BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1486—1489 (1969)

Mössbauer Effect of ^{119}Sn in Molecular Complexes of Tin(IV) Chloride with Several Aromatic Compounds

Sumio ICHIBA, Mitsuo MISHIMA*[1] and Hisao NEGITA

Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima

(Received October 4, 1968)

The Mössbauer spectra of molecular complexes of tin(IV) chloride with some oxygen-containing aromatic compounds, such as hydroxybenzaldehydes and cinnamic acid, were investigated. Most of these complexes show the quadrupole splitting resulting from the addition of aromatic molecules to tin(IV) chloride, although in some cases broad absorption curves are observed. The isomer shifts of these complexes are 0.25—0.45 mm/sec, much smaller than that of tin(IV) chloride itself. These values are almost the same as those of the complexes of tin(IV) chloride with aliphatic compounds. From these results, the bond nature and structures of these complexes, which had not previously been studied, were discussed in some detail.

In a previous paper[1)] dealing with the ^{119}Sn Mössbauer effect in the molecular complexes of tin (IV) chloride with some aliphatic compounds, it was shown that the spectra for most of the complexes were doublets caused by the quadrupole splitting, and that the isomer shifts of the molec-

---

*[1] Present address: Department of Chemistry, Shimane University, Matsue.

1) S. Ichiba, M. Mishima, H. Sakai and H. Negita, This Bulletin, **41**, 49 (1968).

ular complexes with respect to SnO_2 were in the range from 0.30 to 0.45 mm/sec.

In the present work, the 1 : 2 molecular complexes of tin(IV) chloride with some aromatic compounds have been investigated by Mössbauer spectroscopy. The structures of these complexes have not been investigated. However, the preparations of most of the complexes have been reported by Pfeiffer[2,3] and by Rosenheim *et al.*[4]

In the molecular compolexes of tin(IV) chloride (electron acceptor) with oxygen-containing aromatic compounds (electron donor), there are two possibilities in the way of coordination, unlike the aliphatic compounds, because the oxygen-containing aromatic molecule has two parts serving as electron donors, *i. e.*, the benzene ring and the oxygen-containing group. In the complex of tin(IV) chloride with benzaldehyde, for example, the chlorine atom in tin(IV) chloride may be bonded to the benzene ring of benzaldehyde through its π-electron, but it is equally, or even more, likely that the oxygen atom of the aldehyde group will be coordinated to the tin atom in tin(IV) chloride directly through the lone-pair electrons of the oxygen, as in the case of aliphatic compounds reported previously. In the former case the chlorine atoms around the tin atom remain in the tetrahedron form in complexing, whereas in the latter case they change to an octahedron.

The purpose of the present study is to clarify the difference between the aliphatic and aromatic complexes and to explain, on the basis of the Mössbauer parameters, how tin(IV) chloride is bounded to the aromatic compound in the complex.

Experimental

Preparation of Molecular Complexes. The tin(IV) chloride and all the aromatic compounds were obtained commercially. All the complexes except that of tin(IV) chloride with cinnamyl alcohol were prepared by a method similar to those described by Pfeiffer[2,3] and by Rosenheim and Levy.[4] That is, the complexes were formed by dropping tin(IV) chloride (1/20 mol) into ice-cooled petroleum ether, chloroform, or a benzene solution of an aromatic compound (1/10 mol); they were then dried over silica gel in a vacuum desiccator.

The complex of tin(IV) chloride with cinnamyl alcohol was prepared by adding tin(IV) chloride (1/20 mol) to petroleum ether in which cinnamyl alcohol (1/10 mol) was suspended. Brown nonhygroscopic crystallines with a mp of 82°C were thus obtained. All the complexes except that of tin(IV) chloride with ethyl cinnamate were purified by sublimation under a reduced pressure of 4—7 mmHg. The complexes were identified by their melting points; the results are summarized in Table 1, along with the literature values.

TABLE 1. MELTING POINTS OF $SnCl_4$-COMPLEXES

Complex	Melting point °C	
	Obsd	Lit[a]
$SnCl_4 \cdot 2C_6H_5CHO$	177	187—189
$SnCl_4 \cdot 2C_6H_5COOH$	78—80	90
$SnCl_4 \cdot 2C_6H_4(OH)CHO(o)$	140	—
$SnCl_4 \cdot 2C_6H_4(OH)CHO(p)$	175	185
$SnCl_4 \cdot 2C_6H_4(OCH_3)CHO(p)$	178	158
$SnCl_4 \cdot 2C_6H_5CH{=}CHCH_2OH$	82	—
$SnCl_4 \cdot 2C_6H_5CH{=}CHCHO$	241	225—230
$SnCl_4 \cdot 2C_6H_5CH{=}CHCOOH$[b]	—	—
$SnCl_4 \cdot 2C_6H_5CH{=}CHCOOC_2H_5$	140	134

a) Refs. 2, 3.

b) Melting point could not be measured on account of thermal decomposition.

Measurements. The measurements were made as previously.[1] The activity at a given velocity was accumulated until it reached about 10^5 counts in order to reduce the statistical errors. The γ-ray radiation source was tin(IV) oxide containing 1 mCi ^{119m}Sn. The source was used at room temperature, whereas 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.

Results and Discussion

The results are given in Table 2. The isomer shift, δ, and the quadrupole splitting, 2ε, of the complexes are presented in the first and second columns respectively. The third column gives the half-width, $R_{1/2}$, which was defined in the previous paper.[1] The isomer shift is referred to tin(IV) oxide at room temperature. A positive value means that the source and the absorber are approaching each other, while a negative value means that they are moving apart. When the splitting due to the quadrupole interaction was

TABLE 2. MÖSSBAUER PARAMETERS FOR $SnCl_4$-COMPLEXES

Complex	δ[a] mm/sec	2ε[b] mm/sec	$R_{1/2}$[c] mm/sec
$SnCl_4 \cdot 2C_6H_5CHO$	0.42	0.80	2.10
$SnCl_4 \cdot 2C_6H_5COOH$	0.35	1.16	2.70
$SnCl_4 \cdot 2C_6H_4(OH)CHO(o)$	0.34	0.92	2.28
$SnCl_4 \cdot 2C_6H_4(OH)CHO(p)$	0.45	0	1.50
$SnCl_4 \cdot 2C_6H_4(OCH_3)CHO(p)$	0.35	0.64	1.90
$SnCl_4 \cdot 2C_6H_5CH{=}CHCH_2OH$	0.27	0	1.50
$SnCl_4 \cdot 2C_6H_5CH{=}CHCHO$	0.42	0.75	2.05
$SnCl_4 \cdot 2C_6H_5CH{=}CHCOOH$	0.40	0.92	2.28
$SnCl_4 \cdot 2C_6H_5CH{=}CHCOOC_2H_5$	0.25	1.20	2.80

a) δ is the isomer shift relative to the source of SnO_2 crystal. The accuracy of the measurement is ±5%.

b) 2ε is the quadrupole splitting.

c) $R_{1/2}$ is the half-width.

---

[2] P. Pfeiffer, *Ann.*, **376**, 285 (1910).

[3] P. Pfeiffer, *Z. anorg. Chem.*, **71**, 97 (1911); *ibid.*, **112**, 81 (1920); *ibid.*, **133**, 91 (1924).

[4] A. Rosenheim and W. Levy, *Ber.*, **37**, 3667 (1904).

observed, the average line position was taken as the δ-value. All the values of δ and 2ε are given in mm/sec.

Isomer Shift. In Table 2 the values of the isomer shift for all the complexes of $SnCl_4$ with oxygen-containing aromatic compounds fall in a range from 0.25 to 0.45 mm/sec. There is no appreciable difference between the δ-values for the complexes with oxygen-containing aliphatic compounds reported previously[1] and those with oxygen-containing aromatic compounds. The values are appreciably smaller than those of tin(IV) chloride, which are 0.7 ± 0.08,[5] 0.78 ± 0.1,[6] 0.8 ± 0.05,[7] and 0.9 ± 0.1[8] with respect to tin(IV) oxide. This means that tin(IV) chloride-complexes have a lower s-electron density at the tin nucleus than does tin(IV) chloride itself. In other words, the formation of the 1 : 2 complex of tin(IV) chloride with an oxygen-containing organic compound results in a decrease in the s-electron density at the tin nucleus.

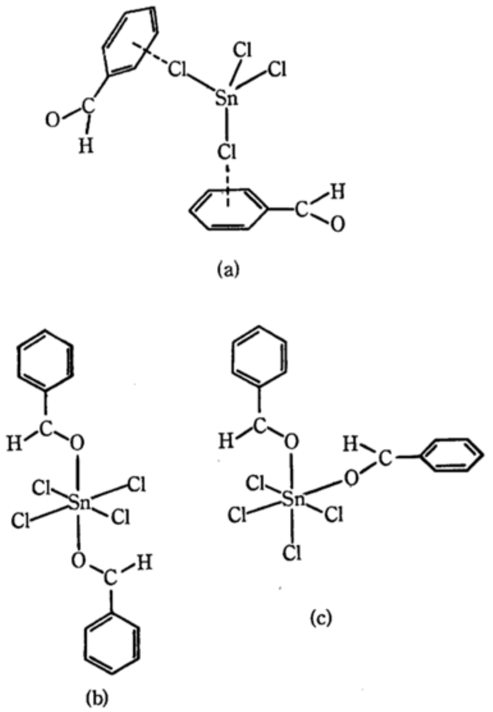

Fig. 1. Bond structures of $SnCl_4$-benzaldehyde complex.

In forming the molecular complex, it is assumed that the coordination of aromatic molecules to tin(IV) chloride permits two bond-structures, as has been mentioned above. For instance, the possible bond-structures of the complex of tin(IV) chloride with benzaldehyde are shown in Fig. 1; in (a) the π-electrons are transferred from the benzene ring to the chlorine atom of tin(IV) chloride, while in (b) and (c) the lone-pair electrons of the oxygen atom are transferred to the tin atom. In the (a) bond-structure the tetrahedral arrangement of the chlorine atoms around the tin atom is preserved, but in the structures (b) and (c) it changes to an octahedron of the *trans*- or *cis*-form.

The electron configuration outside the krypton core of a neutral tin atom is $(4d)^{10}(5s)^2(5p)^2$. In tin(IV) chloride, chlorine atoms are coordinated to the tin atom in a tetrahedral form so that the hybrid bond of the tin atom is sp^3. If the Sn–Cl bond in tin(IV) chloride is completely covalent, as has been discussed in a previous paper,[1] its s-electron character is 0.25. However, the bonds character was deduced to be approximately 40% ionic from the pure quadrupole resonance due to ^{35}Cl[9] and the Mössbauer effect of ^{119}Sn.[8,10]

If the complex has the structure (a), electrons will transfer from the benzene ring of the benzaldehyde to the chlorine atom of tin(IV) chloride. Consequently, the chlorine atom in the complex may be more ionic than that of tin(IV) chloride itself. However, the electron transferred to the chlorine atom may not influence the electron density at the tin nucleus very seriously, since it affects indirectly through the chlorine atom.

On the other hand, in the complex of the bond-structure (b) or (c) the electron-donor atom is the oxygen atom and the acceptor atom is the tin atom in tin(IV) chloride. That is to say, oxygen atoms are directly coordinated to the tin atom, and then oxygen atoms occupy a *cis*- or *trans*-position and the arrangement of atoms around the tin atom is hexacoordinated. Lone-pair electrons of the oxygen atom of the aldehyde group contribute directly to the electron core of the tin atom of tin(IV) chloride and sp^3d^2 hybrid orbitals are formed around the tin atom. If the ligand atoms are completely hexacoordinated, *i. e.*, if the Sn–O and Sn–Cl bonds are entirely equivalent and completely covalent, the s-electron character of the bonds is 0.17. Therefore, the s-electron density at the tin nucleus may be expected to be larger in the complex of the bond-structure (a) than in the complex of the bond-structure (b) or (c). Thus, the complex of the bond-structure (a) should show a larger isomer shift than the complex of the bond-structure (b) or (c). The isomer shifts of the complexes

---

[5] R. A. Stukan, T. N. Sumarokova, V. A. Trukhatanov and V. V. Khrapov, *Dokl. Acad. Nauk. SSSR,* **156,** 400 (1964).

[6] A. Yu. Aleksandrov, N. N. Delyagin, N. P. Mitrofanov, L. S. Poluk and V. S. Shpinel, *Zh. Eksperim. i Teor. Fiz.,* **43,** 1242 (1962); *Soviet Phys. JETP,* **16,** 874 (1963).

[7] S. Khristrov, Tsv. Bonchev and Kl. Burin, *Compt. Rend. Acad. Bulgare Sci.,* **19,** 293 (1966).

[8] M. Cordey-Hayes, *J. Inorg. Nucl. Chem.,* **16,** 915 (1963).

[9] A. L. Schalow, *J. Chem. Phys.,* **22,** 1211 (1954).

[10] D. A. Shirley, *Rev. Mod. Phys.,* **36,** 399 (1964).

between tin(IV) chloride and oxygen-containing aromatic compounds are 0.25 to 0.45 mm/sec, considerably smaller than that of tin(IV) chloride itself; these shifts do not differ appreciably from those of the complexes of tin(IV) chloride with aliphatic compounds, 0.31—0.45 mm/sec. Accordingly, the complex of tin(IV) chloride with aromatic compounds is considered to have the bond-structure (b) or (c). It is uncertain at this stage which of the bond-structures, (b) or (c), is the more probable, for other experimental data is lacking.

Quadrupole Splitting. With the exception of the complexes of tin(IV) chloride with *p*-hydroxybenzaldehyde and with cinnamyl alcohol, small quadrupole splittings were observed for all the complexes. A pair of clearly-split lines were observed in two complexes, those with benzoic acid and with ethyl cinnamate. The spectrum of the complex with benzoic acid is shown in Fig. 2 as an example. When the value of $R_{1/2}$ was below 2 mm/sec, only a broad absorption curve was observed. The value of the quadrupole splitting was found by analysing the curve, assuming that the component lines were of a Lorentzian type with a half-width of 1.50 mm/sec.

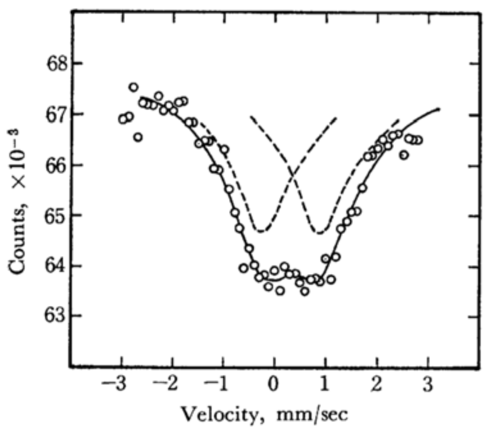

Fig. 2. Mössbauer spectrum of $SnCl_4 \cdot 2C_6H_5$-COOH.

In Table 2, it is interesting to note that the complex with *p*-hydroxybenzaldehyde has no quadrupole splitting, though the complex with *o*-hydroxybenzaldehyde has. This is obviously due to the difference of the molecular structures of the ligands. However, the crystal structures of these complexes have not yet been established. Since the difference in the quadrupole splitting is caused by the relative positions of the OH- and CHO-groups, or the ortho- and para-positions, it is significant to consider how the two isomers are coordinated to the tin atom and how they give rise to the electric field gradient around the tin nucleus.

In the hexacoordinated complex of tin(IV) chloride with *p*-hydroxybenzaldehyde, the OH-groups are coordinated to the tin atom; therefore, the CHO-groups are free from the coordination, being separated from the tin atom or *vice versa*. However, it is more probable that the OH-groups are coordinated, for the complex with benzaldehyde shows splitting. On the other hand, in the complex with *o*-hydroxybenzaldehyde, the non-coordinated group at the ortho-position is very close to the tin atom and so necessarily causes an electric field gradient of some extent at the tin nucleus. Thus, the difference between the relative positions of the OH- and CHO-groups is reflected in the quadrupole splitting.

Small quadrupole splittings are also observed in the complexes with aromatic molecular ligands containing a carbonyl group with which the organic molecules are attached to the tin atom. According to Greenwood and Ruddick,[11] quadrupole interactions in tin(IV) compounds are observed only when there is an imbalance in subsidiary π-interactions.

In the spectrochemical series, carbonyl is ranked as a strong π acceptor and Cl^-, as a strong π donor. This difference in ligand ability will be enough to cause the imbalance in the π-interactions between the π orbitals of the ligands and the d_π orbitals of the central tin atom in the complex. Thus, small quadrupole splittings are observed in the complexes with benzaldehyde, benzoic acid, *etc.*, whereas no quadrupole splitting is observed in the complexes with *p*-hydroxybenzaldehyde and cinnamyl alcohol. This is because the *p*-hydroxybenzaldehyde and cinnamyl alcohol are attached to the tin atom by means of OH-groups which have little or no π-bonding abilities and which do not give rise to an electric field gradient at the tin atom. The small variation in the splitting values results from the inductive effects of the neighbouring groups of the carbonyl coordinated to the tin atom.

---

[11] N. N. Greenwood and M. N. R. Ruddick, *J. Chem. Soc.*, **1967**, 1679.