

Mössbauer Spectroscopic Studies of $(\text{Me}_2\text{NH}_2)_2\text{SnX}_6$ ($\text{X} = \text{Cl}$ or Br) and Their Related Complexes

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The temperature dependence in the ^{119}Sn Mössbauer spectral area for $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnCl}_6$ was found to be almost linear, although a phase transition of the complex has been suggested by IR, ^{35}Cl NQR and NMR studies, while an anomaly in the temperature dependence for $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnBr}_6$ was found at ~ 235 K, which is close to the phase transition temperature ~ 253 K determined by ^{89}Br NQR. These differences are attributable to molecular motion of the dimethylammonium ion in the complexes. The X-ray powder diffraction pattern of $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnCl}_6$ did not change near the phase transition point, but that of $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnBr}_6$ changed at 108 - 123 K and 233 - 253 K.

Key words: Mössbauer Spectroscopy; Phase Transition; SnX_6^{2-} Ion; Molecular Motion.

1. Introduction

Alkylammonium hexahalogenostannates (IV), $\{(\text{C}_n\text{H}_{2n+1})_m\text{NH}_{4-m}\}_2\text{SnX}_6$ ($n = 0, 1, 2, \dots, x; m = 0 - 4; \text{X} = \text{Cl}$ or Br) form a large family of complexes whose physico-chemical properties are interesting from a structural, dynamic and thermodynamic point of view. The structural phase transitions in some of these complexes have been studied by NQR [1 - 15], NMR [7, 11, 16 - 20], Raman [21, 22], IR [23], heat capacity [24, 25], DTA [15, 18, 19, 26], crystal structure [8, 19, 27, 28], and neutron powder diffraction techniques [10, 29].

Mössbauer spectroscopy can provide us with valuable information about the lattice dynamical properties of a solid which are associated with the motion of Mössbauer atoms. The variable temperature ^{119}Sn -Mössbauer spectroscopic studies of $(n\text{-C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{SnCl}_6$ ($n = 6 - 18$) [30] and $(n\text{-C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{SnX}_6$ ($n = 0 - 4; \text{X} = \text{Cl}$ or Br) [31] have also been reported by us. For higher carbon chain alkylammonium hexachloro tin complexes ($n = 6, 8, \dots, 16$) the temperature dependence of the area in-

tensity deviated from a straight line. This deviation increased with the number of carbon atoms in the alkyl groups. The X-ray powder diffraction patterns of the complexes at room temperature show a layer structure in which adjacent alkylammonium ions are intercalated. The motion of the alkylammonium ion can be correlated with the observed temperature dependence. On the other hand, in lower carbon alkylammonium tin complexes a large discontinuity of the temperature dependence of the area intensity was found for $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{SnCl}_6$, $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{SnBr}_6$, $(n\text{-C}_4\text{H}_9\text{NH}_3)_2\text{SnCl}_6$ and $(n\text{-C}_4\text{H}_9\text{NH}_3)_2\text{SnBr}_6$ at phase transition temperatures obtained from the heat anomaly on the DSC curves. However in the cases of $(\text{NH}_4)_2\text{SnCl}_6$ [1, 5, 6, 16, 21, 27], $(\text{NH}_4)_2\text{SnBr}_6$ [1, 10, 16, 21, 24] and $(\text{CH}_3\text{NH}_3)_2\text{SnCl}_6$ [2 - 4, 17, 27] phase transitions have been discovered by many physico-chemical techniques, no anomaly in the temperature dependence of the Mössbauer spectral area was found. This discrepancy may be attributable to the difference in the phase transition type and / or the molecular motion of alkylammonium ions. The molecular motion of the alkylammonium ion may play an im-

portant role in these complexes. Recently the existence of a phase transition of $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnCl}_6$ [11, 13, 23] and $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnBr}_6$ [9] has been reported from IR, ^{35}Cl -NQR and ^{79}Br -NQR studies, respectively. In the present work, variable temperature- ^{119}Sn -Mössbauer spectroscopy has been carried out to study the thermal motion of the tin atom in $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnCl}_6$, $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnBr}_6$ and $\{(\text{CH}_3)_3\text{NH}\}_2\text{SnCl}_6$ in combination with a variable temperature X-ray powder diffraction measurement.

2. Experimental

All complexes were prepared by mixing $(\text{CH}_3)_2\text{NH}_2\text{X}$ and SnX_4 or $(\text{CH}_3)_3\text{NHCl}$ and SnCl_4 ($\text{X} = \text{Cl}$ or Br) in acidic aqueous or ethanol solution. The purity of the complexes was checked by elemental analyses for C, H, and N. Found: C, 11.28; H, 3.85; N, 6.57%. Calcd. for $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnCl}_6$: C, 11.34; H, 3.81; N, 6.61%. Found: C, 6.85; H, 2.24; N, 3.86%. Calcd. for $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnBr}_6$: C, 6.96; H, 2.34; N, 4.06%. Found: C, 15.89; H, 4.54; N, 6.27%. Calcd. for $\{(\text{CH}_3)_3\text{NH}\}_2\text{SnCl}_6$: C, 15.96; H, 4.46; N, 6.20%. The Mössbauer spectroscopic measurements were carried out using a constant-acceleration spectrometer at $78 \text{ K} \leq T \leq 300 \text{ K}$. The observed spectra were fitted with Lorentzian line shapes using the least-squares fitting procedure. The isomer shift values were referred to BaSnO_3 at room temperature. The X-ray powder diffraction patterns were obtained by using Cu K_α radiation.

3. Results and Discussion

The Mössbauer spectra of all the complexes described in this paper showed a singlet due to the high symmetry of the SnX_6^{2-} anion. The Mössbauer isomer shifts (IS) and halfwidths (Γ_{exp}) derived from the observed spectra at 78 K are listed in Table 1. The IS values of the chlorine complexes are smaller than those of the bromine complexes because of the more electronegative ligand. The recoil-free fraction f_a and its temperature dependence provided us with useful information about the lattice dynamics of a solid.

According to the Debye approximation in the high temperature limit, the “relative” value of the recoil-free fraction f_a is given by

$$f_a = \exp \left[-3E_\gamma^2 T / (Mc^2 k\theta^2) \right], \quad (1)$$

Table 1. Mössbauer parameters of alkylammonium hexahaloanionotin(IV) complexes at 78 K.

Complex	IS* [mm s ⁻¹]	Γ_{exp}^* [mm s ⁻¹]	Ref.
$(\text{CH}_3\text{NH}_3)_2\text{SnCl}_6$	0.55	0.92	[31]
$\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnCl}_6$	0.52	0.93	this work
$\{(\text{CH}_3)_3\text{NH}\}_2\text{SnCl}_6$	0.50	0.88	this work
$\{(\text{CH}_3)_4\text{N}\}_2\text{SnCl}_6$	0.53	0.90	[31]
$\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnBr}_6$	0.85	1.02	this work

* The accuracy of these parameters is approximately $\pm 0.02 \text{ mms}^{-1}$.

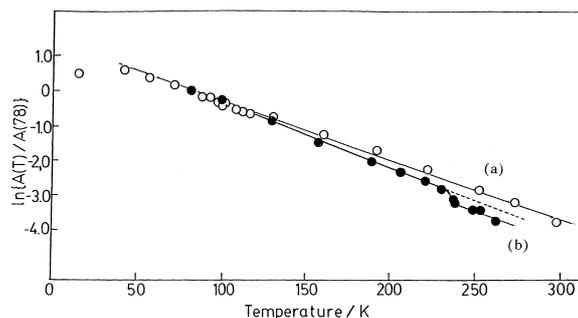


Fig. 1. Temperature dependences of the area intensity for (a) $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnCl}_6$ and (b) $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnBr}_6$.

where E_γ is the energy of the Mössbauer transition, θ the Debye temperature, M the molecular mass, and k the Boltzmann constant. The parameter α of the intermolecular force constant in solid was derived by using the relation

$$k\theta/h = \nu_{\text{max}} \propto (\alpha/M)^{1/2}, \quad (2)$$

where ν_{max} is the maximum lattice frequency. From combining (1) and (2), the following expression was obtained by Matsubara *et al.* [32]:

$$\alpha \propto \theta^2 M = (3E_\gamma^2/kc^2) \left[-d \ln f_a / dT \right]^{-1}, \quad (3)$$

where $3E_\gamma^2/kc^2$ is $2.13 \cdot 10^4$ for ^{119}Sn .

The values of $\theta^2 M$ can be estimated from the temperature dependence of the recoil-free fraction. The coefficient of the temperature term $d \ln f_a / dT$ can be replaced for a “thin” absorber by the observed temperature dependence of the area under the resonance line $d \ln \{A(T)/A(78)\} / dT$ (normalized to 78 K). The temperature dependences of the area for many kinds of tin compounds were observed, and it was found that there is a distribution of the parameters of the intermolecular force constant with respect to the state

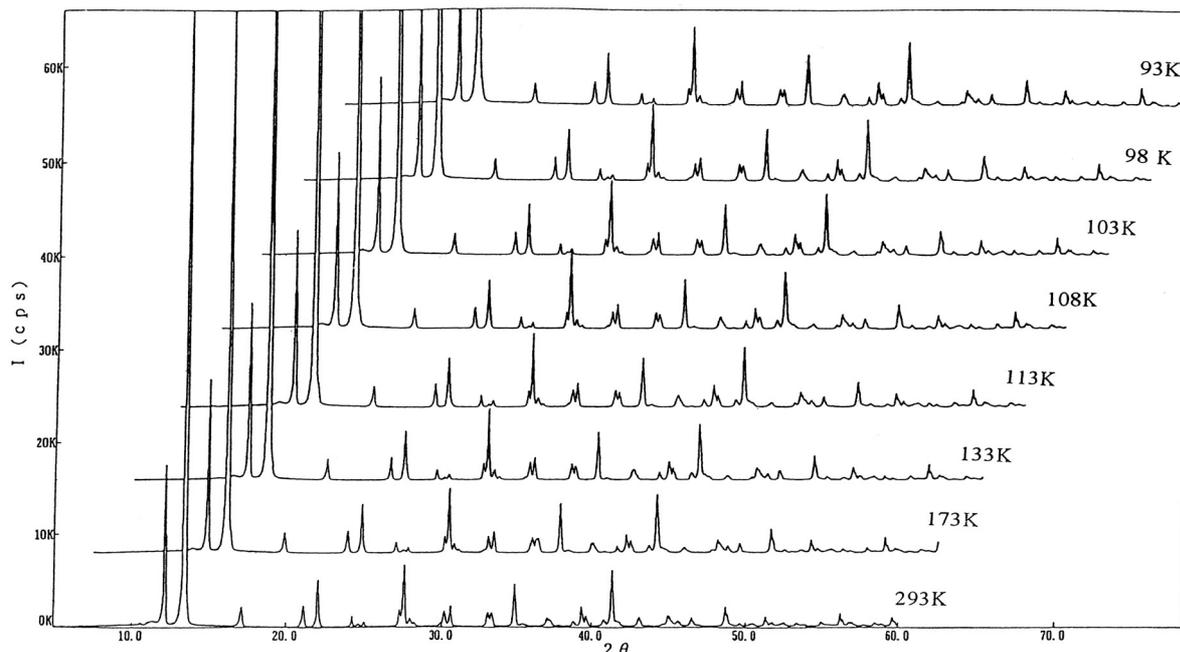


Fig. 2. X-ray powder diffraction patterns of $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnCl}_6$ at various temperatures.

of molecular association in solid state. The values of the parameter $\theta^2 M/10^6$ [$\text{amu}\cdot\text{K}^2$] (amu = atomic mass unit) are distributed around unity for monomer compound. Those of one- and two-dimensional polymer compounds are distributed around 1.3 and 1.7, respectively.

The temperature dependences of the area under the resonance line for $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnCl}_6$ and $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnBr}_6$ are shown in Figure 1. In Fig. 1 (a) the temperature dependence of the area intensity for $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnCl}_6$ is almost linear. From the coefficient of the slope, the value of $\theta^2 M/10^6$ [$\text{amu}\cdot\text{K}^2$] was estimated to be 1.3. This value is close to that for $(\text{CH}_3\text{NH}_3)_2\text{SnCl}_6$ (1.4) reported previously [31]. However these values are smaller than those of $(\text{NH}_4)_2\text{SnCl}_6$ (2.2) and $(\text{NH}_4)_2\text{SnBr}_6$ (2.3). This means that the tin atoms in $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnCl}_6$ is more mobile than those in $(\text{NH}_4)_2\text{SnCl}_6$ and $(\text{NH}_4)_2\text{SnBr}_6$. No anomaly in the temperature dependence of the area intensity of the ^{119}Sn -Mössbauer spectra is consistent with the results of NMR [20] and DTA [20] measurements of $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnCl}_6$, but disagrees with the results of ^{35}Cl NQR [11, 13] and IR [23] studies of the complex, suggesting a phase transition at about 100 K. Horiuchi *et al.* [11, 13] reported the existence of

a phase transition because an unusual temperature variation of frequencies, attributable to the motion of the cation, was observed. They also concluded that the disappearance of the ^{35}Cl NQR signals of the complex below room temperature is attributable to the motion of the cation as a whole. Knop *et al.* also reported the presence of a phase transition at 100 K by observing the splitting of the N-H stretching band of the NHD^+ group into a doublet below 100 K [23].

An anomaly in the temperature dependence of the Mössbauer spectral area for $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnBr}_6$ was found in the vicinity of the phase transition temperature reported by Dillon *et al.* [9]. They found a drastic phase change at (253 ± 1) K from the temperature dependence study of ^{89}Br NQR frequencies. On further cooling, the complex was settled into a low temperature phase at (242 ± 1) K. This temperature is very close to the temperature (~ 235 K) found in the discontinuity for the temperature dependence of the area in Fig. 1 (b). They also suggested the presence of a second phase transition between 135 and 77 K due to the split signal for the lower frequency resonance at 77 K. However, as can be seen from Fig. 1 (b), the temperature dependence of the area intensity does not show any anomaly at the corresponding temperatures.

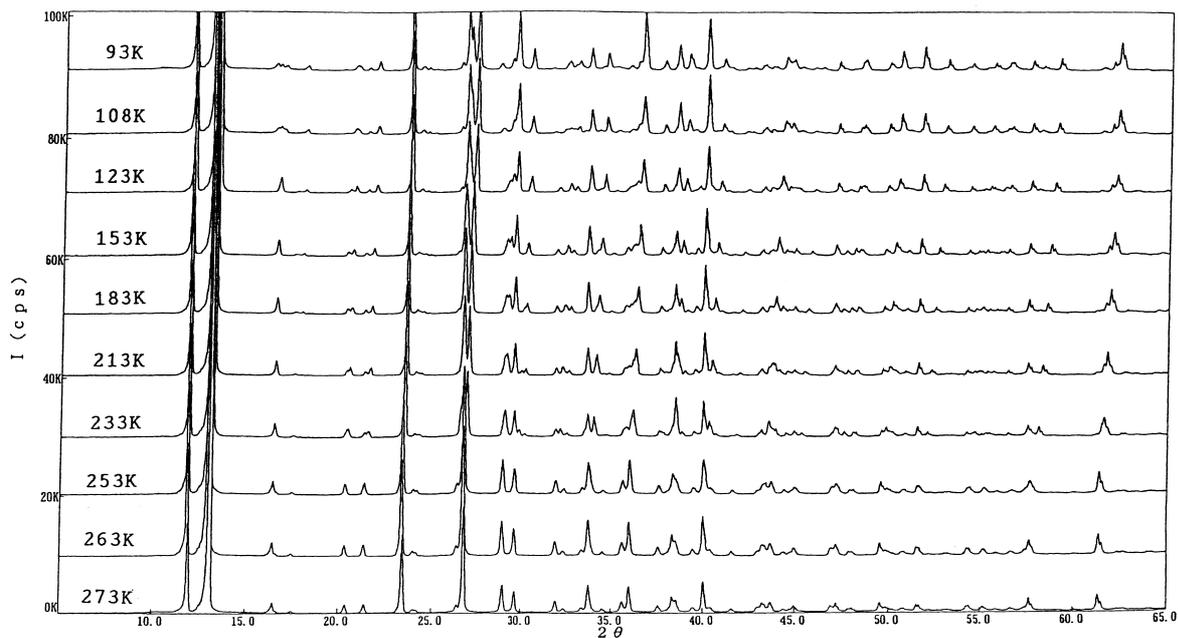


Fig. 3. X-ray powder diffraction patterns of $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnBr}_6$ at various temperatures.

Temperature dependences of X-ray powder patterns of $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnCl}_6$ and $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnBr}_6$ are shown in Figs. 2 and 3, respectively. As can be seen from Fig. 2 the patterns for $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnCl}_6$ did not change at temperatures between 78 and 293 K. However, the patterns for $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnBr}_6$ changed in two temperature ranges, 108 - 123 K and 233 - 253 K. The change in the powder patterns in the high temperature region consists with the results of the Mössbauer and ^{89}Br NQR studies. Although a change in the X-ray powder patterns at low temperature was not detected from the temperature dependence of the area intensity for $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnBr}_6$, a change in the ^{89}Br NQR was detected, as mentioned above. These phase transitions, attributed to the hydrogen bonding, are very sensitive to the ^{35}Cl and ^{89}Br NQR frequencies.

The temperature dependence of the area intensity for $\{(\text{CH}_3)_3\text{NH}\}_2\text{SnCl}_6$ is shown in Fig. 4 together with those for $(\text{CH}_3\text{NH}_3)_2\text{SnCl}_6$ and $\{(\text{CH}_3)_4\text{N}\}_2\text{SnCl}_6$ reported in [31]. The magnitude of the slope depends on the number of methyl groups. With increase of this number the temperature dependences became large. This can be attributed to the rigidity of tin atom in the SnCl_6^{2-} ion. Probably the increase in the number of methyl groups means a decrease

of hydrogen bonding, and thus the packing of the cations and anions becomes loose. The Mössbauer spectra of $\{(\text{CH}_3)_4\text{N}\}_2\text{SnCl}_6$ could not be observed at room temperature because of the weak recoil-free fraction of tin atoms in the complex. An anomaly in the temperature dependence of the area intensity for $\{(\text{CH}_3)_3\text{NH}\}_2\text{SnCl}_6$ was not found. This result agrees with that of DSC measurement and the results of ^1H NMR and ^{35}Cl NQR reported by Ikeda *et al.* [7]. They found two kinds of motions of the $(\text{CH}_3)_3\text{NH}^+$ ion, 1) the intraionic reorientations of the CH_3 groups and 2) the reorientation of the whole cation about its C_3 axis.

The presence of the phase transition for $(\text{CH}_3\text{NH}_3)_2\text{SnCl}_6$ was found by some physico-chemical techniques [2 - 4, 6, 17, 27, 29]. It is suggested that in $(\text{CH}_3\text{NH}_3)_2\text{SnCl}_6$ the reorientational motion of the CH_3NH_3^+ ion changes at the phase transition temperature from a weakly-hindered rotation at high temperature to a more restricted motion at lower temperature. However, the transition has not been observed in NH and DH stretching spectra [23]. This result is consistent with no anomaly in the temperature dependence of the area for $(\text{CH}_3\text{NH}_3)_2\text{SnCl}_6$. It means that the hindered rotational motion of CH_3NH_3^+ ions does not affect the tin site because the rotation is quite

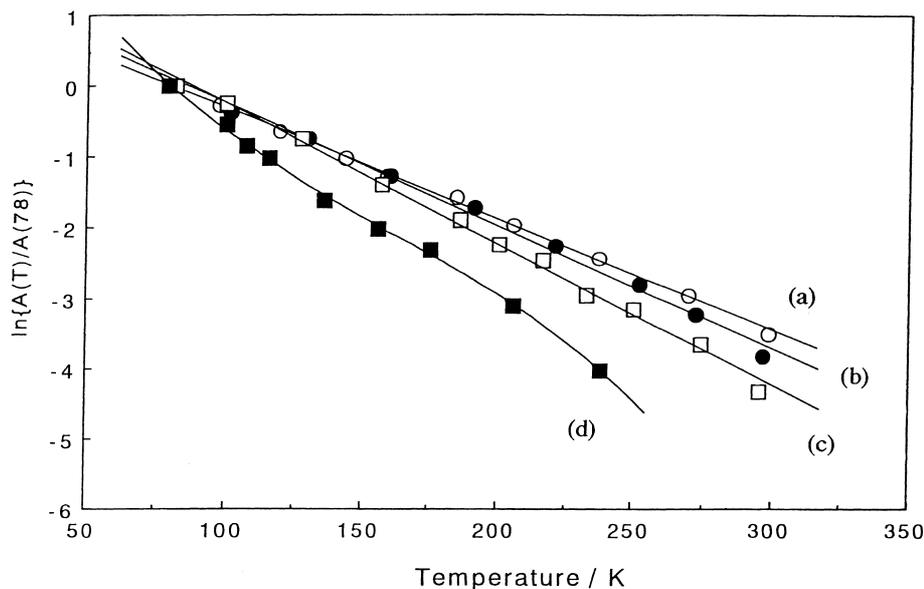


Fig. 4. Temperature dependences of the area intensity for (a) $(\text{CH}_3\text{NH}_3)_2\text{SnCl}_6$, (b) $\{(\text{CH}_3)_2\text{NH}_2\}_2\text{SnCl}_6$, (c) $\{(\text{CH}_3)_3\text{NH}\}_2\text{SnCl}_6$ and (d) $\{(\text{CH}_3)_4\text{N}\}_2\text{SnCl}_6$.

weak. The slope for $\{(\text{CH}_3)_4\text{N}\}_2\text{SnCl}_6$ is not linear. A phase transition at 149 K has been found by Raman spectroscopy [22], NMR [18] and NQR [8] studies. These results agree with the observed discontinuity of the temperature dependence of the spectral area near the phase transition point.

The phase transition is detectable by the temperature dependence of the recoil-free fraction of tin atoms, but its sensitivity is less than that of NQR or NMR. On the other hand, the temperature dependence provides us with useful information about the state of the molecular association in a solid.

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