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Mössbauer Effect of ^{119}Sn in Tetracarbonylcobalt Derivatives of Tin(IV) Halides

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The ^{119}Sn Mössbauer effect was studied in tetracarbonylcobalt derivatives of tin(IV) halides, $X_nSn[Co(CO)_4]_{4-n}$, where X=Cl, Br or I, and $n=0\sim4$. The isomer shift in each halogen series increased as the halogen atom was successively replaced by the $Co(CO)_4$ group. The values of the isomer shift were between those of tin(IV) halides and $XSn[Co(CO)_4]_3$ and did not change lineraly with the number of halogen atoms. The values of the quadrupole splitting were smaller than those of the corresponding organotin halides, X_nSnR_{4-n}, and attained their maximum at dihalides. From the Mössbauer parameters, the chemical bonds in the compounds, especially the Sn–Co bond, were discussed.

A large number of compounds containing metal-metal bonds between a Group IV element and a transition element have been synthesized, and the nature of the bonds and chemical properties of the compounds have been investigated by many workers.[1–5] Recently, Mössbauer spectroscopy has become available for compounds containing tin atoms, and the compounds containing a Sn–M bond, such as Sn–Fe, Sn–Co, Sn–Mn, and Sn–Re, have been studied by this method.[6–13] In particular, compounds containing metalcarbonyl have been investigated in the studies of metal-metal bonding. Karasyov *et al.*[13] have studied $A_nSn(C_6H_5)_{4-n}$ ($A=Mn(CO)_5$, $Re(CO)_5$, or $Co(CO)_4$, and $n=1\sim3$) by Mössbauer spectroscopy and elucidated the electron-donating nature of $Mn(CO)_5$ and $Re(CO)_5$ and accepting nature of $Co(CO)_4$

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as compared to C_6H_5. Goldandkii *et al.*[13] have studied the A_nSnCl_{4-n}, $[C_5H_5Fe(CO)_2]_nSn(C_6H_5)_{4-n}$, and $[C_5H_5Fe(CO)_2]_nSnCl_{4-n}$ compounds and reported that in them metalcarbonyl groups act as electron acceptors. Onaka *et al.*[10] have studied $R_{3-n}X_nSn$-$[Mn(CO)_5]$ and reported that the $Mn(CO)_5$ group is a stronger electron donor than the methyl, phenyl, and halogen groups. Spencer *et al.*[14] have studied $X_nSn[Co(CO)_4]_{4-n}$ and $R_nSn[Co(CO)_4]_{4-n}$ by ^{59}Co nuclear quadrupole resonance (NQR) and reported that there are Sn–Co π-interactions and that $Co(CO)_4$ is more electron-withdrawing than the methyl group. In the present studies, the Mössbauer effects of ^{119}Sn in $X_nSn[Co(CO)_4]_{4-n}$, where X=Cl, Br, or I, and $n=0\sim4$, were investigated in order to study the chemical bond, especially the Sn–Co bond.

Experimental

Materials. Tin(IV) halides and dicobalt octacarbonyl were obtained commercially. Tin(II) chloride was dehydrated completely by heating it in a nitrogen atmosphere. Tin(II) bromide was prepared by dissolving tin metal powder in concentrated hydrobromic acid. Tin(II) iodide was purified by sublimation in a nitrogen atmosphere. The purity of the tin(II) halides was checked by means of the Mössbauer spectrum.

Preparation of the Compounds. The compounds studied were prepared by the method of Patmore and Graham.[1] All the reactions were carried out under a nitrogen atmosphere because of their reactivity with air. The compounds were identified by their melting points and infrared spectra.

Measurements. The measurements were made as has been described previously.[15] The γ-ray source of barium stannate was used at room temperature, whereas the absorber was cooled with liquid nitrogen. The thickness of the absorber was about 20 mg/cm^2 for tin.

Results and Discussion

The Mössbauer spectrum of $Cl_3Sn[Co(CO)_4]$ is shown in Fig. 1, as an example. The solid line in the figure is the computer fit of the experimental points to the Lorentzian curve by the least-squares method. From the curves, the Mössbauer parameters, such as the isomer shift (δ), the quadrupole splitting (2ε), and the half width (Γ), were derived. The values of these parameters are summarized in Table 1.

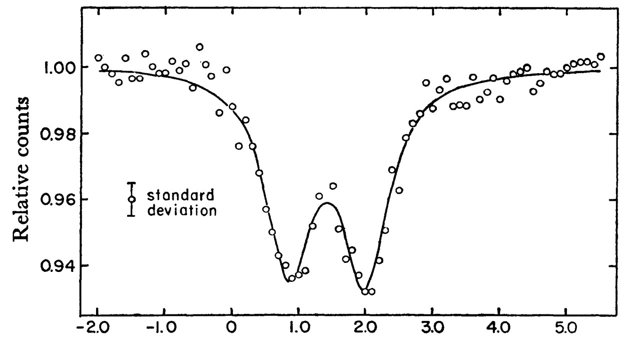

Fig. 1. The Mössbauer spectrum of $Cl_3Sn[Co(CO)_4]$.

Table 1. Mössbauer parameters for tin compounds

Compounds	$\delta^{a)}$ (mm/sec)	2ε (mm/sec)	Γ (mm/sec)
$SnCl_4$	0.86	0	1.08
$Cl_3Sn[Co(CO)_4]$	1.42	1.15	0.82
$Cl_2Sn[Co(CO)_4]_2$	1.74	1.40	0.86
$ClSn[Co(CO)_4]_3$	1.93	1.18	1.10
$SnBr_4$	1.01	0	1.35
$Br_3Sn[Co(CO)_4]$	1.49	1.28	1.23
$Br_2Sn[Co(CO)_4]_2$	1.81	1.46	0.86
$BrSn[Co(CO)_4]_3$	1.97	1.06	0.80
SnI_4	1.54	0	1.10
$I_3Sn[Co(CO)_4]$	1.73	0.71	1.09
$I_2Sn[Co(CO)_4]_2$	2.02	1.07	0.95
$ISn[Co(CO)_4]_3$	2.03	0.95	0.91
$Sn[Co(CO_4)]_4^{b)}$	1.96	0	—

a) Isomer shift with respect to $BaSnO_3$.
b) Ref. 8).

Isomer Shift. According to Cordey-Hayes,[16] the isomer shift of tin (IV) compounds is lower than the value of gray tin, which is completely quadrivalent, with the hybridized configuration $(5s)(5p)^3$, and which is sensitive to the *s*-electron density at the tin nucleus in such a way that the decrease in the value is closely related to the increase in the partial ionic character of the bond. The screening effects of the *s*-electrons by the 5*s*, 5*p* and, in some cases, 5*d* electrons are also taken into account.

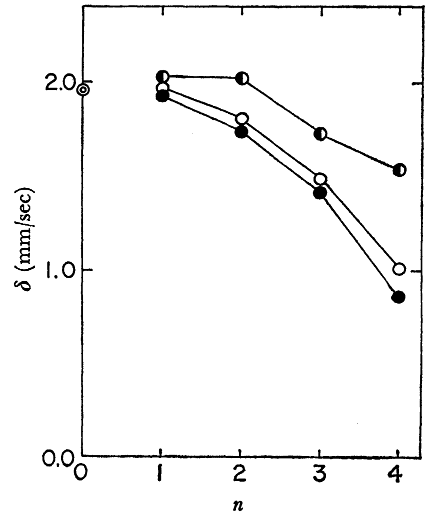

Fig. 2. The isomer shift *vs.* the number of halogens, *n*, in $X_nSn[Co(CO)_4]_{4-n}$ series.
●: Cl, ○: Br, ◐: I and ◎: $Sn[Co(CO)_4]_4$.

In Table 1, the values of the isomer shift of tin tetrahalides agree with the literature values,[13] and the values of the $X_nSn[Co(CO)_4]_{4-n}$ compounds (X=Cl, Br, or I, and $n=1\sim3$) increase as the electronegativities of the halogen atoms decrease. The plots of the values of the isomer shift *versus* the number of halogens, *n*,

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are shown in Fig. 2. Since the value of the isomer shift of $Sn[Co(CO)_4]_4$ is higher than that of each tin (IV) halide, the bonding character of the Sn–Co must be more covalent than those of Sn–X. The values of the isomer shift of the compounds in each series of halogen are between the values of $XSn[Co(CO)_4]_3$ and SnX_4. In each curve, it is observed that the changes in the isomer shift *versus* the number of halogens are not linear. That is, the change in the isomer shift becomes smaller as the number of halogens, *n*, decreases. On the other hand, it has been reported that the ionic character in the Sn–Cl bond increases with the decrease in the *n*, as is shown by the findings concerning the NQR due to ^{35}Cl in $Cl_nSn[Co(CO)_4]_{4-n}$ ($n=2\sim4$).[17–19] Thus, the electrons on the tin atom are more withdrawn to chlorine atoms as their number, *n*, decreases. Furthermore, according to Spencer *et al.*,[14] more π-electrons transfer to the tin atom from $Co(CO)_4$ and, in turn, decrease the isomer shift of tin, as their number, *n*, increases. The observed isomer shift must be the result of the competition of the ionic character in the Sn–X bond with the π-bonding in the Sn–Co bond as the number, *n*, changes.

The same tendency of the isomer shift has been observed in the $[C_5H_5Fe(CO)_2]_nSnCl_{4-n}$ and $[C_5H_5Fe(CO)_2]_nSn(C_6H_5)_{4-n}$ ($n=0\sim3$) series of compounds.[7]

Quadrupole Splitting. In tin(IV) compounds, large quadrupole splittings are generally observed when there is an unequal electron population at the three 5*p* or four $5sp^3$ orbitals. Sizable quadrupole splittings are observed in the $X_nSn[Co(CO)_4]_{4-n}$ compounds (X=Cl, Br, or I, and $n=1\sim3$), as is shown in Table 1. Thus, in these compounds there is an unequal electron population at the three 5*p* orbitals, so that the bonding characters of Sn–X and Sn–Co are considerably different. Many workers have studied the quadrupole splitting of organotin compounds of the type of X_nSnR_{4-n} (R=alkyl or aryl, X=halogen, and $n=1\sim3$).[13,20–22] The results show that the quadrupole splitting in the organotin compound becomes smaller as the electronegativity of the organic group, R, approaches that of the halogen atom. Because the quadrupole splittings of the $X_nSn[Co(CO)_4]_{4-n}$ compounds are smaller than the values of the corresponding organotin compounds, the $Co(CO)_4$ group is more electronegative than the alkyl or aryl group. This result agrees with the conclusions of the NQR study of the compounds by Spencer *et al.*[14] and the Mössbauer study of the $(C_6H_5)_nSn[Co(CO)_4]_{4-n}$ series by Karasyov *et al.*[13]

Bir'yukov *et al.*[23] reported that the Co–Sn–Cl angle in $ClSn[Co(CO)_4]_3$ is 104°, as determined by the X-ray diffraction method. Boer *et al.*[24] reported that, in $Cl_2Sn[Co(CO)_2C_7H_8]_2$ or $(C_6H_5)_2Sn[Co(CO)_2C_7H_8]_2$, the Co–Sn–Co angle is larger than Cl–Sn–Cl or C_6H_5–Sn–C_6H_5, as determined by the X-ray diffraction method. Patmore and Graham[25] reported that the Co–Sn–Co angle in $Cl_2Sn[Co(CO)_4]_2$ is larger than the tetrahedral angle, as determined by IR spectroscopy. They also studied the $(CH_3)_nSn[Co(CO)_4]_{4-n}$ compounds by NMR spectroscopy and showed, from the coupling constants, $J(^{117}Sn\text{–}CH_3)$ and $J(^{119}Sn\text{–}CH_3)$, that an increase in the *s*-character is observed in the Sn–Co bond. All those results may be summarized by Bent's rule,[26] which suggests that the *s*-character is concentrated in the orbitals directed toward more electropositive substituents. In the light of Bent's rule, it is plausible that the *s*-character is concentrated in the Sn–Co bonds, while the *p*-character is concentrated in the Sn–X bonds. In consequence, the Co–Sn–Co bond angle becomes larger than the tetrahedral angle, while the X–Sn–X angle becomes smaller. The resultant imbalance in *p*-electron populations is manifested by quadrupole splitting.

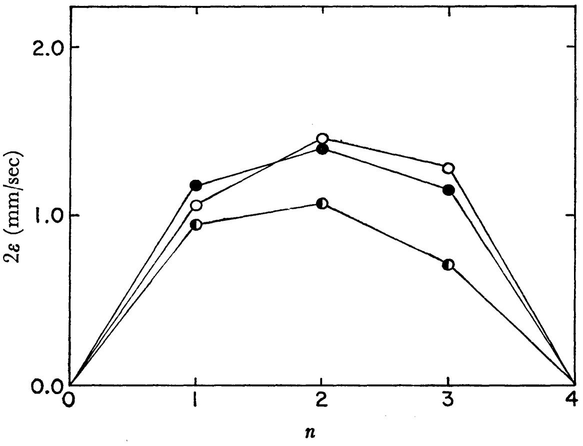

Fig. 3. The quadrupole splitting *vs.* the number of halogens, *n*, in $X_nSn[Co(CO)_4]_{4-n}$ series.
●: Cl, ○: Br, and ◐: I.

In Fig. 3, the values of the quadrupole splitting are plotted *versus* the number of halogen atoms, *n*. From the electronegativity of halogen, it can be expected that the values of the quadrupole splitting will decrease in the order of Cl>Br>I, but this is not true of bromine. The anomaly of bromine compounds seems to result from the distorted tetrahedral structure of tin tetrabromide,[27,28] in accordance with its broad line width.

The values of the quadrupole splitting attain their maximum at $n=2$ in all series of the compounds. An explanation of this phenomenon was attempted using a simple point-charge model. According to Parish and Platt,[21] the coordinates and arrangements of the

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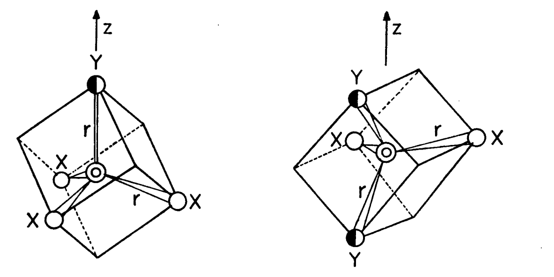

(a) X_3SnY(or $XSnY_3$) (b) X_2SnY_2

Fig. 4. Point-charge models of the tetrahedral bonding.

tetrahedral point-charge model of the X_nSnY_{4-n} type, in which X is the halogen atom and Y is the $Co(CO)_4$ group in the present case, are as is shown in Fig. 4.

The quadrupole splitting of ^{119}Sn, which has spin states of the excited and ground states of the nuclei, 3/2 and 1/2, is given by:

$$2\varepsilon = KV_{zz}(1+\eta^2/3)^{1/2} \tag{1}$$

Where V_{zz} is the electric-field gradient in the direction of the principal axis, which is taken as the z axis, and where the asymmetry parameter, η, is defined by:

$$\eta = \frac{V_{xx}-V_{yy}}{V_{zz}} \tag{2}$$

The electric-field gradients, V_{xx}, V_{yy}, and V_{zz}, can be expressed as follows:

$$\begin{aligned} V_{xx} &= \sum_{\mathrm{L}}(3\sin^2\theta_{\mathrm{L}}\cos^2\phi_{\mathrm{L}}-1)[\mathrm{L}] \\ V_{yy} &= \sum_{\mathrm{L}}(3\sin^2\theta_{\mathrm{L}}\sin^2\phi_{\mathrm{L}}-1)[\mathrm{L}] \\ V_{zz} &= \sum_{\mathrm{L}}(3\cos^2\theta_{\mathrm{L}}-1)[\mathrm{L}] \end{aligned} \tag{3}$$

where [L] represents the nature of the ligand contributing to the electric-field gradient, and where θ_L and ϕ_L are the polar and azimuthal angles of the ligand respectively. Using the three Eqs., (1), (2), and (3), the relative values of the quadrupole splitting for the tetrahedral point-charge model of X_nSnY_{4-n} (n=1∼3) are calculated as follows:

X_3SnY	tetrahedral	$2\varepsilon \sim 2[Y]-2[X]$
X_2SnY_2	tetrahedral	$2\varepsilon \sim 1.15(2[Y]-2[X])(\eta=1)$
$XSnY_3$	tetrahedral	$2\varepsilon \sim -2[Y]+2[X]$

where [X] and [Y] are the parameters of the contributions to the electric-field gradient by the X and Y ligands.

In this interpretation, the dihalides should have a quadrupole splitting larger by 15% than that for the monohalide or trihalide, which have the same value but the opposite sign. The experimental data are consistent with the results of the point-charge treatment for the maximum value at dihalide. However, the values of $X_3Sn[Co(CO)_4]$ and $XSn[Co(CO)_4]_3$ are not equal. This can be explained on the basis of the deviation of the bond angle from the tetrahedral angle. As has been stated above, the X–Sn–Co bond angle is larger than the tetrahedral angle in $X_3Sn[Co(CO)_4]$ and is smaller in $XSn[Co(CO)_4]_3$. The electric-field gradient arises from the imbalances in the charges on the ligands as well as in the valence electron, but the latter is far more effective than the former. Therefore, the sign of the electric-field gradient in the tetrahedral compound, $XSn[Co(CO)_4]_3$, would be positive, because the valence shell of the tin atom will have more electron density concentrated in the x- and y-directions (Sn–Co) than in the z-direction (Sn–X), and the sign in $X_3Sn[Co(CO)_4]$ would be negative. The parameters of the quadrupole splitting are:

$2[X]-2[Y] > 0$	in tetrahedral $XSn[Co(CO)_4]_3$
$2[Y]-2[X] < 0$	in tetrahedral $X_3Sn[Co(CO)_4]$

If the X–Sn–Co bond angle were smaller than the tetrahedral angle in $XSn[Co(CO)_4]_3$ and larger in $X_3Sn[Co(CO)_4]$, the values of the parameter of the quadrupole splitting in both compounds would be decreased. However, the decreasing rate of the quadrupole splitting in $X_3Sn[Co(CO)_4]$ with the increase in the X–Sn–Co angle would be larger than that in $XSn[Co(CO)_4]_3$ with the decrease in the X–Sn–Co angle, because the value of $3(3\cos^2\theta-1)$ decreases more rapidly as θ increases in the neighborhood of the tetrahedral angle and $[X]>[Y]$. Furthermore, it is expected that the parameter, [X], of $XSn[Co(CO)_4]_3$ would become larger than that of $X_3Sn[Co(CO)_4]$. This is the case with the compounds of chloride and iodide.

When all the molecules in the series of the X_nSnY_{4-n} compound are obtained in an isolated state in solid or frozen solutions, the data of quadrupole splitting provide valuable information about the molecular structure, as is shown in the present study. In view of this, the Mössbauer studies of organic tin halides in a frozen solution would be interesting, for in that way all the molecules may be isolated, while it is difficult to discuss the molecular structure from the data in the solid state, where some association occurs.