Introduction

Our interest in halogenoacetic acids salts led us to study [(NH$_2$)$_2$C(CH$_3$)$_2$COO), a new guanidinium salt which we have synthesized and identified by conventional elementary analysis. In recent years there has been a growing interest in salts of chloroacetic acid as some of them exhibit ferroelectric phase transitions. In the large family of chloroacetic acid salts only those containing NH$_4^+$ and N(CH$_3$)$_4^+$ exhibit ferroelectric properties, and the difference between the phases are also reflected in some ammonium or tetramethylammonium bands, as revealed by Raman and IR spectra [1 - 6]. In our investigations we are looking for new salts with different cations which are easy to reorient in the solid state. [(NH$_2$)$_2$C(CH$_3$)$_2$COO) is the first halogenoacetic acid salt containing the guanidinium cation.

Experimental

[(NH$_2$)$_2$C(CH$_3$)$_2$CICOO was prepared by aqueous reaction of stoichiometric quantities of CH$_3$CICOH and (CH$_3$N$_3$)$_2$H$_2$CO$_3$ (2:1). The resulting white precipitate was filtered and recrystallized twice from water. Large single crystals of [((NH)$_2$)$_3$C]CH$_3$CICOO were obtained from aqueous solution at 295 K. The crystals were powdered, dried in a vacuum desiccator and used for measurements after identification by conventional elementary analysis.

The $^{35}$Cl NQR spectra were recorded using an NQR Fourier transform pulse spectrometer FT NQS-150. The resonance frequency was determined to a precision of 1 kHz. The temperature of the sample was stabilized to within 0.1 K by using an Oxford flow cryostat.

Proton NMR second moments as well as spin-lattice relaxation times were studied in a wide range of temperatures.

Measurements of the NMR second moment were carried out with a wide-line spectrometer operating at 28 MHz. The second moment values found by numerical integration of the absorption curve derivatives were corrected for the finite modulated field.

The relaxation times in the laboratory $T_1$ and rotating frame $T_{1p}$ were measured at 60 MHz using a home-made pulse spectrometer. $T_1$ was determined by a saturation recovery method and $T_{1p}$ by spin-locking the magnetization in a rotating field of 22 G.

The temperature of the sample was monitored with a Pt resistor to an accuracy of 1 K. All measurements were taken with increasing temperature.
Results and Discussion

The $^{35}$Cl NQR spectrum consists of two widely spaced and strong lines of equal intensity at 77 K, which indicates the existence of two crystallographically inequivalent chlorine atoms in the crystal. The temperature dependence of the pure quadrupole frequency is shown in Figure 1. With increasing temperature up to 332 K the NQR frequencies and their separation decreases. A gradual broadening of the lower NQR line and a decrease of the signal amplitude with increasing temperature was also observed. The lower NQR line vanishes at about 350 K.

The negative temperature coefficients of the NQR frequencies may be interpreted as the averaging effect on the electric field gradient (EFG) caused by the torsional oscillations of the $\text{CClH}_2$ groups of the anion [7, 8]. Assuming anharmonicity of the oscillations by taking the temperature dependence of their frequencies in the form

$$\omega_i = \omega_i^0(1 - g_i T) \quad (1)$$

we obtained the best fit of the experimental $\nu_Q(T)$ values to the Brown theory equation [8]

$$\nu_Q(T) = a_0 + a_1 T + a_2 T^2, \quad (2)$$

Table 1. Fit parameters of the experimental $\nu_Q(T)$ values for [($\text{NH}_2)_3\text{C}$]$\text{CH}_2\text{ClCOCO}_2$ to the Brown formula.

<table>
<thead>
<tr>
<th>$a_0$ (MHz)</th>
<th>$a_1 \cdot 10^{-3} (\text{MHz K}^{-1})$</th>
<th>$a_2 \cdot 10^{-5} (\text{MHz K}^{-2})$</th>
<th>$g$</th>
<th>$\kappa$</th>
</tr>
</thead>
<tbody>
<tr>
<td>34.2277</td>
<td>-1.8201</td>
<td>-0.9434</td>
<td>0.52</td>
<td>0.49</td>
</tr>
<tr>
<td>34.9499</td>
<td>-2.7853</td>
<td>-1.3760</td>
<td>0.49</td>
<td>0.49</td>
</tr>
</tbody>
</table>

where

$$a_0 = \nu_Q(0), \quad (3)$$

$$a_1 = -\frac{3}{2} k \nu_Q(0) \sum_i A_i / (\omega_i^0)^2 \quad (4)$$

$$= -\frac{3}{2} k \nu_Q(0) M A / (\omega^0)^2,$$

$$a_2 = -3k \nu_Q(0) \sum_i g_i A_i / (\omega_i^0)^2 \quad (5)$$

$$= -3k \nu_Q(0) M g A / (\omega^0)^2.$$  

$A_i$ is a coefficient which for librations is equal to the reciprocal of the relevant moment of inertia $I_i^{-1}$, $M$ is a number of modes in the averaging of the EFG and $k$ is the Boltzmann constant. There are no data for particular modes of vibrations, so for the calculations we used an averaged mode of the average frequency $\omega^0$ and the averaging parameter $g$. The best fit is given by the solid line in Figure 1. The coefficients $a_i$ and the average coefficient $g$ obtained from the fit are given in Table 1.

The gradual broadening of the lower NQR line probably originates from the fluctuations of the external EFG due to the guanidinium cation motion. To reveal the nature of the motion, the NMR study has been undertaken.

The temperature dependence of the proton NMR second moment is shown in Figure 2. The mean value of 18.2 G$^2$ registered at low temperatures is constant up to 250 K, where it starts to decrease slowly and then more rapidly to the plateau value of 10.9 G$^2$ observed up to the melting point at about 365 K.

The theoretical proton second moment value was found numerically, using the van Vleck formula [9]. For a rigid structure of a polycrystalline sample containing one species of magnetic nuclei with spins $I$ and giromagnetic ratio $\gamma_I$ the formula reads

$$M_2 = (3\gamma_I^2 h^2 / 5N) I(I + 1) \sum_{j,k} r_{jk}^{-6}, \quad (6)$$
Fig. 2. Temperature dependence of the proton NMR second moment.

where \( r_{j,k} \) is a distance between respective nuclei and \( N \) is the number of nuclei over which the sum is taken. In our calculations we assumed the standard geometry of the guanidinium cation (e.g., C-N = 1.32 Å, N-H = 1.01 Å and the proton-proton distance in the anion 1.79 Å). The intramolecular part of the second moment for such a geometry was found to be 15.2 G\(^2\). The intermolecular part (3 G\(^2\)) was obtained by a subtraction of the above value from the experimental 18.2 G\(^2\), which could be treated as corresponding to the rigid structure.

On increase in temperature, the second moment is evidently reduced reflecting an onset of ion motions in the crystal lattice. To interpret the reduction to the value of 10.9 G\(^2\) observed at high temperatures we had to consider different models of proton motions. It is very surprising that \( C_3 \) reorientation of the guanidinium cation found in all the guanidinium salts previously studied [10 - 14] had to be excluded. Such a motion would reduce the second moment to the much lower value of about 7 G\(^2\). The best agreement with the experimental value we obtained by supposing guanidinium cation reorientation around its twofold symmetry axis. Such a motion reduces the intramolecular part of the rigid-structure second moment by the factor

\[
\rho = 1 - 3 \sin^2 \alpha \cos^2 \alpha, \quad (7)
\]

where \( \alpha \) is the angle between the interproton vector and the reorientation axis. It leads to a theoretical total value of 11.6 G\(^2\), well comparable with the experimental 10.9 G\(^2\). However, the value obtained can be further slightly reduced if one assumes the oscillation of the protons revealed in the NQR studies. In particular, the slight decrease of the NMR second moment in the temperature range 250 - 300 K can be well interpreted in terms of proton oscillations of about 15°.

The proton spin-lattice relaxation times \( T_1 \) and \( T_{1\rho} \) as functions of inverse temperature are shown in Figure 3. A decrease of \( T_1 \) with increasing temperature and a well defined \( T_{1\rho} \) minimum of 1.2 ms at 345 K was observed. The relaxation experiments enable us to extract precise activation parameters for the \( C_2 \) reorientation of the guanidinium cation. The experimental \( T_1 \) and \( T_{1\rho} \) data can be described by the expressions

\[
\frac{1}{T_1} = \frac{2}{3} \gamma J M_2 \left[ \frac{\tau}{1 + \omega_0^2 \tau^2} + \frac{4\tau}{1 + 4\omega_0^2 \tau^2} \right] \quad (8)
\]

\[
\frac{1}{T_{1\rho}} = \frac{2}{3} \gamma J M_2 \left[ \frac{5\tau}{2(1 + \omega_0^2 \tau^2)} + \frac{\tau}{1 + 4\omega_0^2 \tau^2} + \frac{3\tau}{2(1 + 4\omega_1^2 \tau^2)} \right] \quad (9)
\]
where $\tau$ is a correlation time for the motion considered and $\Delta M_2$ is the second moment reduction value.

The theoretical fits (solid lines in Fig. 3) yielded an activation energy of 42 kJ/mol and a preexponential factor $\tau_0 = 3.9 \times 10^{-13}$ s for the motion considered.

It is noteworthy that a similar value of the activation energy was obtained in many other guanidinium salts [10-14], but for the $C_3$ reorientation of the cation. Regardless of the reorientation, the value of the energy barrier certainly reflects the great number of hydrogen bonds in which the cation is involved.

Acknowledgement

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