

Nuclear Magnetic Resonance of a Layered Organic-Inorganic Hybrid System $(C_8H_{17}NH_3)_2SnCl_6$

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Three successive phase transitions in bis-*n*-octylammonium hexachlorostannate, $(n-C_8H_{17}NH_3)_2SnCl_6$, were studied by means of the 1H nuclear magnetic resonance linewidth and spin-lattice relaxation measurements. Unlike the compounds with longer hydrocarbon chains, the order-disorder and conformational nature were found to coexist in the phase transitions.

Key words : layered organic-inorganic hybrid system, nuclear magnetic resonance, phase transitions

1. Introduction

The hexahalometallates of the general formula A_2MX_6 ($A = K^+, Rb^+, Cs^+, NH_4^+$; $M = Pd, Pt, Sn, Pb, Re, Se, Te, Ir, Os, \dots$; $X = Cl, Br, I$) normally crystallize in the cubic antiferite structure with space group $Fm\bar{3}m(O_h^5)$ in the high temperature phase [1, 2]. They usually undergo structural phase transitions lowering their symmetry with decreasing temperature. If A is replaced by alkylammonium ion, $(R_nNH_{4-n})_2MX_6$ type compounds are formed and the dimensionality of the overall structure is reduced from 3D to 2D. Several examples have been reported for the Sn, Pt and Te metals [3-6].

The bis-*n*-alkylammonium hexachlorostannates $(n-C_nH_{2n+1}NH_3)_2SnCl_6$ (C_nSn for short) are layer compounds, where the $SnCl_6^{2-}$ octahedra do not form a 2D macro-anion but exist separately [2-4]. The NH_3 group of the alkylammonium ion links the three closest octahedra through equivalent hydrogen bonds of the $N-H \cdots Cl$ type, forming a layer. The distance between the ammonium groups or between the tin atoms in C_nSn is large (7.3~7.5 Å, depending on the chain length) for interdigitated interlayer alkylchains. The alkylammonium groups are statically disordered around the three fold-axes at $(1/3, 2/3, z)$ and $(2/3, 1/3, \bar{z})$, with the alkylchains alternately pointing upwards and downwards [4].

In contrast to the case of bis-*n*-alkylammonium tetrachlorometallates $(n-C_nH_{2n+1}NH_3)_2MCl_4$ with $M = Cd, Cu,$

and Mn (C_nM) [7-9], little information is available on the phase transition of C_nSn [2, 4-6]. In our previous 1H nuclear magnetic resonance (NMR) studies of $C_{10}Sn$ and $C_{18}Sn$, two phase transitions, i.e., order-disorder and conformational transitions, were clearly found and the molecular motions of the methyl and ammonium groups, and some defects were characterized in each phase [10-12]. Although both $C_{10}Sn$ and $C_{18}Sn$ show a very similar transition sequence, the transitional behaviors are quite different from each other. In the 1H NMR study of $C_{12}Sn$ [13], the typical transition sequence were also observed as in $C_{10}Sn$ and $C_{18}Sn$. The transitional behavior and the molecular motions in $C_{12}Sn$ were very similar to those in $C_{10}Sn$. However, the transition sequence in C_nSn with $n \leq 8$ are quite different from that in C_nSn with $n \geq 10$ and the nature of the transitions are not known for $4 \leq n \leq 8$ [5, 6]. Nonetheless, it can be expected that the molecular motions in C_8Sn are similar to those in $C_{10}Sn$, in spite of the distinct transition sequence. In this work, 1H NMR was employed for the study of phase transitions and molecular motions in C_8Sn .

2. Experiment

The C_8Sn sample used in this work was synthesized with much care to avoid impurities by the chemical reaction: $2(n-C_8H_{17}NH_3Cl) + SnCl_4 \cdot 5H_2O \rightarrow (n-C_8H_{17}NH_3)_2SnCl_6 + 5H_2O$. After filtering and two recrystallizations, white sugar-like crystals were finally obtained and then

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vacuum-dried and kept in dry condition for further works. The stoichiometry and the structure were checked by elemental analysis and x-ray diffraction (XRD). Differential scanning calorimetry (DSC) carried out between 123 K and 453 K shows three successive phase transitions in agreement with previous works [5, 6]. The linewidth and spin-lattice relaxation time measurements were made using 200-MHz ¹H NMR in the temperature range 200-380 K.

3. Results and Discussion

Figure 1 shows the ¹H NMR FWHM (full width at half maximum) linewidth of C8Sn as a function of temperature. According to previous works [5, 6] and our DSC measurements, C8Sn undergoes three successive phase transitions, at 272 K (*T*_{c1}), 344 K (*T*_{c2}), and 355 K (*T*_{c3}), respectively. However, the linewidth reflects only two of the transitions, at around *T*_{c1} and *T*_{c2}. In compounds of the CnSn type, a reduction of the linewidth is mainly caused by the diminution of the dipolar splitting [13]. Thus, the linear decrease of the linewidth, approaching *T*_{c1}, can be assigned to the decrease of the dipolar splitting. Since the linewidth around *T*_{c1} remains fairly large, a uniaxial reorientation of the rigid alkyl chains, conserving the average chain axis, appears to be responsible for the decrease of the linewidth. Then, the transition at *T*_{c1} may be ascribed to the order-disorder transition of the rigid alkyl chain.

Further decrease of the linewidth from *T*_{c1} to *T*_{c2} may arise from the disorder motion of the chain axis, which

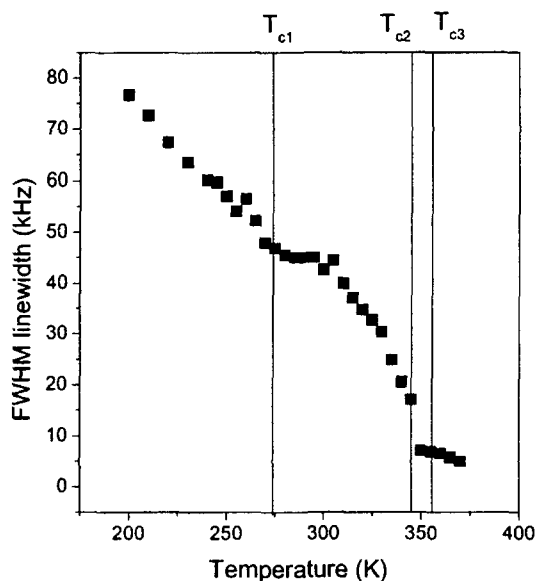


Fig. 1. ¹H NMR FWHM linewidth as a function of temperature.

can reduce the linewidth nearly to zero when the average chain axis is destroyed due to the activated chain defects such as the GG conformer. Then, the transition at 344 K is expected to be accompanied by the conformational transformation. After the average chain axis is destroyed, the hydrocarbon chains are virtually liquid-like in terms of the hydrocarbon chain motion. Since there is no average chain axis and thus no orientational order of the hydrocarbon chain, the chain appears isotropic as in a liquid and the linewidth should go below 1 kHz, as in C10Sn. Around *T*_{c2}, however, the linewidth in C8Sn remains to be about 5 kHz and continues to decrease through *T*_{c3}. Thus, the conformational change is believed to take place through a wide temperature range.

The spin-lattice relaxation of C8Sn showed a single-exponential pattern over the whole temperature range except around *T*_{c3}. The spin-lattice relaxation rate measurement in Fig. 2 shows a discontinuity at *T*_{c3}, characteristic of a first-order phase transition. While *T*_{c1} is assigned to represent the order-disorder transition temperature in this system, no anomaly is apparent in Fig. 2 as in the case of C10Sn and C12Sn [10, 13]. In these compounds, a discontinuity in the spin-lattice relaxation time usually accompany the conformational transition. Thus, the discontinuity around *T*_{c3} is believed to be due to a partial chain melting originating from the conformational transformation. As discussed in Fig. 1, the conformational transition appears to take place through a wide temper-

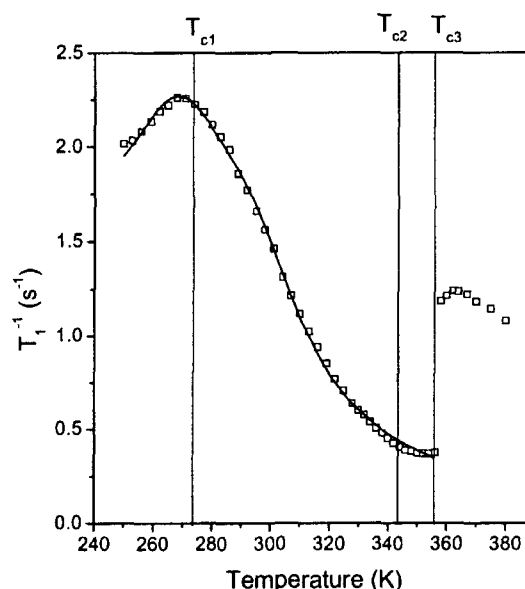


Fig. 2. The ¹H NMR spin-lattice relaxation rate vs temperature taken at 200 MHz. The solid line is fitted to the intramolecular dipole-dipole spin-lattice relaxation by four types of molecular motions according to Eqs. (1) and (2).

ature range, and the partial chain melting appears to take place at T_{c3} .

The spin-lattice relaxation rate data below T_{c3} were well fitted to the intramolecular dipole-dipole interactions modulated by various types of molecular motions [14];

$$T_1^{-1} = \sum_i \frac{2}{3} \gamma^2 M_{2i} \left[\frac{\tau_{ci}}{1 + (\omega\tau_{ci})^2} + \frac{4\tau_{ci}}{1 + (2\omega\tau_{ci})^2} \right],$$

$$i = 1, 2, \dots, n. \quad (1)$$

$$\tau_c = \tau_0 e^{E/RT}, \quad (2)$$

where γ is the proton gyromagnetic ratio, M_2 the second moment, ω the Larmor frequency and E is the activation energy. Four different types of the molecular motions ($n=4$) as in the case of C10Sn were introduced to fit to the experimental data and the results of the fitting according to Eqs. (1) and (2) are shown in Fig. 2 as a solid line. Since the molecular motions in C8Sn are expected to be similar to those in C10Sn, the second moments of the CH₃ and NH₃ groups acquired from C10Sn [10], were assumed for C8Sn.

From analysis of the spin-lattice relaxation data, the activation energies of the CH₃ group were found 8, 10, and 11 kJ/mol in C8Sn, C10Sn, and C12Sn, respectively, which values are very similar. On the other hand, the activation energies of the NH₃ group are 14(±4), 40, and 55 kJ/mol in C8Sn, C10Sn, and C12Sn, respectively. Below T_{c1} , an "unknown defect" motion dominates the spin-lattice relaxation as in C10Sn, where the second moment of the defect is about 1.7 G² and the activation energy is about 46 kJ/mol. Near T_{c3} , another type of defect motion, presumably a chain-end defect, is dominant, whose second moment and activation energy are about 1.2 G² and 51 kJ/mol, respectively.

As discussed in our previous work [13], the activation energy of the ammonium group strongly depends on the chain length and appears to be related to the order-disorder transition of the hydrocarbon chain in the C_nSn systems. The strong chain length dependence of the NH₃ group is confirmed also in C8Sn. However, the presumably order-disorder transition temperatures are very close in C8Sn and C10Sn, in spite of the large difference between the activation energies of the NH₃ groups. Then, the transition in C8Sn at T_{c1} may not be simply assigned to an order-disorder transition.

Figure 3 shows the derivative of the spin-lattice relaxation time with respect to temperature. It shows an anomaly around T_{c2} , where the conformational transition is believed to start, but the spin-lattice relaxation time itself does not show it. In C_nSn systems with $n \geq 10$, the differential anomalies were also observed, around the

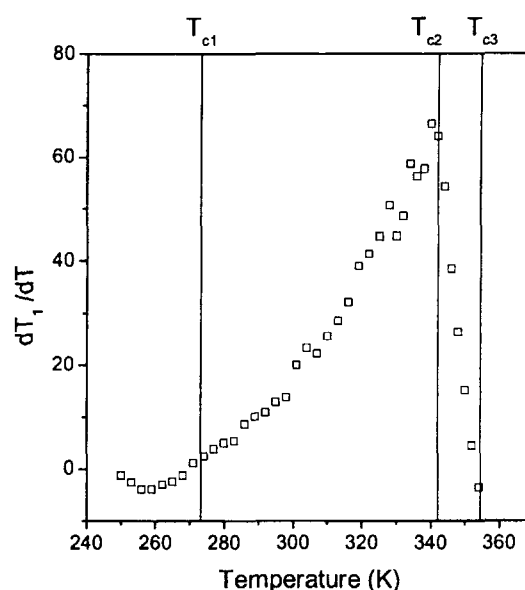


Fig. 3. Differential of the spin-lattice relaxation time with respect to temperature.

order-disorder transition temperature, which is not reflected in the spin-lattice relaxation time. In analogy to C10Sn and C12Sn, it can then be assumed that the transition at T_{c2} bears an order-disorder nature as well as a conformational nature. It then follows that the characteristics of the transitions in C8Sn is fairly distinct from those in C10Sn and C12Sn. In other words, both the order-disorder and conformational natures are mixed in the phase transitions of C8Sn.

In summary, three phase transitions in C₈H₁₇(NH₃)₂SnCl₆ (C8Sn) were found and characterized by means of ¹H NMR. As a result, it was found that unlike in the C_nSn compounds with longer hydrocarbon chains, the phase transitions in the C8Sn system have mixed nature of the hydrocarbon chain molecular motions, order-disorder and conformational dynamics.

Acknowledgments

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