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Mössbauer Effect of ^{119}Sn in Complexes of Tin(IV) Chloride and Dialkyltin Dichlorides with Some Nitrogen Donors

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Abstract

The tin-119 Mössbauer effect was studied in complexes of dimethyltin dichloride, dibutyltin dichloride and tin (IV) chloride with nitrogen donors such as pyridine, phenanthroline, bipyridyl, quinoline, isoquinoline, β-naphthoquinoline or acridine. The data on the quadrupole splitting revealed that the alkyl groups in all the complexes of dialkyltin dichloride are situated in trans position to each other. The isomer shifts for the parent chloride and its complex decreased with an increase in electron-donating ability of R bonded to the tin atom, where R= n-C_4H_9, CH_3 or Cl, while a similar tendency was also found in the difference of the isomer shift between them. These results showed the dependence of the electron-donating ability of R on the group bonded to R.

An extensive study of tin (IV) complexes by means of the Mössbauer effect has established a relation between the bond character of tin (IV) complexes and the Mössbauer parameters. It was suggested that the isomer shift (IS) relates to the electron-donating or -attracting ability of ligand group[1,2], and that the relation between the quadrupole splitting (QS) and the configuration of complex[2,3] surves as an indicator of *cis*- or *trans*-form of complex. Furthermore, it was shown that the IS is smaller for $SnCl_4$-complexes especially with oxygen or nitrogen donors than for $SnCl_4$ itself[4]. On the other hand, it became apparent from this work that the IS for Bu_2SnCl_2 is almost the same magnitude as that for its complex.

The purpose of this investigation is to clarify the origins of the aforementioned difference between the $SnCl_4$-complexes and dialkyltin dichloride-complexes.

Experimental

Preparation of Complexes. The $SnCl_4$-complexes were prepared in the similar manner described previously[4]. The Me_2SnCl_2- and Bu_2SnCl_2-complexes were prepared by mixing benzene, ethanol or pertoleum ether solutions of dialkyltin dichloride and Lewis base in suitable propotions and evacuated for 24 hours. These complexes were used without further purification.

The elemental analyses of N, and the spectra of IR and Mössbauer effect for the complexes gave satisfactory results.

Mössbauer Spectra. The Mössbauer spectrometer was essentially the same as that described elsewhere[5]. The absorber of areal density 15 mg/cm^2 of Sn was cooled with liquid nitrogen, while the source $BaSnO_3$ was kept at room temperature. The spectra were analyzed by fitting the Lorentzian curves to the experimental points by use of of the least square regression method.

Results and Discussion

The Mösssbauer parameters for the complexes with nitrogen donors are summarized in Table 1. Of these complexes the IS,s for pyridine-, bipyridyl- and o-phenanthroline-complexes were in fair agreement with the previous data[6].

Isomer Shift. The IS's for the $SnCl_4$-complexes range from 2.27 to 0.50 mm/sec and are smaller than the parent $SnCl_4$. This indicates that the *s*-electron density at the tin nucleus decreases when $SnCl_4$ forms a complex with nitrogen donors. The increase in the ionic character and/or the increase in *p*- and *d*-electrons in hybrid orbitals are responsible for the decrease in the IS on complexation. The IS's for the complexes of $SnCl_4$ with the nitrogen donors shown in Table 1 are comparable with those for complexes with oxgen donors[4,7], whereas it was shown that the IS,s are somewhat more positive for complexes with nitrogen donors than for analogous complexes with oxygen donors[8]. The magnitude of the IS seems to be mainly influenced by a ligand molecule than a ligand atom in complexes with nitrogen donors and with oxygen donors.

Comparison of the IS for Me_2SnCl_2, $\delta(Me_2SnCl_2)$, with that for its complex, δ(complex), reveals that the formation of a Me_2SnCl_2-complex causes a small or no decrease in the *s*-electron density at the tin nucleus. The decrease in

TABLE 1. MÖSSBAUER PARAMETERS FOR TIN(IV) COMPOUNDS AT 80°K[a]

Compounds	IS[b]	QS	Line width		$\Delta\delta$[c]
$SnCl_4$[d]	0.86				
$SnCl_4$. 2acr	0.27		1.10		−0.59
$SnCl_4$. 2naph	0.37	0.52	1.10	1.10	−0.49
$SnCl_4$. 2qui	0.39		1.33		−0.47
$SnCl_4$. phen	0.43		1.25		−0.43
$SnCl_4$. 2py	0.44		1.10		−0.42
$SnCl_4$. bipy	0.46		0.90		−0.40
$SnCl_4$. 2isoq	0.50		1.10		−0.36
Me_2SnCl_2	1.55	3.58	0.65	0.84	
Me_2SnCl_2. 2py	1.36	3.92	0.82	0.73	−0.19
Me_2SnCl_2. 2isoq	1.38	3.92	0.84	0.85	−0.17
Me_2SnCl_2. bipy	1.45	4.07	0.78	0.89	−0.10
Me_2SnCl_2. phen	1.46	4.16	0.74	0.97	−0.09
Me_2SnCl_2. 2acr	1.49	4.04	0.71	0.84	−0.06
Me_2SnCl_2. 2naph	1.58	4.29	0.92	0.79	0.03
Bu_2SnCl_2	1.59	3.43	1.00	1.05	
Bu_2SnCl_2. bipy	1.58	4.09	0.78	0.93	−0.01
Bu_2SnCl_2. 2py	1.60	4.04	0.72	1.00	0.01
Bu_2SnCl_2. phen	1.62	4.19	0.61	0.93	0.03
Bu_2SnCl_2. 2qui	1.71	4.33	0.99	1.03	0.12
Ph_2SnCl_2[e]	1.36	2.76			
Ph_2SnCl_2. phen[e]	1.21	3.37			−0.15
Ph_2SnCl_2. bipy[e]	1.22	3.39			−0.24

a) All values in mm/sec.
b) Relative to $BaSnO_3$ at room temp.
c) The decrease in the isomer shift on complexation.
d) S. Ichiba, M. Katada and H. Negita, *Bull. Chem. Soc. Japan*, **45**, 1679 (1972).
e) M. A. Mullins and C. Curran, *Inorg. Chem.*, **7**, 2584 (1968).
acr = acridine ; naph = β-naphthoquinoline ; qui = quinoline ; phen = 1, 10-phenanthroline ; py = pyridine ; bipy = 2, 2′-bipyridyl ; isoq = isoquinoline.

the IS on complexation $\Delta\delta(Me_2SnCl_2)[=\delta(\text{complex})-\delta(Me_2SnCl_2)]$ is at the most an extent of less than half $\Delta\delta(SnCl_4)$; $\Delta\delta$ is listed in the last column of Table 1. As $\Delta\delta(Bu_2SnCl_2)$ is nearly equal to zero or positive rather than negative, the *s*-electron density at the tin nucleus is hardly reduced on complexation. $\Delta\delta(Ph_2SnCl_2)$ is *ca.* −0.15 mm/sec which is an intermediate value between $\Delta\delta(SnCl_4)$ and $\Delta\delta(Me_2SnCl_2)$. Thus the *s*-character on the tin atom decreased in the order, $Bu_2SnCl_2 > Me_2SnCl_2 > Ph_2SnCl_2 > SnCl_4$ on complexation, which is consistent with that of the IS for the parent Lewis acids.

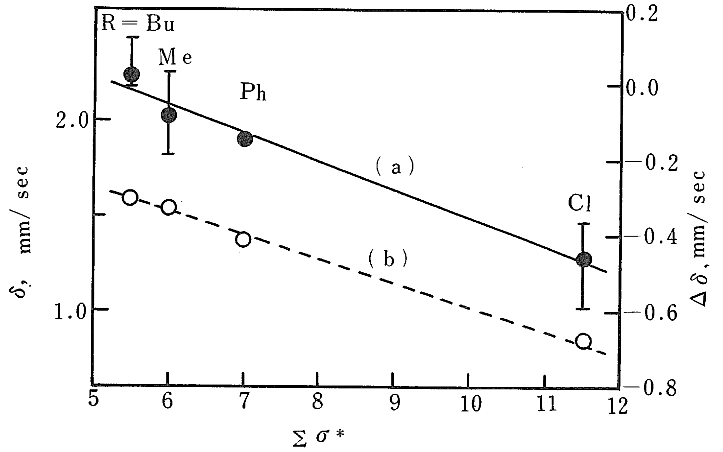

Fig. 1. The relation between the isomer shift and Taft constant
(a) $\Delta\delta$ *vs* $\Sigma\sigma^*$ (b) δ *vs* $\Sigma\sigma^*$

In Fig. 1, the IS and the difference of the IS between the Lewis acid and its complex are plotted to the sum of the Taft constant for R's$^{9)}$, where R = Me, Bu, Ph or Cl. Both the IS and the $\Delta\delta$ is linearly decreased with an increase in the sum of the Taft constant. This seems to indicate that the compound attached by more electron-releasing groups gives a higher *s*-electron character on the tin atom and in such a compound the *s*-character is hardly varied on complexation. However, in a $SnCl_4$ crystal the Cl atoms are spatially directed to the corners of a tetrahedron$^{10)}$. On the other hand, in a Me_2SnCl_2 crystal the enviroment of the tin atoms is considerably distorted from the regular tetrahedral coordination towards octahedral because of the intermolecular interaction$^{11)}$, though the intermolecular interaction is not so strong because of the long distance between one tin atom and the chlorine atom of its nearest neighbors and the arrangement of the nearest atoms around the tin atom is close to a tetrahedron rather than a octahedron. In contrast with the bonds in $SnCl_4$, the Sn-C and Sn-Cl bonds are expected to contain the *s*-character. However, the 5*d*-electrons seem to shield to a lesser extent the *s*-electrons in Me_2SnCl_2 since the influence of the shielding due to the 5*p*-eleetrons on the IS value is less than 1/10 of that of the variation in the 5*s*-electron density$^{12)}$ and the *s*-electrons are shielded much weaker by the 5*d*-electrons than by the 5*p*-electrons. The similar structure is expected for Bu_2SnCl_2 and Ph_2SnCl_2. In the tin(IV) compounds the ionic character of the central tin atom is increased as Lewis acid is attached by electronegetive ligands, and the *s*-electron density is reduced by the electron withdrawal of the ligands, while the electron-releasing group supplies the electron to the central atom and compensated the reduction of the electron population.

It was preposed from the results of the nuclear quadrupole resonance and the Mössbauer effect that in $R_{4-n}SnCl_n$ the electron populations (α_R and α_{Cl}) in the hybrid orbitals directed towards R and Cl are increased with increasing n[13]. On the other hand, it was discussed on the base of the same method that α_R on R_3SnX is increased with increasing electronegativity of X[14]. This means that the electron-donating ability of a given group is increased as the electron-attracting ability of the other group attacted to the common central ion is increased. In other words, the electron-donating ability of R is not constant, but dependent upon a partner group. Our data exhibit that the variation in the electron-donating ability of R becomes progressively greater as the Taft constant of R is increased. In the complex of Bu_2SnCl_2 the decrease in the electron density on the tin atom which is caused by complexation is almost completely compensated by butyl groups. The variation in the electron-donating ability of a methyl group appears to be not so great as that of a butyl group since the IS is somewhat greater for Me_2SnCl_2 than for its complexes. Since $SnCl_4$ has the greatest absolute value of $\Delta\delta$, the donating or attracting ability of a chlorine atom does not vary significantly with a partner group. After all the degree of the variation of the electron-donating ability with partner group increases in the following order ; $Cl < Ph < Me < Bu$.

Quadrupole Splitting. The QS is sensitive to cis-trans isomerism in hexacoordinated tin(IV) complexes. It was reported that *cis*-R_2SnX_4 have QS's of *ca.* 2 mm/sec and *trans*-R_2SnX_4 have splittings of *ca.* 4 mm/sec[2,3]. Since the complexes of dialkyltin dichloride with nitrogen donors exihibited the QS,s of *ca.* 4 mm/sec, it is concluded that alkyl groups in all of these complexes are situated in the trans position to each other.

The small variation of the QS with ligand molecules was found in the complexes with nitrogen donors. The QS is greater for Bu_2SnCl_2-comlex than for Me_2SnCl_2-complex with the same ligand molecules. And the more bulky the ligand molecules, the greater the QS for the complex. The coordination of the bulky groups to Lewis acid is considered to make the octahedron distorted. Such a steric effect affects somewhat the electric field gradient and/or the asymmetric parameter.

In $SnCl_4$-complexes the complex with bulky groups also exhibited a small QS or a broad absorption peak. Our conclusion is in accord with the previos ones[7,8].

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