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Phase transition of pyridinium tetrachloroiodate(III), $PyHICl_4$, studied by a single crystal X-ray analysis and dielectric and heat capacity measurements

Tetsuo Asaji [a,*], Kazuo Eda [b], Hiroki Fujimori [a], Toshinobu Adachi [a],
Takayoshi Shibusawa [a], Masaharu Oguni [c]

[a] Department of Chemistry, College of Humanities and Sciences, Nihon University, Sakurajosui, Setagaya-ku, Tokyo 156-8550, Japan
[b] Department of Chemistry, Faculty of Science, Kobe University, Nada-ku, Kobe 657-8501, Japan
[c] Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8551, Japan

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Abstract

Change of a local environment of a polar pyridinium ion, which is associated with the phase transition of crystalline pyridinium tetrachloroiodate(III) at $T_c = 217$ K, was investigated by a single crystal X-ray analysis and dielectric and heat capacity measurements. The site symmetry $2/m$ of the ion at $T > T_c$ indicates an orientational disorder in the high-temperature phase (HTP). The energy difference ΔE between the stable and meta-stable orientations of the pyridinium ion at the $2/m$ site was estimated to be $\Delta E/R \leqslant 560$ K at 280 K in the HTP. Below the T_c, an antiferroelectric ordering of the ions was revealed.

Keywords: Phase transition; Crystal structure; Heat capacity; NQR

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1. Introduction

When reorientational motion of pyridinium ion in the crystal is discussed it might be assumed that pyridinium ion has a pseudohexad C_6' axis [1–3]. However, the order–disorder process of pyridinium ion in the solid state is not so simple enough to be explained by the 6-fold disorder in the orientation. In the low-symmetry crystalline phase, site symmetry of pyridinium ion should be taken into account for the potential wells in order to explain reorientational motion of the pyridinium ions [4,5]. Besides, our calorimetric study of pyridinium tetrabromoaurate(III) revealed the temperature dependence of the energy difference, which characterizes the nonequivalence of the potential wells, through a cooperative effect of pyridinium orientation [6].

For the better understanding of the reorientational motion and the ordering process of pyridinium ion in the crystalline state, it is worth to extend study to the other pyridinium salts. It is known from ^{35}Cl NQR and DTA/DSC measurements that pyridinium tetrachloroiodate(III), $PyHICl_4$, undergoes a phase transition at $T_c = 217$ K [7,8]. The single NQR line observed in high-temperature phase (HTP) splits into a doublet in low-temperature phase (LTP). In our previous study [8] the following points were recognized. (i) The temperature dependence of the NQR frequencies and a very broad thermal anomaly observed in DTA suggest a second-order nature of the phase transition. (ii) The temperature dependence of the NQR spin–lattice relaxation time associated with a critical relaxation around T_c suggests the phase transition is of an order–disorder type with pyridinium ions. (iii) The large splitting of the NQR frequency in LTP suggests a strong deformation of ICl_4^- anion as well, which is coupled with the order–disorder of pyridinium ions.

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[*] Corresponding author. Tel./fax: +81 3 5317 9739.
E-mail address: asaji@chs.nihon-u.ac.jp (T. Asaji).

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In the present study, we have determined crystal structure of $PyHICl_4$ both in HTP and LTP, and temperature dependencies of heat capacity, C_p, and dielectric constant, ε', attempting to get more detailed information about the ordering process of the pyridinium ion in $PyHICl_4$.

2. Experimental

2.1. Preparation and identification

$PyHICl_4$ was prepared according to the method described in the literature [9] and identified by elemental analysis at Center for Organic Elemental Microanalysis, Kyoto University. Anal. Calcd. for $PyHICl_4$: C, 17.2; H, 1.7; N, 4.0; I, 36.4; Cl, 40.7%. Found: C, 17.2; H, 1.7; N, 4.1; I, 36.2; Cl, 40.4%.

2.2. Crystal structure determination

Single crystal X-ray measurements of HTP as well as LTP were carried out at 233 and 113 K, respectively, using a SMART 1000/CCD diffractometer (Bruker) with graphite-monochromated Mo Kα radiation ($2\theta < 55°$). The crystal structure was solved by direct method and refined by full-matrix least-squares calculations based on F_0^2 with empirical absorption corrections by using a program package SHELXL [10]. The crystal data and the details of the experiments and refinements are given in Table 1.

2.3. Dielectric measurements

The dielectric measurements were carried out for a pressed polycrystalline pellet (ca. 0.7 mm thick and 10 mm in diameter) sandwiched by graphite-pellet electrodes (ca. 0.5 mm thick and 10 mm in diameter). To ensure electric contact between sample-pellet and graphite-pellet, a colloidal carbon (PELCO Conductive Graphite) was used as adhesive. Silver-paste (Dotite, Fujikura Kasei Co., Ltd) was used to connect electric lead wire on the graphite-pellet electrode and to mount the sample capacitor on a copper block as a counterelectrode. For the measurements in the frequency range of 0.11–10 kHz, a bridge type instrument Ando Denki TR-1C was employed. Temperature was determined by use of a copper vs. constantan thermocouple and a germanium resistance thermometer N2G from Scientific Instruments, respectively, above and below 77 K.

2.4. Heat capacity measurements

Heat capacity was measured in the temperature range between 18 and 340 K by use of an adiabatic calorimeter employing 2.383 g (6.832 mmol) of $PyHICl_4$. A platinum resistance thermometer (Minco Products S1059, USA), which had a nominal resistance of 100 Ω at 273.16 K, was used after the temperature scale was transferred from the other thermometer calibrated on the ITS-90. The imprecision and inaccuracy of the heat capacity measurements with apparatus were estimated previously to be less than 0.04% and 0.4%, respectively [11].

3. Results and discussion

3.1. Crystal structures of HTP and LTP

The positional parameters of the atoms in HTP and LTP, and the geometric parameters in both the phases are listed in Tables 2–4, respectively. The crystal structures of the HTP and LTP are shown in Figs. 1 and 2, respectively. In Fig. 2, the convenient axes a' ($=a$), b' ($=-b$), c' ($=-a-c$) were chosen as to be easy to compare the structural change through the transition. The site symmetry of the pyridinium ion is $2/m$ in the HTP and there must exist an orientational disorder. In the LTP the ions are ordered in their orientation. The one-dimensional hydrogen-bond network $\cdots PyH \cdots ICl_4 \cdots PyH \cdots ICl_4 \cdots$ is formed in the crystal. Fig. 3 shows geometry of the hydrogen-bonded chain and stacking scheme of the adjacent chains in the plane parallel to the $a'c'$-plane for LTP. Since the distance $H1 \cdots Cl2$ (2.615 Å) $< W_H + W_{Cl}$ while $H4 \cdots Cl1$ (2.964 Å) $> W_H + W_{Cl}$ as compared with the sum of van der Waals radii of hydrogen ($W_H = 1.20$ Å) and chlorine ($W_{Cl} = 1.75$ Å) atoms [12], the presence of a hydrogen bond is expected between Cl2 and the NH hydrogen (H1) atoms. The interaction between the CH hydrogen (H4) and Cl1 atoms seems to be weak although the chain structure can be recognized. The nearest inter-chain distance is ca. 3.3 Å in the crystallographic mirror plane (parallel to the $a'c'$-plane) and ca. 6.2 Å between the chains on the adjacent mirror plane along the b'-axis. Therefore, a two-dimensional array of the hydrogen-bonded chains can be recognized in the mirror plane. The orientation of the pyridinium ions is ordered ferroelectrically within each plane and arranged in the opposite direction in alternate planes along the b'-axis, resulting in an antiferroelectric ordering as a whole crystal. The antiferroelectric order of pyridinium ions is consistent with the temperature dependence of the real part of dielectric constant, ε', depicted in Fig. 4. That is, a strong increase at $T \to T_c$ below T_c and much weaker temperature dependence at $T > T_c$ without showing sharp maximum at T_c are characteristic of temperature evolution of the dielectric constant in antiferroelectric crystals [13,14]. Similar behavior of the dielectric constant was also reported for the antiferroelectric phase transition of pyridinium hexafluorophosphate [15]. Therefore, we suggest that the phase transition at 217 K is antiferroelectric.

In [8], we have reported the temperature dependence of ^{35}Cl NQR frequencies of $PyHICl_4$. The single frequency observed in HTP split into a doublet below T_c. In the present study, we have extended the NQR measurements down to 4.2 K. The frequencies were observed at 25.398 and 19.872 MHz at 77 K, and 25.448 and 19.901 MHz at 4.2 K. The separation $\Delta\nu$ of the split frequencies is very