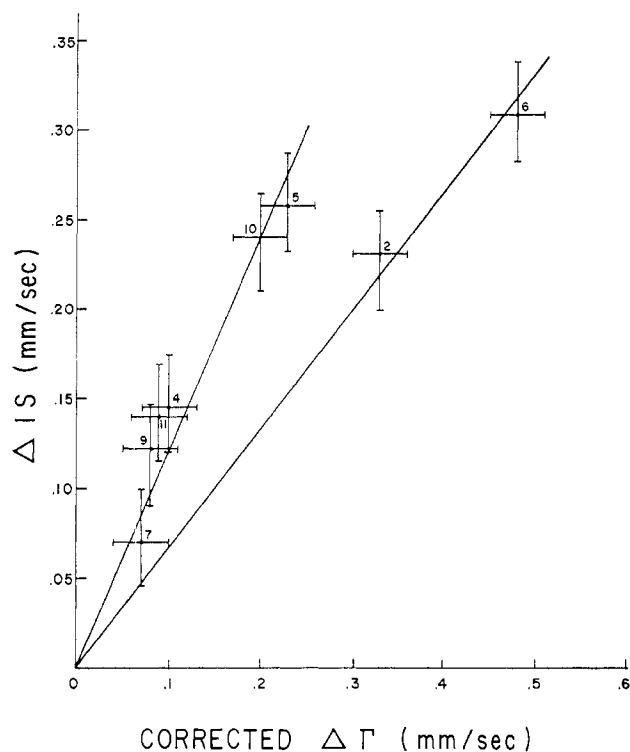(13) R. Hoppe and W. Dahne, *Naturwissenschaften*, 49, 254 (1962).

Figure 3.—|Δ isomer shift | *vs.* ΔΓ. (Data points are numbered according to the listing of compounds in Table II. The line of greater slope is a least-squares fit to all points except 2 and 6.)

the symmetry had been lowered from O_h to C_{2v}. The absorber thickness was maintained between 8 and 9 mg of Sn/cm² for all compounds and the source-absorber geometry was maintained constant for all experiments; thus, it is a safe assumption that the line broadening is the result of unresolved quadrupole splitting.[14] If the line broadening in the mixed halides is a result only of the imbalance in electron-withdrawing ability of the halides which induces an asymmetry in the electric yield, a relationship might be expected between the difference in electron-withdrawing ability of the halides

(14) V. G. Bliznakov and K. Petrov, *Z. Anorg. Allgem. Chem.*, **354**, 307 (1967).

(as determined from isomer shift data) and the line broadening. The absolute value of the difference in isomer shift between $SnX_6{}^{2-}$ and $SnX_4Y_2{}^{2-}$ should be a measure of the difference in electron-withdrawing ability between two Y ligands and two X ligands in a tin environment containing four additional X ligands. These values which are written as |ΔIS|, are plotted in Figure 3 against ΔΓ, where ΔΓ is the difference in line width between $SnX_4Y_2{}^{2-}$ and $SnX_6{}^{2-}$. ΔΓ is a measure of the line broadening as a result of replacing two X ligands with two Y groups. All values were corrected for the inherent differences in line widths between the symmetrical $SnX_6{}^{2-}$ and $SnY_6{}^{2-}$ species. The corrected ΔΓ values reflect the line broadening attributable only to unresolved quadrupole splitting. Figure 3 shows that as the difference in electron-withdrawing ability between X and Y increases in the $SnX_4Y_2{}^{2-}$ complexes, the line broadening also increases. It is interesting that this relationship appears to be linear with all of the data points for the mixed halides except those containing a fluoride ligand falling on one line and the data for the fluoride-containing complexes falling on another line. The fact that such a relationship is established lends support to the suggestion that the line broadening in the mixed-halo species is the result of unresolved quadrupole splitting. Thus, it appears that line-width data in tin(IV) complexes can be used to obtain information about the asymmetry in the stereochemistry of the tin coordination.

The fact that a smaller difference in electron withdrawal between the halides in the fluoride-containing complexes results in a larger line broadening, or greater unresolved quadrupole splitting, (ΔE_0), as compared to the other mixed halides, may be an indication that these complexes are in the *trans* configuration rather than *cis*, since $\Delta E_q(trans)/\Delta E_q(cis) = 2$.[15] These data do not of course confirm the *trans* configuration for these species but are simply compatible with that interpretation.

(15) R. R. Berrett and B. W. Fitzsimmons, *J. Chem. Soc.*, 525 (1967).