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Mössbauer Effect of the ^{119}Sn in the Molecular Complexes of Tin Tetrachloride with Some Aliphatic Compounds

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Molecular complexes of tin tetrachloride with some aliphatic compounds, such as alcohols and esters, were investigated by means of the Mössbauer effect due to ^{119}Sn, irradiation being made by 23.8 keV γ-rays from the ^{119m}Sn in tin dioxide. Most of these complexes show quadrupole splittings resulting from the addition of organic molecules to tin tetrachloride, although broad absorption curves are observed in some cases. The isomer shifts range from 0.30 to 0.45 mm/sec. They are much smaller than that of tin tetrachloride itself. The results are interpreted by taking account of the electronic structures of the complexes.

A number of molecular complexes of tin tetrachloride with oxygen-containing aliphatic compounds, *i. e.*, Lewis bases, have been examined by means of the Mössbauer effect due to ^{119}Sn. Previous structural studies of these complexes have been made mostly by means of the infrared spectra, though sometimes, rarely, by X-ray analysis.[1-3] When tin tetrachloride complexes with such monofunctional donors as alcohols, esters, and ketones, 1 : 2 complexes are generally formed, and the molecular shape changes from a tetrahedron to a octahedron which has either a cis- or a trans-form. On the basis of the infrared spectra of several 1 : 2 complexes, it has been suggested[1,4] that small ligands tend to give cis-complexes. In the course of this work, however, both cis- and trans-complexes were examined.

The purpose of the present study is to clarify the changes in the electron density and the bond character in the $SnCl_4$-complexes. Some of the results obtained are similar to those obtained by Stukan *et al.*,[5] but they are slightly different from those obtained by Khristrov *et al.*[6] The Mössbauer spectra of most of the complexes are doublets. These doublets are caused by quadrupole splitting, 2ε, and are regarded as a direct measure of the electric-field gradient at a tin nucleus or, in qualitative terms, as a measure for the deviation from spherical symmetry of the electron cloud around the tin nucleus.

The difference between the center of the splitting and the zero Doppler velocity, δ, is the isomer shift, which is a relative value with respect to the source. It gives a measure of the s-electron density at the tin nucleus. The source in the present work was radioactive tin dioxide, $^{119m}SnO_2$, and was used at room temperature. Although a small quadrupole splitting is observed in tin dioxide,[7,8] it is preferable as a source because it has a large recoilless fraction of 23.8 keV γ-rays, even at room temperature.

All the δ-values of the molecular complexes fall in the range from 0.3 to 0.45 mm/sec with respect to tin dioxide and are smaller than that of tin tetrachloride. This means that the s-electron density at the nucleus decreases when tin tetrachloride complexes with oxygen-containing organic compounds.

Experimental

Preparation of Molecular Complexes. The $SnCl_4$-complexes were prepared by mixing reactants in benzene or petroleum ether, or by adding tin tetrachloride to ice-cold bases in suitable proportions. Generally the complexes precipitated immediately. They were then filtered off in a dry air stream, washed with a pure solvent, and recrystallized or sublimed under reduced pressure. The complexes with alcohols were prepared by a method previously reported in the literature.[9,10]

The 1 : 2 complexes were obtained by adding the tetrachloride (1/10 mol) to an ice-cold benzene solution of an alcohols (2/10 mol) except ethyl alcohols. The complexes were then purified by sublimation under reduced pressure. The complex of tin tetrachloride

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[9] D. C. Bradley, E. V. Caldwell and W. Wardlaw, *J. Chem. Soc.*, **1957**, 3039.

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with ethyl alcohol was prepared by adding tin tetrachloride to ice-cold ethyl alcohol directly. The crystalline tin trichloride monoethoxide ethanolate was obtained when the tetrachloride and ethyl alcohol were mixed in benzene. It was recrystallized from a benzene solution.

The 1 : 4 complex of tin tetrachloride with isopropyl alcohol was prepared by refluxing tin tetrachloride (27 g) and isopropyl alcohol (40 g) for several hours; it was crystallized spontaneously on cooling. A crop of cubic crystals was obtained.

The complexes of tin tetrachloride with ester, tetrahydrofuran (THF), dioxane, acetone, cyclohexanone, and acetonitrile were prepared by adding tin tetrachloride to a petroleum ether solution of the bases in accordance with the usual method.[4,11] The complexes were then purified by sublimation under reduced pressure.

The compound was identified by measuring its melting point. The results are summarized in Table 1, along with the literature values. They are in good agreement with each other.

TABLE 1. MELTING POINTS OF $SnCl_4$-COMPLEXES

Complexes	Melting point, °C[a]	
	obs.	lit.
$SnCl_4 \cdot 2CH_3OH$	99—106	98—103[b]
$SnCl_4 \cdot 2C_2H_5OH$	51— 58	53—56[b]
$SnCl_4 \cdot 2n\text{-}C_3H_7OH$	106—108	95—98[b]
$SnCl_4 \cdot 2(CH_3)_2CHOH$	112—113	104—106[b]
$SnCl_4 \cdot 4(CH_3)_2CHOH$	61— 68	
$SnCl_4 \cdot 2(C_2H_5)_2O$	80.0—86.5	78—80,[b] 92,[c] 80.6[d]
$SnCl_4 \cdot 2(CH_2)_4O$	S : 155—	S : 165—175[b]
$SnCl_4 \cdot 2O(CH_2)_4O$	S : 175—	S : 175—195[b]
$SnCl_4 \cdot 2(CH_3)_2CO$	93—96	94—96[b]
$SnCl_4 \cdot 2(CH_2)_5CO$	75.5—76.5	74—76[b]
$SnCl_4 \cdot 2CH_3CN$	104—117	
$SnCl_3 \cdot OC_2H_5 \cdot C_2H_5OH$	190—197	191—193,[b] 187[d]

a) Sublimation temperature is designated by " S."
b) Ref. 11.
c) Ref. 10.
d) W. Hieber and E. Reindl, *Z. Electrochem. Angew. Phys. Chem.*, **46**, 559 (1940).

Measurements. The isomer shift and the quadrupole splittings were observed by changing the Dopplevelocity of the absorber. An apparatus of this type was supplied by the Nuclear Science Engineering Company (NSEC, Model B).

The detector was a single channel γ-ray spectrometer made by the Nippon Musen Irigaku Kenkyusho Company. It was equipped with an NaI (1 mm in thickness) scintillation detector. The γ-ray radiation source was tin dioxide containing 2mCi ^{119m}Sn. The source was used at room temperature, while the absorber was cooled with liquid nitrogen. The thickness of the absorber was about 15 mg/cm^2 for Sn. X-Rays were cut off by a Palladium foil attached to the absorber. The activity at a given velocity was accumulated until it reached about 10^5 counts in order to reduce the statistical errors. The accuracy of the apparatus was checked by observing the Mössbauer spectrum of barium stannate, $BaSnO_3$. The isomer shift obtained by this apparatus was in good agreement with the literature value ($\delta < 0.1$ mm/sec).[12] The resonant absorption of the sample was not examined at room temperature.

Results and Discussion

The results of the Mössbauer effect measurement are summarized in Table 2. The isomer shift and quadrupole splitting in molecular complex are presented in the first and second columns of this table, while the third column gives the half-width of the absorption curve, $R_{1/2}$, which will be defined below. All the shifts are shown relative to that of tin dioxide; the positive values indicate the motion of the absorber toward the source. The quadrupole splittings were determined by a procedure to be described below. All the numerical values of δ and 2ε are given in mm/sec.

TABLE 2. MÖSSBAUER PARAMETERS FOR $SnCl_4$-COMPLEXES

Complexes	δ mm/sec[a]	2ε mm/sec[b]	$R_{1/2}$ mm/sec[c]
$SnCl_4 \cdot 2CH_3OH$[d]	0.43	0.70	2.00
$SnCl_4 \cdot 2C_2H_5OH$[d]	0.33	0.70	2.00
$SnCl_4 \cdot 2n\text{-}C_3H_7OH$	0.43	0.50	1.80
$SnCl_4 \cdot 2(CH_3)_2CHOH$[d]	0.35	0.70	2.00
$SnCl_4 \cdot 4(CH_3)_2CHOH$	0.30	0	1.50
$SnCl_4 \cdot 2(C_2H_5)_2O$[d]	0.45	1.10	2.65
$SnCl_4 \cdot 2(CH_2)_4O$[e]	0.43	1.14	2.70
$SnCl_4 \cdot 2O(CH_2)_4O$	0.45	1.10	2.60
$SnCl_4 \cdot 2(CH_3)_2CO$[d]	0.40	small	1.70
$SnCl_4 \cdot 2(CH_2)_5CO$	0.35	0	1.50
$SnCl_4 \cdot 2CH_3CN$	0.43	0.70	2.00
$SnCl_3 \cdot OC_2H_5 \cdot C_2H_5OH$	0.33	small	1.65

a) δ is the isomer shift relative to the source of SnO_2 crystal. The accuracy in the measurement is ±5%.
b) 2ε is the quadrupole splitting.
c) $R_{1/2}$ is the half-width.
d) D. Khristrov *et al.* (Ref. 6) obtained values of δ and 2ε different from those in this table.
e) δ-value obtained by Stukan *et al.* (Ref. 5) is 0.70 relative to SnO_2. They did not observe the quadrupole splitting.

Isomer Shift. The values for all the molecular complexes fall in a range from 0.30 to 0.45 mm/sec. It may be noted that these values are smaller than those of $SnCl_4$, 0.78 ± 0.07,[13] 0.9 ± 0.1,[14] 0.7±

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[11] E. T. Hitchcock and P. J. Elving, *Anal. Chim. Acta*, **28**, 417 (1963).

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0.08,⁵⁾ and 0.8±0.05,⁶⁾ with respect to SnO_2. The isomer shift can be expressed as follows:

$$\delta = (4\pi Ze^2R^2c/5E_\gamma)[|\psi(0)_a|^2 - |\psi(0)_s|^2](\Delta R/R)$$

where $|\psi(0)_a|^2$, $|\psi(0)_s|^2$, Z, R and E_γ are the s-electron densities at the nucleus of the absorber and the source, the nuclear charge, the mean nuclear radius, and the energy of the γ-rays respectively. The value of $\Delta R/R$, which is the fractional change of the radius from the ground state to the excited state, was found to be 1.16×10^{-4} ¹⁵⁾ (1.1×10^{-4} by Boyle *et al.*,¹⁶⁾ and 1.2×10^{-4} by Cordey-Hayes¹⁴⁾). Thus, the fact that the complexes have a smaller isomer shift means that the s-electron density at the tin nucleus decreases when the complexes are formed.

The outer electron configuration of a tin atom in $SnCl_4$ is expressed by the tetrahedral sp^3 hybrid. If the Sn–Cl bond in $SnCl_4$ is completely covalent, its s-electron character is 0.25. The ionic character of the Sn–Cl bond in $SnCl_4$ was estimated to be 0.38 by the pure quadrupole resonance (PQR) resulting from chlorine atom,¹⁷⁾ while it was deduced to be 0.42 or 0.50 from the isomer shift of the Mössbauer effect.¹⁴,¹⁵⁾ If the ionic character is approximated by 0.40, the 5s-electron character of the tin atom will amount of $0.25\times(1-0.40)=0.15$, since a quadrivalent tin ion has the $(4d)^{10}$ configuration outside the krypton core. Accordingly, the value of $|\psi(0)_a|^2$ is smaller for $SnCl_4$ than for β-Sn, in which tin networks are formed by sp^3 hybrid orbitals, and the isomer shift is diminished.

When tin tetrachloride forms molecular complexes with oxygen-containing organic compounds, atoms around the tin atom in the $SnCl_4\cdot2D$ complex (D : donor) occupy the corners of a distorted octahedron formed approximately by sp^3d^2 hybrid orbitals. The lone-pair electrons of oxygen atoms serve as the 5d-electrons, and one of the 5s-electron of the tin atom is promoted to the 5p-orbital, as in the complexes of $SnCl_4\cdot2(CH_2)_4S$¹⁾ and $SnCl_4\cdot2SeOCl_2$.³⁾ If each of the bonds is formed by the sp^3d^2 hybrid, its s-character would be 0.17. From the PQR data in the $SnCl_4\cdot2(C_2H_5)_2O$ complex,¹⁸⁾ it may be seen that the ionic character of the Sn–Cl bond is about 10 percent larger than that for $SnCl_4$ itself. That is, the ionic character may be assumed to be 0.44. Therefore, the 5s-electron character of the tin atom may be estimated to be $0.17\times(1-0.44)=0.09$. However, it should be kept in mind that the pure sp^3d^2 hybrid bonds are not formed in the complexes with nonequivalent ligands, as listed in Table 2. Furthermore, the 5s-electron will be shielded, especially by the 5d-electron. When the results of tin tetrachloride are compared with those of its complexes with oxygen-containing organic compounds, it is expected that the $|\psi(0)_a|^2$ of the tin atom will decrease and that the isomer shift will be reduced in forming the complex. This is the case in the present work.

It is difficult to understand why the isomer shift for the $SnCl_4\cdot2C_2H_5OH$ complex is small in comparison with those of other alcohol complexes. For the 1 : 4 complex $SnCl_4\cdot4(CH_3)_2CHOH$, in which the quadrupole splitting has not been observed, it is not evident how four isopropyl alcohol molecules coordinate to a tin atom. Its structural analysis has not been performed as yet, but it seems plausible that two of them coordinate to a tin atom through oxygen atoms of the donors.

As for the isomer shift of $SnCl_4\cdot2(CH_2)_4O$, the present value (0.43 mm/sec) differs from that of Stukan *et al.* (0.70 mm/sec).⁵⁾ According to them, both $SnCl_4$ and $SnCl_4\cdot2(CH_2)_4O$ have the same isomer shift. This seems unreasonable in light of the s-electron density described above.

Quadrupole Splitting. The quadrupole splitting was observed for almost all the compounds. The observed values of the splitting are given in the second column of Table 2. The quadrupole

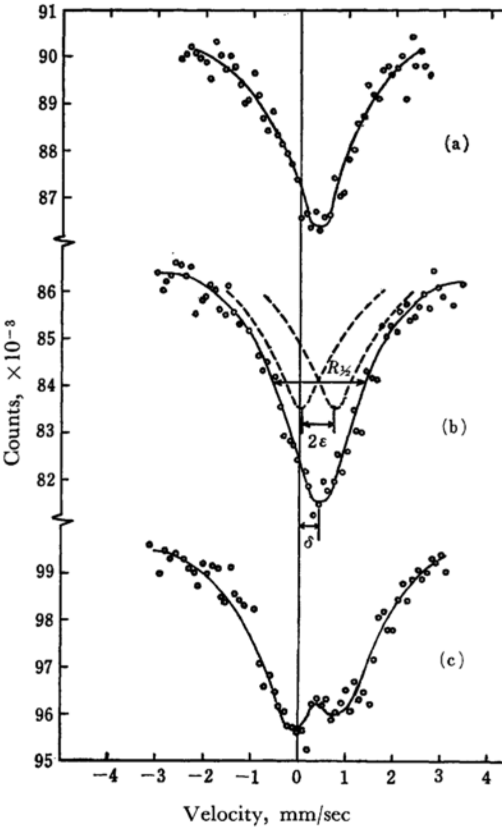

Fig. 1. Mössbauer spectra of $SnCl_4$-complexes.
(a) $CnCl_4\cdot2(CH_2)_5CO$ (b) $SnCl_4\cdot2CH_3CN$
(c) $SnCl_4\cdot2(CH_2)_4O$

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splittings were clearly observed only in complexes with esters, while broad absorption curves were found in the other complexes. A few examples of the spectra are shown in Fig. 1. The minimum value of the observed width, 1.5 mm/sec, is almost equal to that of $BaSnO_3$, which shows no splitting. In the example of the $SnCl_4 \cdot 2CH_3CN$ complex shown in Fig. 1(b), the observed spectrum seems to have a single peak. However, the half-width, $R_{1/2}$, is larger than 1.5 mm/sec, so that there must be some quadrupole splitting. Here $R_{1/2}$ was used to distinguish it from the notation, $\Gamma_{1/2}$, usually used for natural half-widths.

Assuming that the observed curve is composed of Lorentzian curves with the half-width of 1.5 mm/sec, the magnitude of the quadrupole splitting can be deduced easily. The component curves obtained in this way reproduce the original when they are combined. If the components have a width other than 1.5 mm/sec, *e. g.*, 1.4 or 1.6 mm/sec, the combined curves deviate from the experimental curves at the tail part or at the peak. However, this procedure for the derivation of the quadrupole splitting cannot be free from some small errors, since various factors may affect the line width.

In general, the electric field gradient may be caused by two sources, *i. e.*, the charges of the distant ion and the nonspherically distributed electrons around the nucleus. In ionic crystals, the latter effect vanishes, and only the former appears. On the contrary, in covalent crystals the electric field gradient arises mostly from the latter.

In the $SnCl_4$-complexes, both cis- and trans-forms exist, as may be seen in Fig. 2. Among the complexes examined in the present study, both $SnCl_4 \cdot 2CH_3CN$ and $SnCl_4 \cdot 2(CH_3)_2CO$ are known to exist in the cis-form in a benzene solution,[4] but their crystal structures have not yet been determined. If each of these complexes preserves the cis-form in the solid, a twofold axis exists, as in the $SnCl_4 \cdot 2SeOCl_2$ complex shown in Fig. 2(a). Thus the field gradient will appear at tin nuclei, and the quadrupole splitting will be observed to some extent. This is confirmed in Table 2.

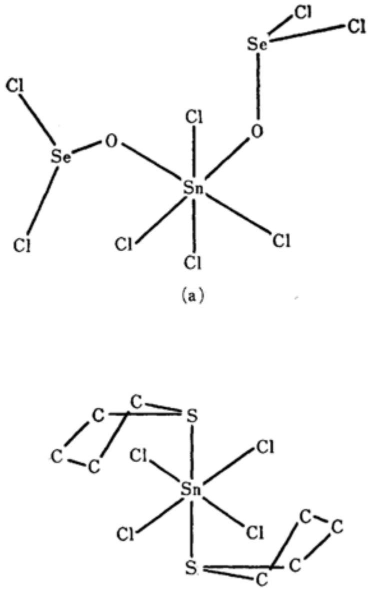

Fig. 2. Structures of tin(IV) chloride complexes.
(a) *cis*-Diseleninylchloride tin(IV) chloride
(b) *trans*-Bis(tetrahydrothyophen) tin(IV) chloride

The quadrupole splitting of the $SnCl_4 \cdot 2(CH_2)_4O$ complex has been observed, contrary to the results reported by Stukan *et al.*,[5] though its crystal structure has not yet been determined. Beattie *et al.*[1] indicated that a similar molecular complex, $SnCl_4 \cdot 2(CH_2)_4S$, is a centrosymmetric molecule with a trans-form; they ascertained this by studying the X-ray diffraction as well as the Raman and infrared spectra (*cf.* Fig. 2(b)). The infrared investigations[19,20] of the $SnCl_4 \cdot 2(CH_2)_4O$ complex show that the two donor molecules coordinate to a tin atom to yield a trans-form. Thus, the shape of the $SnCl_4 \cdot 2(CH_2)_4O$ complex may be almost the same as that of the $SnCl_4 \cdot 2(CH_2)_4S$ complex, which has a twisted form. Consequently, the distribution of the electric charge around the tin nucleus in the $SnCl_4 \cdot 2(CH_2)_4O$ deviates from spherical symmetry, and the quadrupole coupling arises. An interesting fact is that the magnitude of the quadrupole splitting is larger for a trans-complex than for a cis-complex.

The complex compound $SnCl_3OC_2H_5 \cdot C_2H_5OH$ was investigated by means of measurements of the vapor pressure of a benzene solution and the infrared absorption of the solid by Laubengayer *et al.*,[10] as well as by means of the dipole moment in a benzene solution by Osipov *et al.*[21] From these results the dimer structure shown in Fig. 3 was proposed. According to the Mössbauer effect on this compound, the quadrupole splitting is very small, although the value was not determined. Therefore, it seems likely that the compound exists as a cis-form in the solid state.

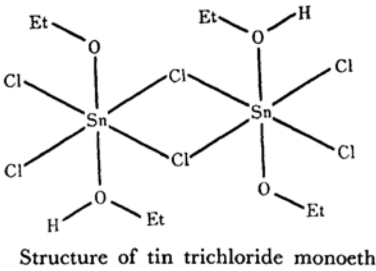

Fig. 3. Structure of tin trichloride monoethoxide ethanolate.

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