¹H and ¹⁹F NMR Study of Cation and Anion Motions in Guanidinium Hexafluorozirconate

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Proton and fluorine NMR second moments and spin-lattice relaxation times of polycrystalline guanidinium hexafluorozirconate and its deuterated analogue were studied in laboratory (60 MHz) and rotating ($H_1 = 20$ G) frames over a wide range of temperature. An analysis of the experimental results enabled us to reveal a dynamical inequivalence of two crystallographically independent cations and an unexpected high mobility of nonspherical anion dimers. A comparison of the ions dynamics in 2:1 complex studied with the guanidinium 1:1 and 3:1 complexes has shown a significant contribution of the hydrogen bonds to the potential barriers hindering the anion reorientations. At low temperatures a proton motion in the hydrogen bond and at 400 K a solid-solid phase transition have been discerned.

Key words: NMR, Ion Motions, Hydrogen Bonds, Phase Transitions.

Introduction

Our X-ray as well as ¹H and ¹⁹F nuclear magnetic resonance studies of crystal structures and ion motions in guanidinium salts containing fluorinated anions enabled us to describe the dynamics of both ionic sublattices and to reveal an interesting interaction of cations and anions leading to a coupling of their reorientational frequencies at phase transitions [1–6].

In the compounds studied the cation undergoes reorientation around its C_3 symmetric axis hindered by an energy barrier of about 40 kJ/mol. In 1:1 complexes like guanidinium tetrafluoroborate [1] or hexafluorophosphate [2] the activation energy for reorientation of the anion was found to be much lower (about 20 kJ/mol) than for the cation. In 3:1 complexes such as tris-guanidinium hexafluoroaluminate [4] and hexafluorogallate [5] the hindering barrier for the anion is much higher (about 65 kJ/mol) than for the cation. This seems to result from a greater number of hydrogen bonds in which the anion is involved as compared to the cation.
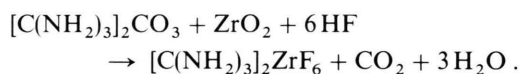
It seemed interesting to study cation and anion dynamics in a 2:1 complex and compare it with 3:1 and 1:1 complexes previously studied. Therefore we have chosen bis-guanidinium hexafluorozirconate

$[C(NH_2)_3]ZrF_6$ for studies of proton and fluorine NMR second moments as well as spin-lattice relaxation times as functions of temperature, complemented by differential thermal analysis.

The crystal structure of the guanidinium hexafluorozirconate has been already determined [7]. The compound crystallizes in triclinic space group P1̄ with $a = 8.168$, $b = 9.919$, $c = 8.264$ Å, $\alpha = 100.38°$, $\beta = 115.38°$, $\gamma = 102.47°$, $Z = 2$. The structure consists of two crystallographically inequivalent guanidinium cations and anion dimers. Both ion-sublattices are connected by a number of hydrogen bonds N–H...F into a three-dimensional network. Such a structure seems to be additionally interesting for NMR study of ion dynamics and possible proton motion in hydrogen bonds. A question arises whether the structural inequivalence may affect the cations motional freedom and what type of reorientation of the asymmetrical dimer is possible.

Experimental Details

Guanidinium hexafluorozirconate was prepared from guanidinium carbonate, zirconium dioxide and hydrofluoric acid according to the reaction

$$[C(NH_2)_3]_2CO_3 + ZrO_2 + 6\,HF$$
$$\rightarrow [C(NH_2)_3]_2ZrF_6 + CO_2 + 3\,H_2O\,.$$

To remove iron paramagnetic impurities revealed in the product by electron paramagnetic resonance purity control, the compound was recrystallized form 20% solution of hydrofluoric acid with a small amount of tartaric acid added. The product was then ground to a powder, dried, degassed and sealed off. The deuterated analogue was obtained from purified $[C(NH_2)_3]_2ZrF_6$ by multiple exchange with D_2O.

The measurements of proton and fluorine NMR second moments were carried out with a wide-line spectrometer operating at 28.0 MHz for protons and 26.3 MHz for fluorine nuclei. The second moment values found by numerical integration of the absorption curve derivatives were corrected for the finite modulated field [8]. Relaxation times T_1 and $T_{1\varrho}$ were measured at 60 MHz using a home-made pulse spectrometer. T_1 was determined by a saturation recovery method and $T_{1\varrho}$ by spin-locking the magnetization in a rotating field of 20 G. The temperature of the sample was controlled by means of a gas-flow cryostat and monitored with a Pt resistor to an accuracy of 1 K. All measurements were taken with increasing temperature.

Differential thermal analysis (DTA) was made with a Derivatograph Unipan (DSC 605 MD).

Results

The temperature dependences of the proton and fluorine second moments for $[C(NH_2)_3]_2ZrF_6$ and $[C(ND_2)_3]_2ZrF_6$ are shown in Figure 1. For protons, the second moment of 23 G^2 diminishes at 180 K to 21 G^2, a value which is maintained constant up to 280 K, where it starts to decrease to 4 G^2 achieved above 410 K. The fluorine second moment has two plateaux: the first one of 12.5 G^2 is observed up to 260 K, and the second one of 1 G^2 above 370 K. For the deuterated sample, a plateau of 5.4 G^2 is observed up to 290 K and another one of 0.3 G^2 above 370 K.

The proton and fluorine spin-lattice relaxation times T_1 and $T_{1\varrho}$ as functions of inverse temperature, measured for $[C(NH_2)_3]_2ZrF_6$, are shown in Figs. 2 and 3, respectively. At low temperatures both T_1^H and T_1^F show shallow minima of 8.4 s for protons and 10.3 s for fluorine nuclei. Strongly nonexponential decays of the ^{1}H and the ^{19}F magnetization observed at temperatures higher than 150 K and 250 K, respectively, were decomposed into two exponential T_1-terms. At high temperatures, a T_1 minimum of 23 ms
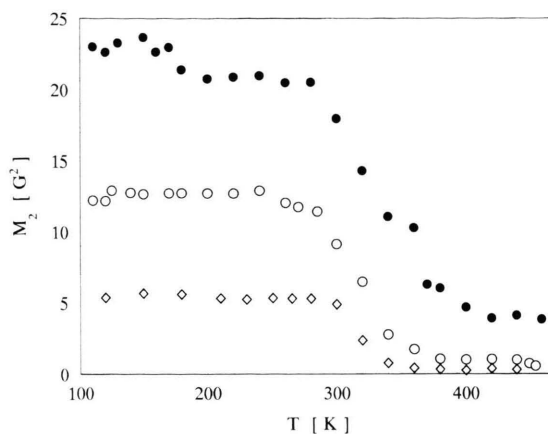

Fig. 1. Temperature dependences of the second moments: proton (●), fluorine (○); ◇: fluorine for the deuterated sample.
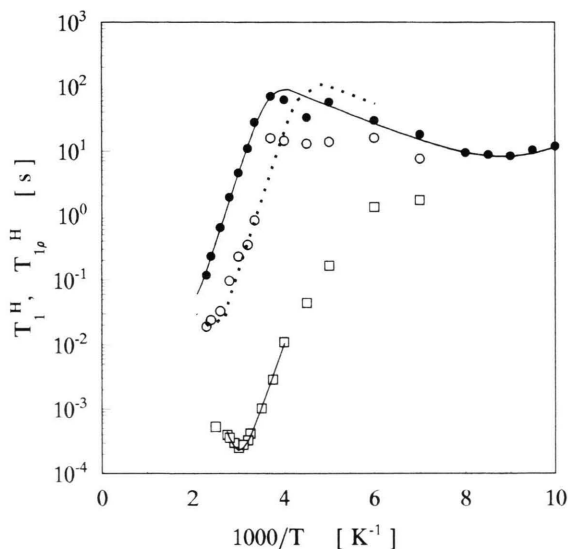
Fig. 2. Temperature dependences of the proton spin-lattice relaxation time T_1 (○ and ●: main component) and $T_{1\varrho}$ (□). The curves are theoretical fits (for T_1, solid line: λ_H^{-1}, dotted line: λ_F^{-1}).

at 425 K is revealed for the fluorine nuclei (Fig. 3), while for protons (Fig. 2) only a linear decrease of T_1^H with increasing temperature is observed. The relaxation times in the rotating frame $T_{1\varrho}^H$ and $T_{1\varrho}^F$ as a functions of temperature show well-defined minima: of 0.25 ms at 333 K for protons and of 0.26 ms at 345 K for fluorine nuclei.

A DTA study has revealed two specific heat anomalies: a strong one at about 400 K and a very weak one
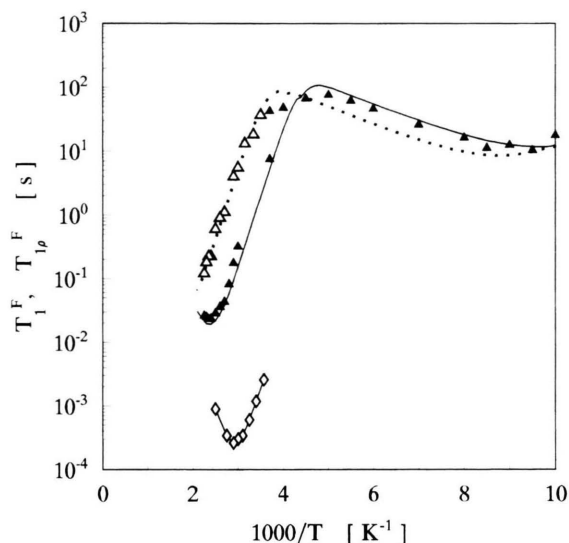
Fig. 3. Temperature dependences of the fluorine spin-lattice relaxation times T_1 ($\triangle$ and $\blacktriangle$: main component) and $T_{1\varrho}$ ($\diamond$). The curves are theoretical fits (for T_1, solid line: λ_F^{-1}, dotted line: λ_H^{-1}).

Table 1. Proton and fluorine second moment values calculated for the rigid cation and anion sublattices.

¹H Second moment (G²)				¹⁹F Second moment (G²)			
Inter-action	Intra-	Inter-	Total	Inter-action	Intra-	Inter-	Total
Gu 1				**ZrF₆ dimer**			
H–H	14.96	3.06	18.02	F–F	4.31	0.26	4.57
H–N	1.98	–	1.98	F–Zr	0.25	0.01	0.26
H–Zr		0.01	0.01	F–H		7.26	7.26
H–F		3.16	3.16	F–N		0.01	0.01
			23.17				12.10
Gu 2							
H–H	14.96	2.43	17.39				
H–N	1.98	–	1.98				
H–Zr		0.01	0.01				
H–F		1.86	1.86				
			21.24				

at 460 K on heating. The latter anomaly seems to be connected with the decomposition of the compound. The former one appears to be reversible and shows a pronounced thermal hysteresis. A new sample, heated up to 420 K, reveals an anomaly at about 360 K when cooled, indicating that the transition should be of first order.

Discussion

Second Moment

Using structural data obtained for the guanidinium hexafluorozirconate [7] and correcting the hydrogen atom locations similarly as in [1], we calculated the theoretical proton and fluorine second moments by applying Van Vleck's formula [9]. Table 1 presents the values obtained for the rigid structure of both ions, taking intra- and intermolecular contributions into account.

As one can see, structural inequivalence of the guanidinium cations (Gu1 and Gu2) leads to slightly different second moments. The mean value of 22.2 G² agrees well with the experimental $M_2^H = 23$ G² registered at low temperatures. Similarly, for ¹⁹F a very good agreement between the experimental (12.5 G²) and theoretical value (12.1 G²) was found. It can thus

be concluded that both ion sublattices at low temperatures are rigid in the NMR time scale. A subtraction of the fluorine second moments registered at the low temperatures for the undeuterated and deuterated samples produces a value of the fluorine-proton interaction. The value obtained, 7.1 G², compares very well with the calculated $M_2(F-H) = 7.26$ G², thus confirming the significant fluorine-proton interaction.

The small decrease (2 G²) of the experimental proton second moment at 180 K seems to be associated with a reorientation of NH₂ group, as was evidenced in other guanidinium salts [1, 2, 4, 10]. The hindering barrier for this reorientation obtained, from the Waugh-Fiedin formula [11] would be about 26 kJ/mol.

At higher temperatures the C_3 reorientation of both structurally inequivalent guanidinium cations strongly reduces the second moment to 4 G². The slightly visible existence of two components of the proton NMR spectrum in the temperature range 240–400 K points to a small difference in dynamical freedom of both cations.

The observed reduction of the fluorine second moment to 1 G² for the undeuterated sample and to 0.3 G² for the deuterated one can be explained in terms of quasi-isotropic reorientation of the anions. Isotropic anion motion has already been found in other guanidinium salts, like tetrafluoroborate [1], hexafluoro-phosphate [2], -aluminate [4], -gallate [5] and -antimonate [6]. Since the anions in all these salts were of a high, close to spherical symmetry, the similar dynamical behaviour of the ZrF₆ anions, which form

non-spherical dimers, seems surprising. The question arises how the dimer can reorient producing a so low second moment value at high temperatures. Our calculations of the second moment, for different models of the anion motion show that a reorientation around one of three two-fold symmetry axes reduces *intramolecular* part of the fluorine second moment only to about 2.7 G^2. If one assumes a simultaneous reorientation around all three two-fold symmetry axes occurring in the dimer, the value is reduced to 1.1 G^2.

To find a precise value of the *intermolecular* part of the second moment reduced by both cation and anion motions, we have undertaken a study of the deuterated sample. A subtraction of the second moments of both samples at high temperatures yielded the motionally reduced intermolecular part equal to 0.7 G^2. Thus the total second moments (3.4 G^2 or 1.8 G^2) evidently exceed the experimental value. So both considered models do not explain the experimental value of 1 G^2. Considering the anion dimer structure, we can see that its main two-fold symmetry axis can be roughly treated as a four-fold one. So, if one assumes the dimer reorientation about two two-fold axes and one four-fold symmetry axis, we have obtained the total reduced value of 1.2 G^2, close to the experimental result. However, the question arises, how in spite of evident steric constraints such a reorientation of a nonspherical dimer can take place.

Alternatively one could assume that in spite of the dimer structure each separate ZrF_6 anion reorients quasi-isotropically around its center of gravity. It is not clear whether the anion dimer structure can be broken to allow for such a motion. However, our preliminary study of potassium hexafluorozirconate K_2ZrF_6 shows that even the chain-like anion structure can be broken at high temperatures, leading to self-diffusion [12].

It is noteworthy that the structural phase transition revealed in the DTA study at about 400 K does not affect the experimental second moment values. The probable reason is that below the phase transition the reorientation of both ions has already begun, greatly reducing all intermolecular interactions. Hence any structural change at the phase transition can not noticeably affect the values of the second moments.

Spin-lattice Relaxation

The proton T_1 minimum of 8.4 s observed at low temperatures can not be explained in terms of any reorientation considered above. An expected change of the second moment corresponding to such a high T_1 minimum ($\Delta M_2 = 0.01$ G^2) is too small to be observed in the wide-line experiment. Since the compound studied forms a network of rather strong inter-ionic hydrogen bonds N–H...F, it is reasonable to assume that there is a proton motion in an asymmetric two-well potential, similarly as in guanidinium nitrate [10]. It could thus explain the high value of T_1 observed in the experiment, a value which strongly depends on the energy difference between two potential wells, characterized by a higher E_A and a lower E_B energy barrier. The spin-lattice relaxation rate for such a proton motion can be given by [13]

$$T_1^{-1} = a/(1+a)^2 C \left[\tau/(1+\omega^2\tau^2) + 4\tau/(1+4\omega^2\tau^2)\right], \quad (1)$$

where a is a population parameter defined by

$$a = \exp(\Delta/RT), \quad (2)$$

$$\Delta = E_A - E_B, \quad (3)$$

and

$$\tau = \tau_0 \exp(E_A/RT)/[1 + \exp(-\Delta/RT)]. \quad (4)$$

C stands for the relaxation constant depending on the geometry of the motion considered.

At higher temperatures the motions, which evidently modulate dipolar interactions and strongly affect the relaxation mechanism, are certainly those revealed in the second moment experiment, i.e. C_3 reorientation of the guanidinium cation and quasi-isotropic reorientation of the anion. Thus the reorientations of both these ions and the proton motion in the hydrogen bonds must be considered in the calculation of the spin-lattice relaxation times. (The reorientation of the NH_2 group suggested in the second moment analysis but not revealed by a T_1 minimum was not taken into account in our calculations.)

Since the compound studied is a multispin system, we have considered the total relaxation matrix for four unlike spins (^{1}H, ^{14}N, ^{19}F, ^{91}Zr) [2] as a sum of three matrices corresponding to three different motions:

$$R = R_{\text{cation}} + R_{\text{anion}} + R_{\text{proton}}. \quad (5)$$

For each relaxation matrix we had to calculate its diagonal and off-diagonal elements using the formulae

$$R_{II} = \frac{2}{3}\gamma_I^2 \Delta M_2^{II} g_1(\omega_I, \tau) + \frac{1}{2}\sum_S \gamma_I^2 \Delta M_2^{IS} g_2(\omega_I, \omega_S, \tau), \quad (6)$$

$$R_{IS} = \tfrac{1}{2} \gamma_S^2 \Delta M_2^{SI} g_3(\omega_I, \omega_S, \tau) N_S/N_I, \qquad (7)$$

where

$$g_1(\omega_I, \tau) = \tau/(1 + \omega_I^2 \tau^2) + 4\tau/(1 + 4\omega_I^2 \tau^2), \quad (8)$$

$$g_2(\omega_I, \omega_S, \tau) = \tau/[1 + (\omega_I - \omega_S)^2 \tau^2]$$
$$+ 3\tau/(1 + \omega_I^2 \tau^2) + 6\tau/[1 + (\omega_I + \omega_S)^2 \tau^2]. \quad (9)$$

$$g_3(\omega_I, \omega_S, \tau) = -\tau/[1 + (\omega_I - \omega_S)^2 \tau^2]$$
$$+ 6\tau/[1 + (\omega_I + \omega_S)^2 \tau^2]. \quad (10)$$

Here τ denotes a correlation time for the reorientation considered. To find the relaxation matrix elements we had to calculate the respective reduction of the second moment values (ΔM_2) assuming different models of the ion reorientations. We have considered the cation and anion motions resulting from our second moment experiment, taking into account the possible different mobilities of two crystallographically inequivalent guanidinium cations. Thus assuming one guanidinium cation (Gu 1) being rigid, another (Gu 2) rotating around its C_3-axis and quasi-isotropic reorientation of the anion we have found the following reduction of the second moment: for the cations: $\Delta M_2(H-H) = 8.5\ G^2$, $\Delta M_2(H-F) = 0.8\ G^2$, $\Delta M_2(H-N) = 0.7\ G^2$, and for the anions: $\Delta M_2(F-F) = 4.4\ G^2$, $\Delta M_2(H-F) = 1.7\ G^2$ and $\Delta M_2(F-Zr) = 0.2\ G^2$. For the proton motion in the hydrogen bonds it was difficult to calculate the respective values of ΔM_2, and hence we treated them as fitting parameters. Then we have calculated the total relaxation matrix and found its eigenvalues λ_H, λ_F, λ_N and λ_{Zr}. The inverses λ_H^{-1} and λ_F^{-1} were then compared with the respective experimental T_1^H and T_1^F values.

The fitting procedure was performed simultaneously for T_1 and $T_{1\varrho}$ data. The experimental proton and fluorine $T_{1\varrho}$ data can be described by the following expression, taking only proton-proton or fluorine-fluorine interaction into account:

$$T_{1\varrho} = C' g_\varrho(\omega_0, \omega_1, \tau), \qquad (11)$$

where

$$g_\varrho(\omega_0, \omega_1, \tau) = \frac{5}{2} \frac{\tau}{1 + \omega_0^2 \tau^2} + \frac{\tau}{1 + 4\omega_0^2 \tau^2}$$
$$+ \frac{3}{2} \frac{\tau}{1 + 4\omega_1^2 \tau^2} \qquad (12)$$

and

$$C' = \frac{2}{3} \gamma^2 \Delta M_2. \qquad (13)$$

The analysis confirmed an expected dynamical inequivalence of two guanidinium cations. A least-squares fit to the experimental T_1 and $T_{1\varrho}$ data yielded the activation parameters for the C_3 reorientation of the guanidinium cation Gu 2 and isotropic reorientation of the anion as well as for the proton motion in the hydrogen bond. All the parameters obtained are listed in Table 2.

Table 2. The activation parameters for the motions considered.

	E [kJ/mol]	τ_0 [s]
Proton motion	$E_B = 6.5$ $\Delta = 2.4$	1.4×10^{-12}
C_3 reorientation of the cations Gu 2	41.1	1.2×10^{-13}
Quasi-isotropic reorientation of the anions	46.2	1.0×10^{-13}

The activation energy obtained for the C_3 reorientation of the guanidinium cation Gu 2 is very similar to those reported for other guanidinium salts [1–6]. As far as the anion motion goes, it is interesting to note that its obtained activation energy turns out to be intermediate between the analogous values in 1:1 and 3:1 complexes. While in the former complexes the activation energy was about 20 kJ/mol [1, 2], in the latter it was 67 kJ/mol [4, 5]. Thus the value of 46 kJ/mol found for the anion in the compound studied evidently reflects the intermediate number of hydrogen bonds in which the anion is involved.

[1] A Kozak, M. Grottel, A. Kozioł, and Z. Pająk, J. Phys. C, Solid State Phys. **20,** 5433 (1987).

[2] M. Grottel, A. Kozak, A. Kozioł, and Z. Pająk, J. Phys.: Condens. Matter **1,** 7069 (1989).

[3] Z. Pająk, A. Kozak, and M. Grottel, Solid State Commun. **65,** 671 (1988).

[4] M. Grottel, A. Kozak, H. Małuszyńska, and Z. Pająk, J. Phys.: Condens. Matter **4,** 1837 (1992).

[5] A. Kozak, M. Grottel, and Z. Pająk, Acta Phys. Polonica, **83,** 219 (1993).

[6] M. Grottel, A. Kozak, and Z. Pająk, Z. Naturforsch. **50 a,** 742 (1995).

[7] B. Bukveckij, A. Gerasimenko, I. Kondratiuk, R. Davidovich, and M. Medkov, Koord. Chimia **13,** 661 (1987).

[8] E. R. Andrew, Phys. Rev. **91,** 425 (1953).

[9] J. H. Van Vleck, Phys. Rev. **74,** 1168 (1948).

[10] J. Wąsicki, M. Grottel, A. Kozak, and Z. Pająk, J. Phys.: Condens. Matter **6,** 2491 (1994).

[11] J. S. Waugh and E. I. Fiedin, Fiz. Tverd. Tela, **4,** 2233 (1962).

[12] to be published.

[13] D. C. Look and I. J. Lowe, J. Chem. Phys. **44,** 3437 (1966).