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An ^1H NMR Study on the Motion of Guanidinium Cations in Some Crystals Formed with Tetrahedral or Octahedral Complex Anions Having Halide Ions as Ligands

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Synopsis. The temperature dependences of ^1H NMR spin-lattice relaxation times were determined at 20 MHz for $[C(NH_2)_3]_2ZnX_4$ (X=Cl, Br), $[C(NH_2)_3]_2MCl_6$ (M=Sn, Te, Pt), and $[C(NH_2)_3]_2PtBr_6$. Above room temperature, the D_{3h} cation undergoes reorientational motion by 120° about the cationic C_3 axis. For $[C(NH_2)_3]_2TeCl_6$ crystals, two phase transitions were located at 312 and 373 K.

Recently, we studied the temperature dependences of ^1H NMR second moments and ^1H spin-lattice relaxation times (T_1) in various guanidinium (guH^+) salts involving simple salts such as guanidinium halides and the salts with D_{4h} tetrahalo complexes, such as tetrahaloaurates(III), and obtained information about the motion of the cation in solids.[1-3] From these investigations, it becomes apparent that with increasing temperature the cation undergoes 120° reorientations as a whole, i.e., the C_3 reorientation, about the principal axis of the D_{3h} cation. The observed activation energies (E_a) for this motion are distributed in a fairly wide range from 78 kJ mol^{-1} for (guH)Cl to 20 kJ mol^{-1} for the high-temperature phase and its supercooled state of $(guH)AuBr_4$. This is presumably due to the following reasons. The strength of hydrogen bonding formed between the cation and the counter anion is considered to vary to a large extent from salt to salt. Furthermore, steric hindrance to perform the C_3 reorientation may be largely determined by the loosely or densely packed crystal structure, where the size and/or the shape of the counter anion might play a crucial role. To clarify which is the most important factor, the accumulation of much more data is required. Therefore, the present investigation of ^1H T_1 has been undertaken for some guanidinium salts containing tetrahalo T_d and hexahalo O_h complex anions.

Experimental

$(guH)_2ZnCl_4$ and $(guH)_2ZnBr_4$ were prepared by adding the corresponding guanidinium halide to a hydrohalogenic acid solution of $ZnCl_2$ and $ZnBr_2$, respectively. Colorless crystals were obtained for both complexes. Colorless $(guH)_2SnCl_6$ and yellow $(guH)_2TeCl_6$ crystals were obtained by mixing a concd aqueous solution of (guH)Cl with concd hydrochloric acid solutions of $SnCl_4 \cdot xH_2O$ and TeO_2, respectively.[4,5] Orange colored crystals of $(guH)_2PtCl_6$ were obtained from $(guH)_2PtCl_4$ which had been synthesized in the previous work[1] by oxidizing it with chlorine gas in a concd hydrochloric acid solution. Reddish brown $(guH)_2PtBr_6$ crystals were prepared by adding a concd aqueous solution of (guH)Br to a concd hydrobromic acid solution of hexabromoplatinic(IV) acid. All samples prepared were identified by usual chemical analysis. Anal. Calcd for $[C(NH_2)_3]_2ZnCl_4$: N, 25.7; Cl, 43.3%. Found: N, 26.0; Cl, 43.6%. Calcd for $[C(NH_2)_3]_2ZnBr_4$: N, 16.6; Br, 63.3%. Found: N, 16.8; Br, 63.5%. Calcd for $[C(NH_2)_3]_2SnCl_6$: N, 18.6%. Found: N, 18.9%. Calcd for $[C(NH_2)_3]TeCl_6$: N, 18.3; Cl, 46.2%. Found: N, 18.5; Cl, 46.0%. Calcd for $[C(NH_2)_3]_2PtCl_6$: N, 15.9; Cl, 40.3%. Found: N, 16.2; Cl, 40.2%. Calcd for $[C(NH_2)_3]_2PtBr_6$: N, 10.6; Br, 60.3%. Found: N, 10.7; Br, 60.2%.

A pulsed NMR spectrometer[6] was employed for the measurements of the temperature dependence of ^1H T_1 observed at 20 MHz. A usual π-τ-$\pi/2$ pulse sequence was used for the determination of T_1. Differential thermal analysis (DTA) curves for $(guH)_2TeCl_6$ were recorded by use of a homemade apparatus.[7] Sample temperatures were determined within the accuracy of ±1 K using copper-constantan thermocouples.

Results and Discussion

The temperature dependences of ^1H T_1 observed at 20 MHz are shown in Fig. 1 for $(guH)_2ZnCl_4$ and $(guH)_2ZnBr_4$, and in Fig. 2 for $(guH)_2SnCl_6$, $(guH)_2TeCl_6$, $(guH)_2PtCl_6$, and $(guH)_2PtBr_6$. All of these complexes showed a single ^1H T_1 minimum above room temperature having approximately the same T_1 minimum value. The present complexes except $(guH)_2TeCl_6$ yielded usual T_1 curves explainable by the simple BPP theory.[8] The ^1H T_1 curve of $(guH)_2TeCl_6$ showed anomalies suggesting the presence of phase transitions.

When $(guH)_2TeCl_6$ was heated from room temperature, ^1H T_1 observed decreased monotonously up to ca. 315 K where it increased discontinuously. With further increasing temperature, $\log T_1$ again decreased linearly with decreasing T^{-1} although it decreased discontinuously at 373 K. Above this temperature, $(guH)_2TeCl_6$ yielded a usual BPP curve.

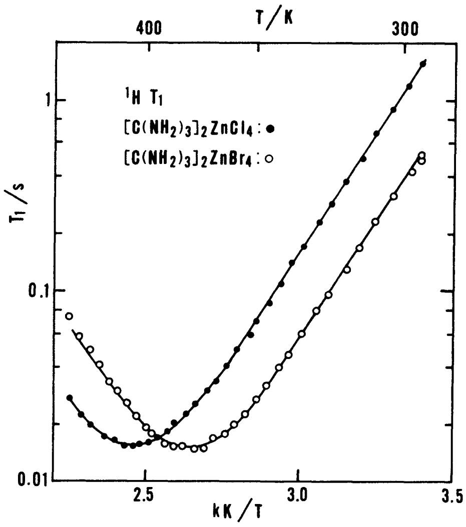

Fig. 1. Temperature dependences of ^1H T_1 determined at 20 MHz for guanidinium tetrachloro- and tetrabromozincate(II). Best-fitted BPP curves are depicted by solid line.

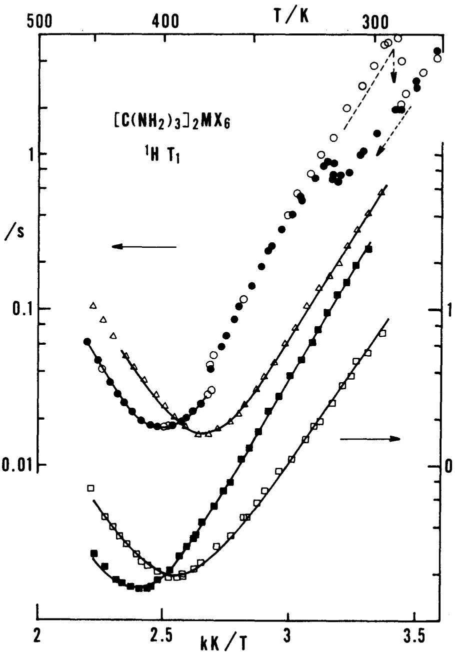

Fig. 2. Temperature dependences of ^{1}H T_1 determined at 20 MHz for $[C(NH_2)_3]_2SnCl_6$ (△), $[C(NH_2)_3]_2PtCl_6$ (■), and $[C(NH_2)_3]_2PtBr_6$ (□). The data of $[C(NH_2)_3]_2TeCl_6$ are also plotted by ● and ○ for the heating and cooling runs, respectively. Best-fitted curves are indicated by solid line. Broken lines with arrows show heating and cooling processes.

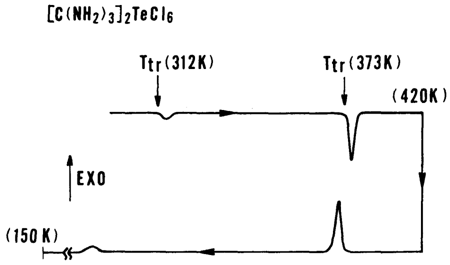

Fig. 3. DTA curves recorded for guanidinium hexachlorotellurate(IV).

When the temperature was lowered from ca. 450 K, the ^{1}H T_1 value observed followed the same curve down to ca. 330 K as that obtained on the heating run. Below this temperature, $\log T_1$ values obtained deviated from the curve observed on the heating run and increased almost linearly against T^{-1} down to ca. 290 K. Around this temperature, ^{1}H T_1 shortened drastically to the value which was observed on the heating run. Below this temperature, $\log T_1$ increased linearly with increasing T^{-1}.

To confirm the occurrence of phase transitions and to determine the phase-transition temperature, T_{tr}, DTA experiments were carried out for $(guH)_2TeCl_6$ (see Fig. 3). When the sample was heated, small and large endothermic peaks appeared at 312 and 373 K, respectively. With decreasing temperature, exothermic anomalies corresponding to the above ones were detected at 372 and near 290 K. Since the latter heat anomaly was weak and broad, a definite transition temperature could not be located on the cooling run. However, it can be said that this phase transition shows marked hysteresis phenomenon as was also observed in the foregoing T_1 experiments. Thermal hysteresis could also be detected for the high-temperature phase transition. Accordingly, it is concluded from the DTA experiments that $(guH)_2TeCl_6$ crystals undergo two first-order phase transitions at 312 and 373 K.

Table 1. ^{1}H T_1 Minimum Value, $T_{1\,\mathrm{min}}$, Observed at 20 MHz, Activation Energy, E_a, and Correlation Time, τ_0, Obtained from T_1 Measurements for the C_3 Reorientation of Guanidinium Ions in the Crystals of Several Complexes

Compound (phase)	$T_{1\,\mathrm{min}}$/ms	E_a/kJ mol^{-1}	τ_0/s
$[C(NH_2)_3]_2ZnCl_4$	16	48	3.2×10^{-15}
$[C(NH_2)_3]_2ZnBr_4$	15	48	1.0×10^{-15}
$[C(NH_2)_3]_2PtCl_6$	16	53	1.2×10^{-15}
$[C(NH_2)_3]_2PtBr_6$	19	45	5.2×10^{-15}
$[C(NH_2)_3]_2SnCl_6$	16	52	3.9×10^{-16}
$[C(NH_2)_3]_2TeCl_6$ (highest-temp.)	17	57	2.2×10^{-16}

The all complexes investigated yielded a single T_1 minimum, the values of which were in the range of 15—19 ms. These values are approximately the same as those found for various guanidinium salts already studied.[1—3,9,10] In the preceding works, those T_1 minima could be attributed to the C_3 reorientation of the cation as a whole about its principal axis on the basis of the theoretical value calculated for the cation using the geometrical values obtained by the X-ray analysis of $(guH)ClO_4$.[2,3,9,10] Therefore, each T_1 minimum detected in the present complexes can be assigned to the magnetic dipolar relaxation due to the cationic C_3 reorientations.

Since guH^+ cations include $-NH_2$ groups in which two kinds of magnetic nuclei, ^{1}H and ^{14}N, exist although ^{14}N nuclei have a small magnetic moment, we should take into account two kinds of magnetic dipolar interactions, ^{1}H-^{1}H and ^{1}H-^{14}N, to calculate motionally averaging ^{1}H T_1. Therefore, the observed ^{1}H T_1 can be written for the present complexes as,[2,8)

$$T_1^{-1} = C\left(\frac{\tau}{1+\omega_H^2\tau^2} + \frac{4\tau}{1+4\omega_H^2\tau^2}\right) + C'\left[\frac{\tau}{1+(\omega_H-\omega_N)^2\tau^2} + \frac{3\tau}{1+\omega_H^2\tau^2} + \frac{6\tau}{1+(\omega_H+\omega_N)^2\tau^2}\right]. \quad (1)$$

Here, ω_H and ω_N denote the Larmor frequencies of a proton and a ^{14}N nucleus, respectively. The motional constants, C and C', are determined by the dipolar interactions operative between protons and between the hetero nuclear spins, respectively. The correlation time, τ, of the motion is assumed to obey the Arrhenius relationship,

$$\tau = \tau_0 \exp(E_a/RT), \quad (2)$$

where E_a and τ_0 are the activation energy for the motion of the cation and its correlation time at the limit of infinite temperature.

The ^{1}H T_1 values observed at various temperatures for each complex except $(guH)_2TeCl_6$ were fitted to Eqs. 1 and 2 by changing the values of E_a and τ_0 as adjustable parameters. The calculation was performed using a personal computer Model PC-9801 from NEC by the least-squares method using a program written by us. For $(guH)_2TeCl_6$, the same method of fitting calculation was used for the ^{1}H T_1 values obtained in the highest-temperature phase. However, only the E_a values of this complex were roughly estimated from the gradient of each linear portion of $\log T_1$ vs. T^{-1} curves observed in the middle- and low-temperature phases as 60 and 42 kJ mol^{-1}, respectively. It is interesting to note that the low-temperature phase of $(guH)_2TeCl_6$, which is stable below room temperature, has the considerably smaller E_a than those estimated for the higher-temperature phases. This suggests that $(guH)_2TeCl_6$ forms more loosely packed crystals in the low-temperature phase as compared with those at the other high-temperature phases.

The best-fitted curves calculated by the least-squares method are shown by solid lines in Figs. 1 and 2. The most probable values of E_a and τ_0 are listed in Table 1 along with the observed T_1 minimum values.

For the C_3 reorientation of the cation in the crystal of $(guH)_2ZnCl_4$ and $(guH)_2ZnBr_4$, the same E_a value was observed as 48 kJ mol^{-1}. Although the anionic size of the former is smaller than the latter and the ionic characters of halide ligands estimated from the NQR frequencies reported are fairly small,$^{11)}$ both complexes exhibit rather small and the same E_a value. This suggests that the size difference of the complex anions and the formation of hydrogen bonding between the cations and halide ligands give negligible effect on the hindering barrier of the cationic C_3 reorientation. Among octahedral complexes, only $(guH)_2PtBr_6$ gave fairly small E_a. This suggests that the cations placed in the large openings surrounded by the bulky anions which practically determine the lattice, can be reoriented more easily than those in the crystals of the hexachloro complexes. Hindering barrier for the C_3 reorientation of the cation due to hydrogen bonding between $-NH_2$ groups and the ligands may be neglected because $(guH)_2SnCl_6$ having more ionic ligands than $(guH)_2PtCl_6$$^{12)}$ gives lower E_a. Since no information about the crystal structure of the present complexes is available, no further discussion can be made.

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