^{13}C CP/MAS NMR Study of Motion and Local Structure of Phenethylammonium Ion in $[C_6H_5CH_2CH_2NH_3]_2PbX_4$ (X = Cl, Br, I)

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Ionic motion and local structure of phenethylammonium ion ($C_6H_5CH_2CH_2NH_3^+$) in a series of phenethylammonium lead(II) halides, $[C_6H_5CH_2CH_2NH_3]_2PbX_4$ (X = Cl, Br, I) were studied by means of ^{13}C cross polarization/magic angle sample spinning (CP/MAS) NMR technique. Among the three salts, remarkable differences in the spectra were observed in the signals corresponding to the phenyl carbons. The peaks from C2, C3, C5, and C6 in the phenyl group were split into three for the chloride and into two for the bromide, although in the iodide those were observed as a single peak. Coalescence of those peaks, as well as line broadening were observed on heating. This indicated that peak split brings about disorder of the orientation in the phenyl group around the C1-C4 axis, suggesting to have three and two orientations for the chloride and the bromide, respectively. Above room temperature the phenyl group undergoes chemical exchange among these orientations, and at higher temperature, reorientation with a large amplitude takes place around its axis. The apparent activation energies of the reorientation of the phenyl group for the chloride and bromide were estimated from the temperature dependence of the linewidth of the resonance peaks to be about 24 kJ mol^{-1}, 25 kJ mol^{-1}, respectively, which is similar to in the iodide (25.0 kJ mol^{-1}). Ab initio molecular orbital energy calculation was carried out to evaluate the potential barrier of the internal rotation of the phenyl group in a free phenethylammonium ion. The intramolecular interaction was evaluated to be 13.9 kJ mol^{-1} from the calculation, and the intermolecular interaction results to be 10 kJ mol^{-1}.

Key words: ^{13}C CP/MAS NMR; Layered compound; Disorder; Reorientation; Activation energy.

Introduction

Phenethylammonium lead(II) halides, $[C_6H_5CH_2CH_2NH_3]_2PbX_4$ (X = Cl, Br, I), form a layered perovskite-type structure [1]. They have attracted much interest, being nano-composites made up of organic and inorganic parts. Especially their optical and electronic properties, originating from their multi-quantum well structure, have extensively been investigated in these [2, 3] and analogous compounds [4 - 10]. Their organic layer can be regarded as a two-dimensional crystal. In the two-dimensionally restricted space, the dynamics of the phenethylammonium ion (Fig. 1) is closely related to phase transition and glass formation [11, 12]. However, the dynamics of the phenethylammonium ion has not yet been studied in detail.

In [13] we have studied the motion of the phenethylammonium ion in $[C_6H_5CH_2CH_2NH_3]_2[CH_3NH_3]_{n-1}Pb_nI_{3n+1}$ ($n = 1, 2$), and in [14] in $[C_6H_5CH_2CH_2NH_3]_2PbX_4$ (X = Cl, Br, I). In [13], ^{13}C CP/MAS NMR measurement revealed that the phenyl group in the phenethylammonium ion undergoes a 180° flip motion around the two-fold(C1-C4) axis and that the potential barrier for the reorientation of the phenyl group depends little on the stacking number, n, of the inorganic layers. In [14], the anomalous lattice extension along the stacking direction of the inorganic layers was found by X-ray powder diffraction measurements. The interlayer distance increases in the order of I < Br < Cl, in contrast with the decrease in the ionic radius in this order. Furthermore, ^1H T_1 measurements gave us one of the explanations about the

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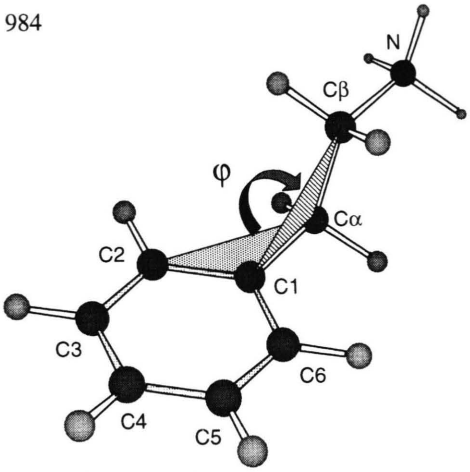

Fig. 1. Structure of phenethylammonium ion.

anomalous lattice extension. We found that the NH_3 moiety and the CH_2CH_2 alkyl chain become mobile in the order $X = I < Br < Cl$ for the series of the $[C_6H_5CH_2CH_2NH_3]_2PbX_4$. That is, the increase in the free volume around the organic cations results in a lattice extension along the stacking direction of the layers.

In the present work, in order to study the influence of the halogen ion of PbX_4^{2-} on the local structure and the dynamics of the phenyl group, we have measured the ^{13}C CP/MAS NMR spectra of phenethylammonium ion in $[C_6H_5CH_2CH_2NH_3]_2PbX_4$ (X = Cl, Br, I). Examining the temperature dependence of the spectra, we discuss the local structure and the dynamics of the phenyl group. Furthermore, we have carried out ab initio molecular orbital energy calculation to evaluate the potential barrier of the rotational motion of the phenyl group.

Experimental

$[C_6H_5CH_2CH_2NH_3]_2PbX_4$ were synthesized as described in [13, 14]. The powder samples were dried *in vacuo* at *ca.* 60°C and packed into the sample rotor (ø 4 mm × 18 mm) under N_2 atmosphere.

^{13}C CP/MAS NMR spectra were measured by using a Bruker MSL-400 spectrometer operating at a Larmor frequency (ν_0) of 100.613 MHz for ^{13}C. A sample spinning rate of *ca.* 6 kHz was employed by use of a ZrO_2 sample rotor. The contact time between the ^{1}H and ^{13}C spin systems to enhance the ^{13}C magnetization was between 1 ms and 3 ms. The FID signals of ^{13}C were recorded under ^{1}H irradiation with a decoupling field (ν_1) of 58 kHz. The repetition time was between 10 s and 100 s, depending on ^{1}H T_1, and the signals were accumulated between 32 and 1024 times. The spectra were obtained at 295 to 378 K. The temperature was controlled within ±2 K and monitored with a Bruker VT-1000 unit. Methyl carbon (17.17 ppm from TMS) in hexamethylbenzene was used as the external standard of the chemical shift of carbon-13 [15].

The structure of a free phenethylammonium ion was optimized by using a GAUSSIAN94 molecular orbital program package [16] with 6-31G* base set, and the total energy of the cation was evaluated with the optimized structure. The potential energy of the internal rotation of the phenyl group was defined as the energy difference between the most stable conformation and the other conformation creating as a function of the dihedral angle, φ, being from C2, C1 Cα and Cβ as shown in Figure 1.

Results and Discussion

Figure 2 shows ^{13}C CP/MAS NMR spectra for $[C_6H_5CH_2CH_2NH_3]_2PbX_4$ at room temperature. According to the assignment in our previous work [13], the observed resonance peaks are assigned to the carbons in the phenethylammonium ion as listed in Table 1. The chemical shift values of the aliphatic carbons (Cα and Cβ) a little changed among three substances. Among these substances, the spectra show the most remarkable difference in the ^{13}C chemical shift range from 129 ppm to 132 ppm, in which the resonance peaks from C2, C3, C5, and C6 in the phenyl group are observed. The iodide gives rise to a single peak and/or the structures at 130.7 ppm, whereas the corresponding peak was split into three for the chloride and into two for the bromide. By contrast, each of C1 and C4 carbon, which is lying on the two-fold axis of the phenyl group gives rise to a single peak without any structure in all the three substances.

The splitting of the resonance peak from the phenyl carbons means that the local structure of the phenyl group in the chloride and the bromide is different

Table 1. ^{13}C chemical shift for phenethylammonium ion in $[C_6H_5CH_2CH_2NH_3]_2PbX_4$ determined from ^{13}C CP/MAS NMR spectra.

	^{13}C chemical shift in ppm from TMS						
Halogen	C1	C2, C3, C5, C6			C4	Cα	Cβ
Cl	137.8	131.7,	130.1,	129.1	127.1	34.9	44.1
Br	137.9	131.1,	130.0		127.3	34.5	44.2
I	137.6	130.7			127.7	34.1	44.5

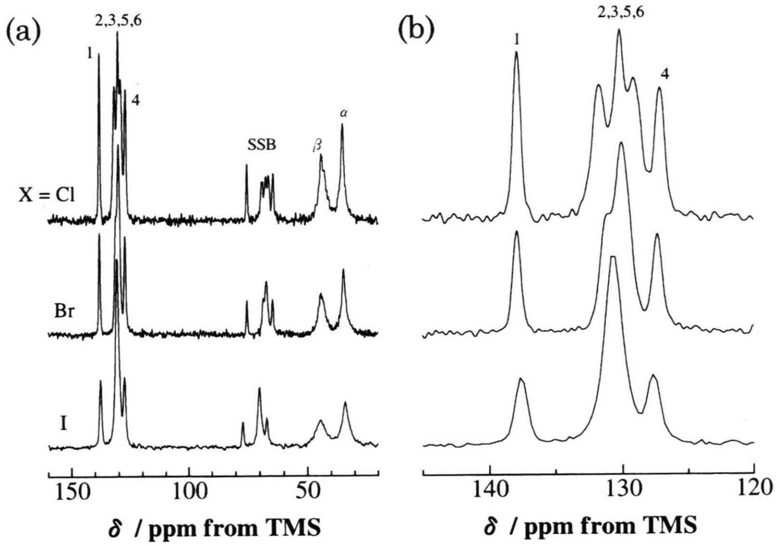

Fig. 2. ^{13}C CP/MAS NMR spectra for $[C_6H_5CH_2CH_2NH_3]_2PbX_4$ (X = Cl, Br, I) at room temperature; (a) full spectra and (b) the enlarged spectra covering the frequency region of the aromatic carbons.

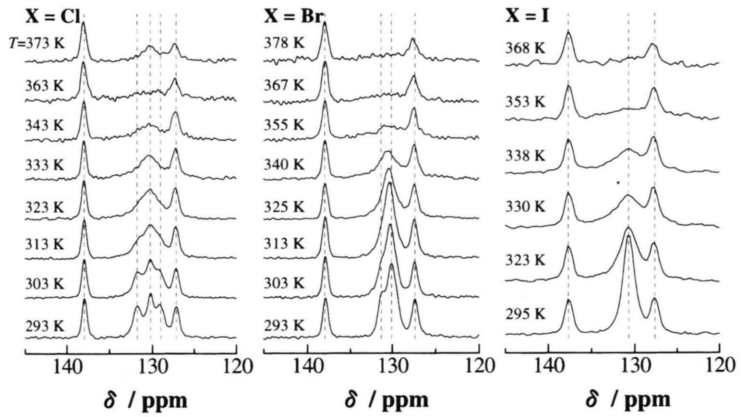

Fig. 3. Temperature dependence of resonance peaks from the phenyl carbons in $[C_6H_5CH_2CH_2NH_3]_2PbX_4$.

from that in the iodide. This is a very useful information to discuss the local structure of the phenethylammonium ion at the interface between the inorganic layers. The observed separation of the split peaks is between 1.0 ppm and 1.6 ppm. There are two possibilities to bring about the split; one is the difference in the chemical and/or magnetic environments of C2(C6) and C3(C5), and the other is the difference in the crystallographic environments of C2(C6) and C3(C5), coming from the disorder in the orientation of the phenyl group around the axis connecting C1 and C4 (hereafter, we abbreviate this axis as '1-4 axis'). In the former case, however, the chemical shift difference between C2(C6) and C3(C5) is expected to be less than 0.5 ppm even in solution [17]. Therefore the latter case is more probably the origin of the peak split. These two possibilities can clearly be confirmed by examining the temperature dependence of the spectra. That is, as the temperature varies, the split will remain constant in the former case, whereas it may disappear in the latter case by the averaging of those peaks due to the chemical exchange between the orientations.

Figure 3 shows the temperature dependence of ^{13}C CP/MAS NMR spectra for each substance. Drastic changes are found in the resonance peaks corresponding to C2, C3, C5, and C6, although the peaks of C1 and C4 are independent of the temperature.

In the chloride and the bromide, the split peaks coalesce on heating, and a sucessive line broadening is observed. In the bromide, two peaks approach each other and coalesce at the averaged value of the chemical shifts for each peak on heating from 293 to 313 K. The peak shows further broadening above the 313 K

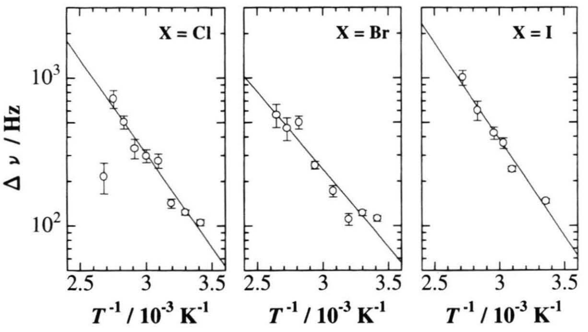

Fig. 4. Temperature dependence of the line width ($\Delta\nu$) for C2, C3, C5 and C6, the logarithm of which is plotted against the reciprocal temperature ($1/T$).

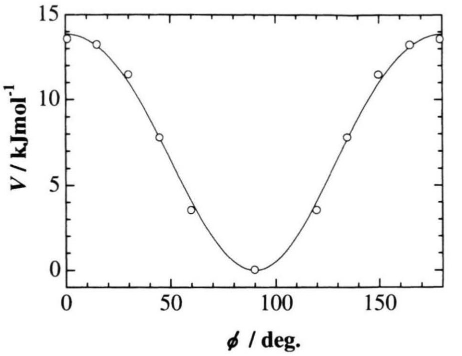

Fig. 5. Calculated potential barrier for the internal rotation of the phenyl group in a free phenethylammonium ion. The potential barrier of each conformation is determined by referring to the most stable conformation with the dihedral angle of 90°. The solid line is the result of the curve fitting by a potential function with the two-fold symmetry (see text).

and assumes the maximum line width at 378 K. In the chloride, the three peaks merge at about 323 K, and the coalesced peak broadens on further heating. The maximum broadening of the peak takes place at 363 K, and the peak becomes narrow again. This finding suggests that the split observed at room temperature is caused by the crystallographic difference in the environment of the phenyl group in the phenethylammonium ion. It is concluded that there are two and three kinds of orientations of the phenyl group in the bromide and chloride, respectively, and that the phenyl group undergoes chemical exchange between the possible orientations around the 1-4 axis with similar frequency of the ^{1}H decoupling rf strength (*ca.* 60 kHz).

In order to discuss the dynamic processes of the phenyl group, the activation energy (E_a) was evaluated from analysis of the NMR line width. The full width at the half maximum of the resonance peak, $\Delta\nu$, at each temperature is inferred by a least square's curve fitting using Lorentzian shape functions. In the chloride and the bromide the line broadening is brought about by the chemical exchange processes, and also by the loss of the efficiency of the ^{1}H decoupling due to the molecular motion. In the chemical exchange process the maximum broadening of the line width occurs after the coalescence of the peaks is just completed, and the faster the exchange rate, the narrower the line. On the other hand, the loss of the efficiency of the ^{1}H decoupling due to the molecular motion brings about the maximum broadening when the frequency of the molecular motion approaches the decoupling frequency. The experimental results show that the maximum broadening occurs above 360 K, a tempereature at which the coalescence of the peaks have already been finished. This suggests that the loss of the efficiency of the ^{1}H decoupling due to the molecular motion dominates the temperature dependence of the line broadening after the coalescence of the peaks. In the coalescence process, however, both mechanism will contribute to the line broadening. In the present work it is not possible attribute with certainty the broadening mechanism of the chemical exchange because of the small separation among the peaks and the lack of spectra at the lower temperature, at which the molecular motion is frozen. So, in the temperature range from 293 K to 313 K the mean value of the line width for the split peaks was used to discuss the temperature dependence of the line width quantitatively. Figure 4 shows $\Delta\nu$ vs. $1/T$ plots for the three substances, of which the slope gives the E_a value of the motion of the phenyl group as described in [18]. These values of E_a are 24 kJ mol^{-1} and 25 kJ mol^{-1} for the chloride and the bromide, respectively, both of which are comparable to that of the iodide (25.0 kJ mol^{-1}). This means that the potential barrier for the reorientation of the phenyl group around the 1-4 axis is similar among three compounds.

The ab initio MO calculation yields the contribution of the intramolecular interaction to the potential barrier of the phenyl rotation, extracting the intermolecular interaction feeling the phenyl group in the interface between the inorganic layers. Figure 5 shows the calculated potential barrier for the internal rotation of the phenyl group in a free phenethylammonium ion.

The lowest energy of the phenethylammonium ion was given in a conformation with φ = 90°. In order to evaluate the potential barrier quantitatively, the calculated value in Fig. 5 was fitted by a potential function assuming the two-fold symmetry as

$$V = \frac{V_2}{2}[1 - \cos(\varphi)] + \frac{V_4}{2}[1 - \cos(2\varphi)]$$

The potential barrier of the internal rotation of the phenyl group in a free phenethylammonium ion was evaluated to be $V_2 = 13.9$ kJ mol^{-1} and $V_2 = 0.8$ kJ mol^{-1}. The V_2 value reflects approximately the maximum energy difference in the potential function with the two-fold symmetry, which is determined by only the intramolecular interaction. Comparing this value with the experimental values of E_a for the phenyl reorientation, the intermolecular interaction contributing to E_a will be evaluated to be 10 kJ mol^{-1} for the three compounds. This value is relatively small, suggesting that the phenyl groups interact weakly with each other in the interface between the inorganic layers, and that the free volume in the surrounding of the phenyl group is relatively large.

Further information about the local structure around the phenyl group and the mode of the motion of the phenyl group can be obtained by the second moment analysis of the line width at the maximum broadening. The line width of the maximum broadening is characterized by the ^{1}H-^{13}C dipolar interaction which is averaged out by some motion of the phenyl group. The line width at the maximum broadening ($\Delta\nu_{\max}$) is smaller in both the chloride (*ca.* 700 Hz) and the bromide (*ca.* 550 Hz) than in the iodide (*ca.* 1000 Hz). In [13] we used the second moment analysis to identify the mode of the motion in the iodide, and the $\Delta\nu_{\max}$ value is interpreted very well by the reorientation of the phenyl group with a 180° flip angle. The second moment due to the ^{1}H-^{13}C dipolar interaction is reduced by the factor F, which is determined by the mode of the motion for the phenyl group. The reduced part of the second moment, which is averaged by the motion of the phenyl group, is represented by $\Delta M_2 = (1 - F)M_2$ (rigid), in which M_2 (rigid) is the second moment in the rigid lattice and is calculated to be 4.5×10^9rad^{2}s^{-2} for the phenyl group. The ΔM_2 value dominates the line width at the maximum broadening. When the reorientation of the phenyl group with 180° flip angle takes place, the theoretical value of ΔM_2 is calculated to be 2.5×10^9rad^{2}s^{-2}. On the other hand, the experimental values of ΔM_2 are evaluated from the line widths of the maximum broadening by use of the relation $\Delta M_2 \equiv 4\pi^2 \Delta\nu_{\max}\nu_1$ [18], yielding 1.6×10^9rad^{2}s^{-2} and 1.3×0^9rad^{2}s^{-2} for the chloride and bromide, respectively. These values are much smaller than the theoretically calculated ones. It is considered that these discrepancies in ΔM_2 are caused by the pre-reduction of the dipolar interaction due to the chemical exchange processes between the disordered orientations as described above. Thus, the differences in ΔM_2 between the experimental and the theoretical ones, which are 0.9×10^9rad^{2}s^{-2} for the chloride and 1.2×10^9rad^{2}s^{-2} for the bromide, are regarded as the ΔM_2 reduced by the chemical exchange processes. Using the above values, we can estimate the mean angles made by the phenyl groups in each of the disordered orientations. For simplification, we assumed the two-site jump model, and the reduction factor F is provided from the expression of ΔM_2 derived by Andrew and Latanowicz [19] as

$$F = 1 - \frac{3}{4}\left[\sin^2 2\theta \sin^2\left(\frac{\Delta\varphi}{2}\right) + \sin^4\theta \sin^2 \Delta\varphi\right],$$

where θ is the angle between the C-H vectors and $\Delta\varphi$ the flip angle of the C-H vector around the 1-4 axis. In the phenyl group, the typical value of θ is 60° when we assume rotation around the 1-4 axis. This relation leads to a mean jump angle of the chemical exchange of the phenyl group of about 35° for the chloride and about 42° for the bromide. This result suggests that the phenyl group in the bromide has two possible orientations around the 1-4 axis with flip angle of 42°, and that in the chloride has three possible orientations within the flip angle of 35° around the 1-4 axis. In the temperature range from 293 to 313 K the phenyl group undergoes chemical exchange among these orientations within the range of the flip angle $\Delta\varphi$ of each compound. Above 313 K, reorientation of the phenyl group with larger flip angle such as $180 - \Delta\varphi$ may take place.

In the present work, the following new aspects are found: (1) Disorder in the phenyl group is existing in the chloride and the bromide. (2) The apparent activation energy of the motion of the phenyl group is similar among the three compounds. (3) The mean intramolecular interaction dominating the internal rotation of the phenyl group is evaluated to be 15kJmol^{-1} by ab initio MO calculation, and the intermolecular interaction is found to be about 10 kJ mol^{-1}. (4) Chemical exchange processes take place between the disordered orientations in the chloride and bromide.

These findings provide a new picture of the local structure: the orientation of the phenyl group in the phenethylammonium ion. the subsitution of the halogen atom in the inorganic layer, PbX_4^{2-}, brings about an anomalous elongation of the *a*-axis for the $[C_6H_5CH_2CH_2NH_3]_2PbX_4$ crystal as the ionic radius of the halogen decreases, whereas for the *b*- and the *c*-axis an extension was observed in the order Cl < Br < I (see Table 1 in [14]). Thus, the distance between neighboring phenyl groups in the organic layer, which is proportional to both the *b*- and *c*-axis, will be enlarged in the order Cl < Br < I. This enlargement will mainly affect the intermolecular interaction for the rotation of the phenyl group, expecting that the activation energy of the phenyl rotation becomes large in this order. However, the observed activation energy and the estimated intermolecular interaction for the phenyl reorientation are similar in the three compounds. It is considered that the increases in the intermolecular distance do not effectively decrease the repulsion between the neighboring phenyl groups. Thus, the variation in the intermolecular distance will bring about a change of the delicately balanced intermolecular interaction. This aspect reflects the molecular packing in the organic layers and results in the disordered orientations of the phenyl group in the bromide and the chloride.

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