# Mössbauer Study of the Complex Compounds
# of Tin (II) Halides

Mitsuo MISHIMA, Masatoshi IDOGAKI and Hisao NEGITA*

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*Department of Chemistry, Faculty of Literature and Science, University of Shimane, Matsue*
*\* Department of Chemistry, Faculty of Science, University of Hiroshima, Hiroshima*

## Abstract

Mössbauer spectra of $^{119}$Sn were observed in tin (II) chloride, bromide and their complexes of the types $MSnX_3 \cdot H_2O$ and $M_2SnX_4 \cdot H_2O$, where M = NH$_4$, K or Cs, and X = Cl or Br. All of the complexes exhibited small quadrupole splittings. In comparison with the parent halides $SnX_2$, the complex chlorides have smaller isomer shifts, whereas this is not the case for the complex bromides. The isomer shift was related to the strength of the ligand field, and the decrease in the isomer shift was interpreted by $s$-$p$ mixing due to the field stabilization.

In the past several years Mössbauer spectra of complex tin (II) compounds were reported[1-4]. The isomer shifts (IS) for tin (II) halides increase with increasing electronegativity of ligand halogen except the fluoride[5]. It was shown that the extent of covalent $s$-$p$ hybridization of the central tin atom in the tin (II) halides increases with decreasing electronegativity of the ligand. On the other hand, the anomalously small IS for tin (II) fluoride is explained in terms of $s$-$p$ mixing due to the crystal field stabilization[5]. The trend in the IS as seen in the trihalotin (II) complexes[2,3] does not always relate to hybridization.

The purpose of the present investigation is to find the origin of the variation in the IS and to clarify the bond character in the complex tin (II) compounds.

## Experimental

*Materials.* Anhydrous tin (II) chloride obtained commercially was purified by the usual method, and anhydrous tin (II) bromide was prepared by a method given in the literature[6]. The preparation of the complexes are described previously[6-8]. These complexes were identified by analyzing tin and halogen.

*Measurement.* The Mössbauer spectrometer was essentially the same as that described previously[9]. The absorber of areal density 15 mg/cm$^2$ of Sn was cooled to 80°K, while the source of $Ba^{119m}SnO_3$ was kept at room temperature.

## Results and Discussion

The Mössbauer parameters for tin(II) compounds are listed in Table 1. The IS was larger for anhydrous tin(II) chloride than for the bromide as reported previously[5,10,11].

Table 1. MÖSSBAUER PARAMETERS FOR COMPLEX TIN(II) HALIDES AT 80° K

| Compound | IS[a], mm/sec | QS, mm/sec |
|---|---|---|
| $SnF_2$[b] | 3.78 | |
| $NH_4SnF_3$[b] | 3.38 | |
| $SnCl_2$ | 4.03 | 0 |
| $NH_4SnCl_3 . H_2O$ | 3.48 | 1.04 |
| $(NH_4)_2SnCl_4 . H_2O$ | 3.52 | 0.99 |
| $KSnCl_3 . H_2O$ | 3.73 | 0.91 |
| $K_2SnCl_4 . H_2O$ | 3.68 | 0.89 |
| $CsSnCl_3$ | 3.53 | 1.03 |
| $SnBr_2$ | 3.95 | 0 |
| $NH_4SnBr_3 . H_2O$ | 3.92 | 1.01 |
| $(NH_4)_2SnBr_4 . H_2O$ | 3.96 | 0.98 |
| $KSnBr_3 . H_2O$ | 3.96 | 0.93 |
| $(NH_4)_2SnCl_2Br_2 . H_2O$ | 3.66 | 0.70 |

a) Isomer shift measurement refers to $BaSnO_3$.
b) Ref. 1.

The quadrupole splittings (QS) for tin(II) halide and its complexes show that there exists greater electric field gradient around the tin nucleus in the complex than in tin(II) halide. It is therefore expected that the arrangement of atoms around the tin atom and/or the distribution of electronic charge around the tin nucleus is less symmetric in the complex than in the corresponding tin(II) halide. The chlorostannite gave a small IS compared with tin(II) chloride, whereas the difference in the IS between the bromostannite and tin(II) bromide was not so remarkable.

The fact that $MSnX_3 \cdot H_2O$ has almost the same Mössbauer parameters as $M_2SnX_4 \cdot H_2O$ suggsusts that there exists only the trihalostannite ion, $SnX_3^-$,

common between the trihalostannite and the tetrahalostannite. Thus no tetrahalostannite ion, $SnX_4^{2-}$, exists in a crystalline state as it does not exist in molton mixtures of tin (II) chloride and potassium chloride[12], though the solubility data suggested the presence of the tetrachlostannite ion in solutions[13]. According to the X-ray diffraction[7], potassium tetrachlorostannite is a hydrated double salt, $KCl \cdot KSnCl_3 \cdot H_2O$, containging $SnCl_3^-$.

The ammonium dichlorodibromostannite, $(NH_4)_2SnCl_2Br_2 \cdot H_2O$, which was prepared from tin (II) bromide and ammonium chloride, is considered to have an ionic species $SnCl_2Br^-$ or $SnClBr_2^-$. It is not apparent, however, which kind of ion is contained in the above compound. The IS for the compound, 3.66 mm/sec, is close to that estimated for the ion $SnCl_2Br^-$. Probably a bromine atom on tin (II) bromide is substituted by a chlorine atom of ammonium chloride to form the ion $SnCl_2Br^-$.

The values of the IS's for tin (II) halides, $SnX_2$, and ammonium trihalostannites, $NH_4SnX_3$ or $NH_4SnX_3 \cdot H_2O$, are compared in (a) or (b) of Fig. 1, respectively. The IS for the trihalostannite decreases with an increase in the electronegativity of the ligand halogen. This trend can be seen in the IS's for tetraalkylammonium trihalostannites[2,4] and pyridine complexes of tin (II) halides[14]
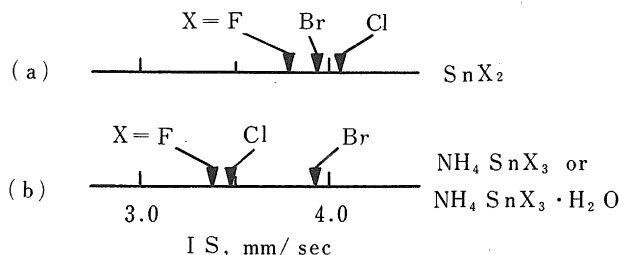
Fig. 1. Isomer shift of tin (II) halide and their complexes

The IS is smaller for the fluorostannite and the chlorostannite than for the corresponding tin(II) halide. This means the decrease of $5s$ electrons and/or the increase of the $5p$ electrons around the tin atom on complexing. It was shown by Orgel [15] that the ions with outer electronic configuration $ns^2$ are stabilized by mixing with $p$-orbitals of the same subshell in the ligand field and that the enviroment around the central ion is distorted. This is true in stannous ion with the outer electronic configuration $5s^2$. The mixing of $s$- and $p$-orbitals of the stannous ion causes the decrease of the $5s$-electron

population. Since the field strength is inversely propotional to the cube of the interionic distance, an increase in bond distance with increasing radius of the ligand atom results in rapid weakening of the field strength on the central metal ion. The fact that the IS for tin(II) bromide is almost the same as that for its complex may come from the large size of $Br^-$ ion. The $s$-character of the tin atom is therefore expected to increase in the order, fluoride $<$ chloride $<$ bromide. This is consistent with the results of the IS's for the halostannites.

The tin atom in $SnCl_2$ is coordinated by the three nearest chlorine atoms at 2.67, 2.78 and 2.78 Å and the three next nearest chlorine atom at 3.06, 3.18 and 3.28 Å [16]. The similar distorted octahedron is formed in KCl. KSn-$Cl_3 \cdot H_2O$, the tin atom being surrounded by six chlorine atom st 2.54, 2.54, 2.63, 3.31, 3.35 and 3.35 Å [7]. The enviroment around the tin atom in the latter is more distorted along a three-fold axis of a octahedron, and the similar situation is expected in the other complexes. Accordingly, the complex is more stabilized and has greater $s$-$p$ mixing, since a strengthening of the ligand field makes the octahedron increasingly distorted [15]. Consequently, it is supposed that a strengthening of $s$-$p$ mixing causes the decrease in $s$-character of the tin atom and the increase in the shielding due to the increase of $p$-electrons, and that they are responsible for the decrease in the IS on complexing. Further, such a distortion increases the asymmetry of the electronic charge distribution around the tin atom and results in the increase in the QS.

Metal ions were classified in two groups [17]; group A which forms more stable complexes with more electronegative ligands and group B which forms more stable complexes with less electronegative ligands. $Sn^{2+}$ ion lies on the border region between the two groups [17]. The stability data on complex tin (II) halides, however, suggest that $Sn^{2+}$ ion belongs to the group A [18]. The smaller IS for the complex and the larger decrease in the IS from its parent halide reflect greater $s$-$p$ mixing, which makes the enviroment around the tin atom more distorted and forms stronger bonds between the central atom and ligands [14]. Thus the results of the Mössbauer effect suggest that the stability of the complex tin (II) halide becomes greater in the order, bromide $<$ chloride $<$ fluoride. This is consistent with the results of the stability data.

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