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^{1}H NMR Study of the Motion of Guanidinium Ions in Guanidinium Dichloroiodate(I) and Tetrachloroiodate(III)

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Synopsis. The temperature dependence of the ^{1}H NMR spin-lattice relaxation time, T_1, was measured for $C(NH_2)_3ICl_2$ and $C(NH_2)_3ICl_4$. For the dichloro complex, three T_1 minima were observed and assigned to the reorientations of crystallographically inequivalent $C(NH_2)_3^+$ ions about the three-fold axes, each of which has an activation energy of 21, 15, and 8.4 kJ mol^{-1}. The tetrachloro complex yielded a single T_1 minimum with an activation energy of 33 kJ mol^{-1}. A phase transition in $C(NH_2)_3ICl_2$ was found at 399 K by NMR and differential thermal analysis.

The dynamical properties of planar guanidinium cations ($C(NH_2)_3^+$, abbreviated as guH^+) in various crystalline compounds were studied using ^{1}H NMR techniques.[1–9] In the present study, we measured the temperature dependence of the ^{1}H NMR spin-lattice relaxation time, T_1, for $guHICl_2$ and $guHICl_4$, in which the anions are rod-like and planar, respectively, to obtain further information about the dynamics of the guH^+ ions in crystals.

Experimental

Guanidinium dichloroiodate(I) was crystallized from concd hydrochloric acid solution saturated with equimolar guHCl and ICl, and purified twice by recrystallization from its hydrochloric acid solution. The crystals of thin plates were orange and very soft. The X-ray powder pattern taken at room temperature was too complex to be indexed.

Guanidinium tetrachloroiodate(III) was obtained by the following method. guHCl and a slight excess of ICl_3 were dissolved in a 1:1 hydrochloric acid–acetic acid mixture; then, chlorine gas was bubbled into the solution. When the yellow solution, thus obtained, was cooled down to ca. 280 K from room temperature, yellow needle-like crystals were obtained. From a hydrochloric acid solution of $guHICl_4$ heated once to ca. 360 K, a mixture of $guHICl_4$ and $guHICl_2$ was obtained upon cooling, indicating that the ICl_4^- ions decomposed into ICl_2^- ions (and Cl_2) at high temperatures. Therefore, all synthetic experiments of $guHICl_4$ were carried out at or below room temperature. The powder diffraction pattern recorded at room temperature suggested that $guHICl_4$ forms a monoclinic lattice isomorphous with that of the room-temperature phase of $guHAuCl_4$.[10]

Analysis: Calcd for $C(NH_2)_3ICl_2$: N, 16.3%; Cl, 27.5%. Found: N, 16.6%; Cl, 27.2%. Calcd for $C(NH_2)_3ICl_4$: N, 12.8%; Cl, 43.1%; I, 38.6%. Found: N, 12.9%; Cl, 43.1%; I, 38.5%.

The spin-lattice relaxation time, T_1, of ^{1}H NMR was measured by the inversion recovery method, using pulse NMR spectrometers.[1,11] Errors in the T_1 measurements were estimated to be less than 5%. The ^{1}H NMR absorption lines were recorded by using a JEOL JNM-MW-40S continuous-wave spectrometer operated at 40 MHz. Differential thermal analysis (DTA) was measured with a home-built apparatus.[12] The temperatures were determined by a copper-constantan thermocouple within an accuracy of ±1 K.

Results and Discussion

Figure 1 shows the temperature dependence of ^{1}H T_1 in $guHICl_2$ measured at resonance frequencies ($\omega/2\pi$) of 20 and 42 MHz. Below room temperature, three T_1 minima were observed. The values of the T_1 minima and the temperatures at which the minima occur at 20 MHz were 41 ms and 266 K, 42 ms and 192 K, and 40 ms and ca. 104 K, respectively. Above room temperature, T_1 increased with increasing temperature and above 399 K the temperature gradient of T_1 changed slightly. DTA experiments were carried out between ca. 90 K and mp (ca. 445 K) of $guHICl_2$. On heating runs, a small endothermic peak was observed at 399 K, confirming that the T_1 anomaly described above is due to a phase transition. Because a thermal hysteresis of ca. 4 K was observed, the transition is of a first-order.

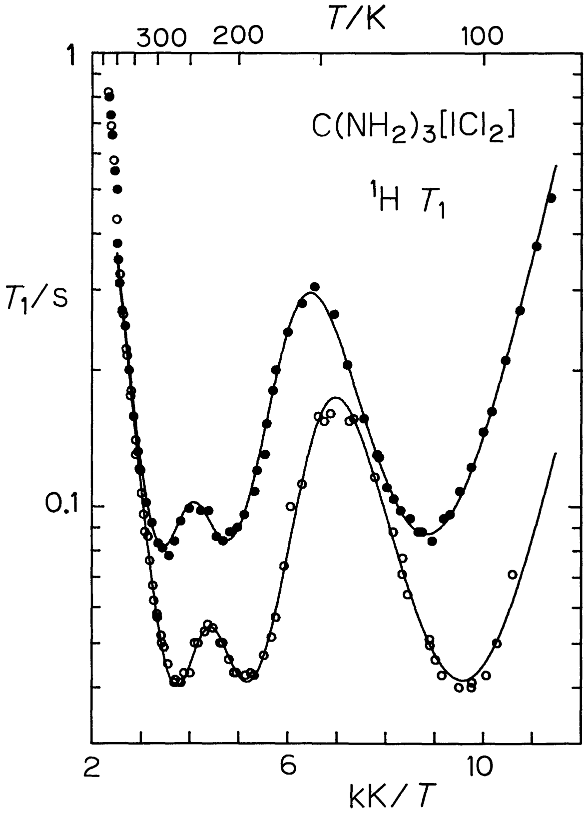

Fig. 1. Temperature dependence of ^{1}H T_1 observed for $C(NH_2)_3ICl_2$. ●: 42 MHz; ○: 20 MHz. Solid curves were calculated by using the best-fit parameters given in Table 1.

Table 1. Motional Parameters of C_3 Reorientations of $C(NH_2)_3^+$ Ions in $C(NH_2)_3ICl_2$ and $C(NH_2)_3ICl_4$ Crystals

Compound	Phase	$C/10^9\ s^{-2}$	$\log(\tau_0/s)$	E_a/kJ mol^{-1}
$C(NH_2)_3ICl_2$	Room-temp	1.91±0.09	−12.3±0.1	20.9±0.6
		2.00±0.06	−12.5±0.2	15.2±0.6
		2.13±0.06	−12.5±0.1	8.4±0.3
	High-temp	—	—	22 ±2
$C(NH_2)_3ICl_4$		4.91±0.13	−14.5±0.1	33.1±0.6

To determine the modes of guH^+ ion motions occurring in this crystal, we recorded the ^1H NMR absorption curves at room temperature, and calculated the second moment, M_2, of the curves to be $0.032\pm0.005\ mT^2$. Theoretical values of ^1H M_2 for a guH^+ ion were calculated for several motional models by considering magnetic dipolar interactions among ^1H and ^1H, and ^1H and ^{14}N spins.[5] They are $0.166\ mT^2$ for a rigid lattice model and $0.043\ mT^2$ for a cation rotating about its C_3 axis. Therefore, it is concluded from a comparison of the observed and calculated M_2 values that all of the guH^+ ions in the crystal perform rapid C_3 reorientation at room temperature.

^1H T_1 due to nuclear dipolar interaction can be approximated as[13]

$$T_1^{-1} = C\left(\frac{\tau}{1+\omega^2\tau^2} + \frac{4\tau}{1+4\omega^2\tau^2}\right), \qquad (1)$$

where τ is the correlation time of the guH^+ ion motion and C is a constant. For simplicity, the contribution from ^{14}N nuclei to ^1H T_1 was neglected in Eq. 1. The usual Arrhenius relation is assumed to hold for τ:

$$\tau = \tau_0 \exp(E_a/RT). \qquad (2)$$

The room-temperature phase of $guHICl_2$ shows three T_1 minima having almost the same depth. This fact suggests that there are three kinds of crystallographically inequivalent guH^+ ions in the crystal and that these cations reorient with correlation times different from each other. Then, the observed temperature dependence of T_1 can be represented in terms of a superposition of three T_1 curves, each of which is expressed by Eq. 1. A least-squares fitting calculation for the T_1 data observed at 20 and 42 MHz was carried out in order to determine the motional parameters of the cations. The best-fit parameters obtained are listed in Table 1 and the calculated temperature dependences of T_1 are drawn by solid lines in Fig. 1.

The observed C values agree satisfactorily with the theoretical value $(1/3)\times5.15\cdot10^9\ s^{-2}$.[5] The E_a values for the C_3 reorientations of the guH^+ ions varied greatly upon changing the counter anions forming crystals with guH^+ ions, probably depending on the crystal packing and/or hydrogen-bonding ability of the anions.[1-9] The E_a values already reported are in the range 20—80 kJ mol^{-1}. The E_a values obtained $guHICl_2$ are widely spread, indicating that the three types of cations are in largely different environments.

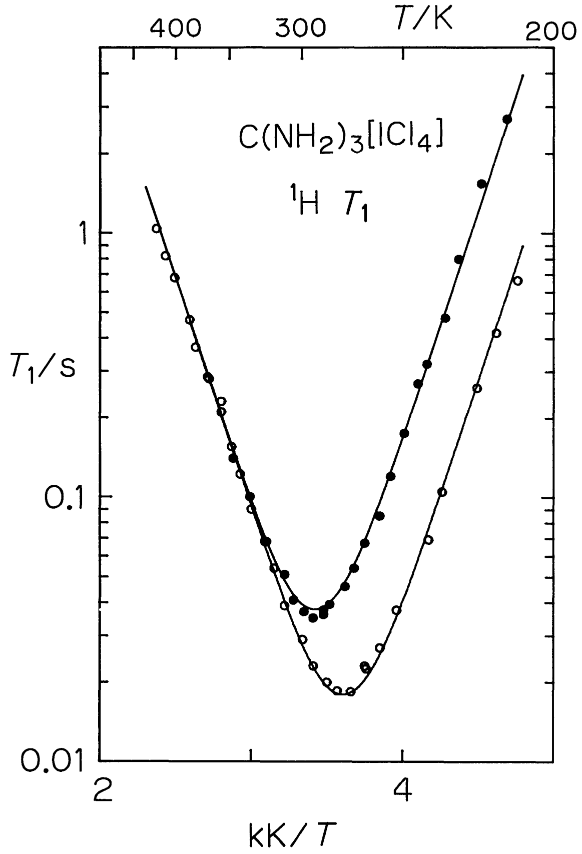

Fig. 2. Temperature dependence of ^1H T_1 observed for $C(NH_2)_3ICl_4$. ●: 42 MHz; ○: 20 MHz.

An E_a of 8.4 kJ mol^{-1} as well as 15.2 and 20.9 kJ mol^{-1} is the smallest one among those for the guH^+ C_3 reorientations determined so far. For the high-temperature phase, an E_a value of ca. 22 kJ mol^{-1} was obtained from the slope of the log T_1 vs. $1/T$ curve.

The temperature dependence of ^1H T_1 for $guHICl_4$ is shown in Fig. 2. Only a single T_1 minimum was observed in each measurement at 20 and 42 MHz. The minimum at 20 MHz was 18.5 ms and appeared at 275 K. The room-temperature M_2 value of $0.034\pm0.005\ mT^2$ indicates that the observed T_1 is attributable to the C_3 reorientation of the guH^+ ions as well. The motional parameters determined by the least-squares fitting are given in Table 1. $guHICl_4$ has a crystal structure either isomorphous with or very similar to that of $guHAuCl_4$. In the latter compounds, the guH^+ ions undergo a reorientation with an E_a of 39 kJ mol^{-1},[3] which is slightly larger than 33 kJ mol^{-1} for the former complex. This can be ascribed, in part, to a larger unit cell of guHICl$_4$ (a~15.8, b~4.0, c~15.0 Å, β~95°) than that of guHAuCl$_4$. DTA and T_1 measurements showed no indication of the occurrence of a phase transition in a temperature range 440—130 K, in contrast to guHAuCl$_4$, which shows a phase transition at 363 K.[1,3]

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