^{35}Cl NQR and Crystal Structure Studies of Salts of Chlorodifluoro- and Dichloroacetic Acid *

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The ^{35}Cl NQR spectra of several chlorodifluoroacetates were studied as a function of temperature, including the acid ClF_2CCOOH. The cations were: Ammonium, guanidinium, paramethylanilinium. Also some acid salts $M^{\oplus}ClF_2CCOO^{\ominus} \cdot n\text{-}ClF_2CCOOH$ ($n \geq 1$) were studied by ^{35}Cl NQR. The bleaching temperatures of the NQR signals were determined. In the para-methylanilinium salt and in the guanidinium salt a phase transition has been observed. The crystal structure of guanidinium chlorodifluoroacetate has been determined at room temperature ($a = 1089$ pm, $b = 845$ pm, $c = 832$ pm, space group Pnma, $Z = 4$). For comparison, guanidinium dichloroacetate was studied by ^{35}Cl NQR and by X-ray diffraction, too: $P2_1/c$, $Z = 4$, $a = 804$ pm, $b = 1202$ pm, $c = 1080$ pm, $\beta = 131.58°$. For guanidinium chlorodifluoroacetate and chlorodifluoroacetic acid, the ^{35}Cl spin lattice relaxation time T_1 and the line width have been followed up as a function of temperature. Therefrom, the activation energies of the reorientation motion of the group $-CF_2Cl$ have been determined to be 14 kJ · mol^{-1} (from T_1) and 12.5 kJ · mol^{-1} (from $\Delta\nu$) for the pure acid and 9.2 kJ · mol^{-1} and 8.8 kJ · mol^{-1}, respectively, for the guanidinium salt.

Introduction

Proton transfer compounds with trichloroacetic acid, (TCA), as proton donating part have been investigated extensively, especially by ^{35}Cl NQR [1–7]. Lynch et al. [8] worked on the problem, particularly by using ^{35}Cl NQR spectroscopy, of acid salts of trichlor- and dichloroacetic acid, and they discussed the results in the light of crystal structure and hydrogen bond of carboxylic acids. A review on the later topic is given by Speakman [9].

Whereas the acidity of the dichloroacetic acid, (DCA), is considerably weaker than that of TCA, leading to a diminuation of the proton transfer power, chlorodifluoroacetic acid, (ClF_2A), is comparable in its acidity with TCA. We have investigated a number of salts of ClF_2A, neutral and acid ones, and shall report here on their properties. Also the pure acid ClF_2CCOOH was studied with ^{35}Cl; ^{35}Cl NQR spectroscopy at 77 K of his compound is reported in [10]. For comparison, we have studied the structure and ^{35}Cl NQR of the guanidinium salts of carboxylic acids and of guanidinium dichloroacetate.

Experimental

The compounds studied were prepared by mixing stoichiometric amounts of an aqueous solution of the carboxylic acid and the base of the cation. The solutions were slightly acidified with the carboxylic acid; in preparation of the acid salts a small excess of the acid above the wanted stoichiometry was present, too. The solutions were crystallized at room temperature by slow evaporation of the solvent H_2O. The basic chemicals were of laboratory grade (Aldrich). In Table 1 the compounds studied are given with the C, H, N elemental analysis for some of them.

For the crystal stucture determination a 4-circle X-ray diffractometer was used. Suitable crystals for the X-ray work were grown from aqueous solution. The experimental conditions for the X-ray work and some crystallographic data of the studied compounds are given in Table 2. The structures were determined by direct methods [11] The hydrogen positions have been taken from difference Fourier synthesis and all atomic coordinates were least squares refined [12].

The ^{35}Cl NQR spectra have been recorded with a superregenerative spectrometer. The wanted temperatures at the sample site were created by a temperature and flow regulated nitrogen gas stream, by immersion of the sample in liquid nitrogen, by thermostats with methanol or silicon oil as the cooling (heating) liquid, respectively, adapted to the temperature range in

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Table 1. Characterization of compounds investigated; chemical analysis in %weight. [a] $n \geq 1$.

Compound	Habitus	Colour	m.p. [K]	C		H		N	
				cals.	found	cals.	found	cals.	found
$X = ClF_2CCOO$									
$C(NH_2)_3^{\oplus} \cdot X^{\ominus}$	plate	colourless	441	19.01	18.95	3.19	3.13	22.17	22.94
$NH_4^{\oplus} \cdot X^{\ominus}$	prism	colourless	360	16.29	15.91	2.73	2.45	9.50	8.47
$4\text{-}(CH_3)C_6H_4NH_3^{\oplus} \cdot X^{\ominus}$	prism	colourless-yellowish	329	42.28	41.74	4.73	4.63	5.48	5.28
$KX \cdot nHX$ [a]	prism	colourless	381	–	15.56	–	0.29	–	–
$RbX \cdot nHX$	prism	colourless	401	–	13.27	–	0.18	–	–
$CsX \cdot nHX$	prism	colourless	359	–	12.02	–	0.21	–	–
$TlX \cdot nHX$	needle	colourless	315	–	8.97	–	0.22	–	–
$X = Cl_2HCCOO$									
$C(NH_2)_3^{\oplus} \cdot X^{\ominus}$	prism	colourless	435	19.11	19.17	3.51	3.75	22.38	22.35

question. For completeness, at some temperatures the ^{37}Cl NQR spectra were observed, too.

Applying the $\pi - \tau - \pi/2$ pulse sequence, the ^{35}Cl spin lattice relaxation time was determined with pulse NMR equipment (Matec). For the sample temperature in the $T_1\,(^{35}Cl)$ measurements a flow and temperature regulated nitrogen gas stream was used.

Results

Crystal Structures of Guanidinium chlorodifluoroacetate (GuClF₂A) and Guanidinium dichloroacetate (GuDCA)

In Table 2 crystallographic data of the title compounds are given together with the experimental conditions for the structure determination. We mention that we have non unique decision about the space group of GuClF$_2$A. Both, the centrosymmetric space group listed in Table 2 and the correlating noncentrosymmetric space group C_{2v}^9-Pna2$_1$ are possible and the crystal structure can be described within both crystal symmetries. In the noncentrosymmetric case the *R*-value is, of course, slightly lower. We return to this question lateron in the paper.

The positional parameters in the unit cell of GuClF$_2$A and GuDCA listed in Table 3 together with the thermal parameters. In Table 4 we have collected the intraionic distances and angles for GuClF$_2$A and GuDCA; included are some interionic distances characterizing the hydrogen bonds.

Figure 1 shows the projection of the unit cell of GuClF$_2$A along the crystallographic *c*-axis. The hydrogen bond system is marked by dashed lines. Figure 2 shows the projection of the unit cell of GaDCA along the *a*-axis. Again the hydrogen bonds are marked.

^{35}Cl Nuclear Quadrupole Resonance

Chlorodifluoroacetic Acid, ClF₂CCOOH

The ^{35}Cl NQR spectra of the compounds listed in Table 1 have been measured as a function of temperature. The ^{35}Cl NQR frequency of the single line spec-

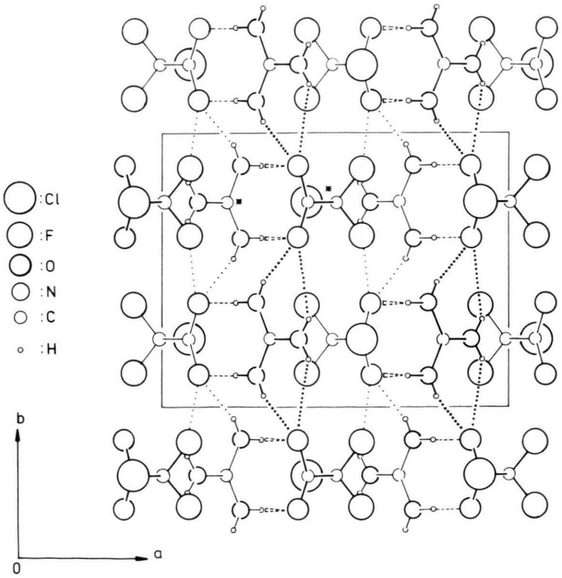


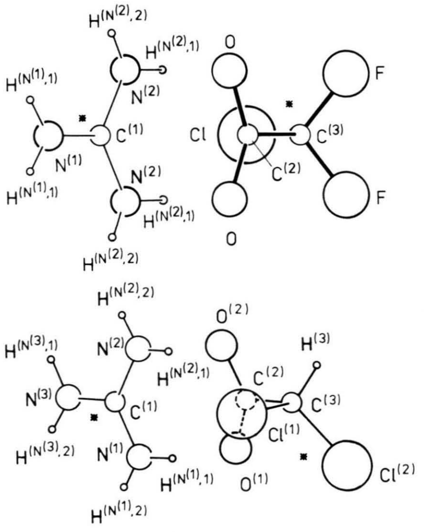
Fig. 1. Projection of the unit cell of guanidinium chlorodifluoroacetate along the axis [001] onto the *ab*-plane. The cation $C(NH_2)_3^{\oplus}$ and the anion $ClF_2CCOO^{\ominus}$ for which the coordinates are given in Table 3 are marked by *. The hydrogen bonds N–H ··· O are shown by dashed lines.

Table 2. Experimental conditions for the crystal structure determination and crystallographic data of $[C(NH_2)_3^{\oplus}] \cdot [ClF_2CCOO^{\ominus}]$ and of $[C(NH_2)_3^{\oplus}] \cdot [Cl_2HCCOO^{\ominus}]$. Diffractometer: Stoe-Stadi 4; wavelength: 71.069 pm (MoKα); monochromator: Graphite (002); scan: $2\vartheta/\omega$; $M = 189.55$ and 188.01, respectively.

Formula	$C_3H_6ClF_2N_3O_2$	$C_3H_7Cl_2N_3O_2$
Crystal size	$(0.3 \times 0.4 \times 1.4)\,mm^3$	$(0.3 \times 0.35 \times 1.4)\,mm^3$
Temperature / K	300	298
Absorption coefficient (μ/m^{-1})	489	781
$(\sin \vartheta/\lambda)_{max}$/pm	0.00538	0.00650
Number of measured reflexions	1996	2163
Symmetry independent reflexions	536	1771
Reflexions considered	531	1644
Number of free parameters	66	111
$F(000)$	384	384
$R(F)$	0.0628	0.0425
$R_w(F)$	0.0650	0.0409
Lattice constants:		
a/pm	1089.3(4)	803.6(3)
b/pm	845.3(3)	1201.6(4)
c/pm	832.4(3)	1080.2(4)
β/°	–	131.583(5)
Volume of the unit cell $V \cdot 10^{-6}/(pm)^3$	766.46(3)	780.19(4)
Space group	Pnma-D_{2h}^{16}	$P2_1/c$-C_{2h}^{5}
Formula units per unit cell	4	4
ϱ_{calc}/Mg · m^{-3}	1.643 (300 K)	1.601 (298 K)
ϱ_{pykn}/Mg · m^{-3}	1.63 (295 K)	1.56 (296 K)
Point positions (F, O, N$^{(2)}$, H) in 8d:	$x, y, z;\ \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z;$ $\bar{x}, \frac{1}{2}+y, \bar{z};\ \frac{1}{2}-x, \bar{y}, \frac{1}{2}+z;$ $\bar{x}, \bar{y}, \bar{z};\ \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z;$ $x, \frac{1}{2}-y, z;\ \frac{1}{2}+x, y, \frac{1}{2}-z$	All atoms in 4e: $x, y, z; \bar{x}, \bar{y}, \bar{z};$ $x, \frac{1}{2}-y, \frac{1}{2}+z;$ $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z.$

(Cl, C, N$^{(1)}$, in 4c: $x, \frac{1}{4}, z; \bar{x}, \frac{3}{4}, \bar{z}; \frac{1}{2}-x, \frac{3}{4}, \frac{1}{2}+z; \frac{1}{2}+x, \frac{1}{4}, \frac{1}{2}-z.$

Numbering of atoms in the molecule (see Table 3 and 4)



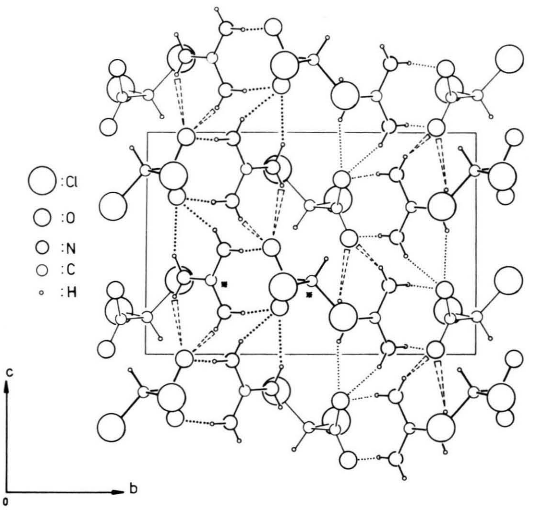


Fig. 2. Projection of the unit cell of guanidinium dichloroacetate along the axis [100] onto the *bc*-plane. The cation $C(NH_2)_3^{\oplus}$ and the anion $Cl_2HCCOO^{\ominus}$ for which the cordinates are given in Table 3 are marked by *. The hydrogen bonds N–H ··· O are shown by dashed lines.

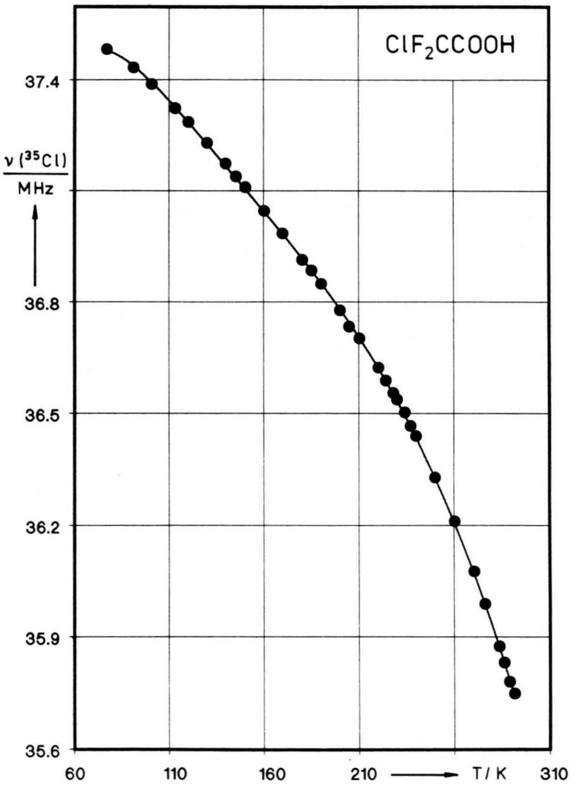


Fig. 3. Temperature dependence of the ^{35}Cl NQR line (single line spectrum) of chlorodifluoroacetic acid.

Table 3. Positional and thermal parameter of $[C(NH_2)_3^{\oplus}][ClF_2CCOO^{\ominus}]$ and $[C(NH_2)_3^{\oplus}][Cl_2HCCOO^{\ominus}]$. The temperature factor is of the form:

$$T = \exp\{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\}.$$

The U_{ij} are given in $(pm)^2$; U is isotropic mean squares thermal amplitude.

Atom	x/a	y/b	z/c	U_{11}, U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$[C(NH_2)_3^{\oplus}][ClF_2CCOO^{\ominus}]$									
Cl	0.4205(2)	0.7500(0)	0.5263(2)	1203(18)	1307(22)	545(13)	0(0)	9(10)	0(0)
F	0.5795(3)	0.8732(5)	0.6950(4)	1356(28)	1803(38)	1170(28)	1044(27)	−467(20)	−284(24)
O	0.3935(3)	0.6191(3)	0.9012(3)	842(20)	359(17)	558(20)	22(15)	−45(15)	22(16)
$C^{(1)}$	0.1864(5)	0.7500(0)	0.2345(8)	493(32)	414(40)	405(34)	0(18)	32(28)	0(0)
$C^{(2)}$	0.4230(5)	0.7500(0)	0.8504(7)	594(34)	499(43)	391(36)	0(0)	86(26)	0(0)
$C^{(3)}$	0.5057(6)	0.7500(0)	0.6990(8)	611(38)	643(47)	664(45)	0(0)	−73(34)	0(0)
$N^{(1)}$	0.1047(6)	0.7500(0)	0.3510(8)	748(42)	607(42)	623(40)	0(0)	−148(32)	0(0)
$N^{(2)}$	0.2277(4)	0.6163(4)	0.1767(5)	801(26)	370(23)	679(30)	−6(21)	−187(20)	50(21)
$H^{(N^{(1)})}$	0.0749(36)	0.6773(51)	0.3829(52)	600					
$H^{(N^{(2)},1)}$	0.2867(31)	0.6175(47)	0.0905(43)	600					
$H^{(N^{(2)},2)}$	0.2063(38)	0.5421(51)	0.2193(46)	600					
$[C(NH_2)_3^{\oplus}][Cl_2HCCOO^{\ominus}]$									
$Cl^{(1)}$	1.2789(1)	0.4190(1)	0.3030(1)	512(4)	969(5)	863(5)	53(3)	492(4)	177(4)
$Cl^{(2)}$	0.9627(1)	0.6006(1)	0.1673(1)	660(5)	791(4)	772(5)	16(3)	430(4)	−257(4)
$O^{(1)}$	0.7842(2)	0.4081(1)	0.2117(2)	347(4)	655(9)	417(8)	93(7)	182(7)	−18(7)
$O^{(2)}$	1.0816(2)	0.3826(1)	0.4786(2)	428(9)	639(9)	413(8)	−20(7)	182(7)	−86(7)
$C^{(1)}$	0.6005(3)	0.1958(2)	0.3351(3)	379(11)	462(11)	469(11)	1(9)	283(10)	19(9)
$C^{(2)}$	0.9810(3)	0.4248(2)	0.3400(3)	364(11)	428(10)	438(12)	−15(9)	252(10)	24(9)
$C^{(3)}$	1.1225(3)	0.5034(2)	0.3294(3)	377(12)	538(12)	469(13)	57(10)	246(11)	56(10)
$N^{(1)}$	0.5135(3)	0.2393(2)	0.1911(2)	419(11)	708(13)	387(11)	129(10)	170(9)	−17(10)
$N^{(2)}$	0.7901(3)	0.2372(2)	0.4722(2)	457(11)	655(12)	367(10)	81(9)	226(10)	0(0)
$N^{(3)}$	0.4990(4)	0.1151(2)	0.3449(3)	554(14)	658(13)	624(14)	132(11)	376(12)	−1(11)
$H^{(N^{(1)},1)}$	0.5841(35)	0.2959(17)	0.1856(25)	600					
$H^{(N^{(1)},2)}$	0.4072(36)	0.2127(18)	0.1101(26)	600					
$H^{(N^{(2)},1)}$	0.8806(34)	0.2893(16)	0.4663(25)	600					
$H^{(N^{(2)},2)}$	0.8389(37)	0.2098(18)	0.5578(27)	600					
$H^{(N^{(3)},1)}$	0.5585(35)	0.0856(16)	0.4444(26)	600					
$H^{(N^{(3)},2)}$	0.3862(37)	0.0880(17)	0.2606(27)	600					
$H^{(3)}$	1.2300(34)	0.5462(16)	0.4295(25)	600					

trum of ClF_2A at 77 K was already reported by Lucken [10], and within the limits of error there is in agreement with the value we found (37.486 MHz this paper, 37.485 MHz [10]). In Fig. 3 the graph $\nu(^{35}Cl) = f(T)$ is shown.

An experimental problem occurred in the study of ClF_2A, the origin of which is not clear yet. The first sample of ClF_2A used showed at $T = 230$ K a small peak in the differential thermoanalysis, DTA. We carefully studied the temperature dependence of $\nu(^{35}Cl)$ around $T = 230$ K but dit not find any sign of a phase transition in the NQR spectrum. A second sample, of the same source (Aldrich), was without a DTA peak, and all the data on ClF_2A we report here have been collected with the second sample. The interesting point is that $\nu(^{35}Cl) = f(T)$ is almost identical for both samples, distinctly differing at 77 K by 20 kHz and merging at temperatures above 200 K. Some impurity effect seems to be responsible for that observation.

ClF_2A melts at 297 K. Approaching the melting point, the width of the ^{35}Cl NQR line broadens strongly, as seen in the $\Delta\nu = f(T)$ curve (Figure 4). $T_1(^{35}Cl)$ decreases strongly with increasing temperature and is < 100 μs shortly below the melting point of the compound; this is seen in Figure 5.

For ClF_2A and all other compounds studied here, we have rationalized the temperature dependence of the ^{35}Cl NQR frequencies by developing $\nu(^{35}Cl) = f(T)$ in a power series

$$\nu(^{35}Cl) = \sum_{i=-1}^{3} a_i T^i. \tag{1}$$

The coefficients of the power series are given in Table 5. In Table 6 we list the ^{35}Cl NQR frequencies at 77 K and at the bleaching out point (or an other chosen temperature) together with the signal to noise ratio, (S/N), and some other data of interest.

Table 4. Selected intra- and intermolecular distances (in pm) and intra- and intermolecular angles (in degree) of $[C(NH_2)_3^{\oplus}][ClF_2CCOO^{\ominus}]$ and $[C(NH_2)_3^{\oplus}][Cl_2HCCOO^{\ominus}]$, determined by X-ray diffraction.

Atoms	Distance	Atoms	Angle
$[C(NH_2)_3^{\oplus}][ClF_2CCOO^{\ominus}]$			
Intramolecular:			
$Cl-C^{(3)}$	171.1(6)	$Cl-C^{(3)}-F$	108.1(4)
$F-C^{(3)}$	131.6(4)	$Cl-C^{(3)}-C^{(2)}$	111.6(4)
$C^{(3)}-C^{(2)}$	155.0(8)	$F-C^{(3)}-F$	104.6(5)
$O-C^{(2)}$	122.7(3)	$F-C^{(3)}-C^{(2)}$	112.1(4)
$N^{(1)}-C^{(1)}$	131.6(7)	$O-C^{(2)}-O$	128.7(6)
$N^{(2)}-C^{(1)}$	130.8(4)	$O-C^{(2)}-C^{(3)}$	115.6(3)
$N^{(1)}-H^{(N(1))}$	74.4(30)	$N^{(1)}-C^{(1)}-N^{(2)}$	120.2(3)
$N^{(2)}-H^{(N(2),1)}$	96.4(34)	$N^{(2)}-C^{(1)}-N^{(2)}$	119.5(5)
$N^{(2)}-H^{(N(2),2)}$	75.7(33)		
Intermolecular:			
$O\cdots N^{(1)}$ (i)	314.8(3)	$N^{(1)}-H^{(N(1))}\cdots O$	141.3(44)
$O\cdots N^{(1)}$ (ii)	328.2(6)	$N^{(1)}-H^{(N(1))}\cdots O$	134.7(45)
$O\cdots N^{(2)}$ (iii)	292.0(5)	$N^{(2)}-H^{(N(2),1)}\cdots O$	173.8(31)
$O\cdots N^{(2)}$ (i)	303.2(5)	$N^{(2)}-H^{(N(2),2)}\cdots O$	160.3(42)
$O\cdots H^{(N(1))}$ (i)	253.4(44)	(i): $\frac{1}{2}-x,\ 1-y,\ \frac{1}{2}+z$	
$O\cdots H^{(N(1))}$ (ii)	271.6(39)	(ii): $\frac{1}{2}+x,\ y,\ \frac{3}{2}-z$	
$O\cdots H^{(N(2),1)}$ (iii)	195.9(36)	(iii): $x,\ y,\ 1+z$	
$O\cdots H^{(N(2),2)}$ (i)	230.9(40)		
$[C(NH_2)_3^{\oplus}][Cl_2HCCOO^{\ominus}]$			
Intramolecular:			
$Cl^{(1)}-C^{(3)}$	178.0(2)	$Cl^{(1)}-C^{(3)}-Cl^{(2)}$	110.2(1)
$Cl^{(2)}-C^{(3)}$	175.9(2)	$Cl^{(1)}-C^{(3)}-H^{(3)}$	106.2(12)
$H^{(3)}-C^{(3)}$	96.9(19)	$Cl^{(2)}-C^{(3)}-H^{(3)}$	106.2(12)
$C^{(3)}-C^{(2)}$	154.0(3)	$Cl^{(1)}-C^{(3)}-C^{(2)}$	107.3(1)
$O^{(1)}-C^{(2)}$	124.6(2)	$Cl^{(2)}-C^{(3)}-C^{(2)}$	113.2(1)
$O^{(2)}-C^{(2)}$	124.3(2)	$H^{(3)}-C^{(3)}-C^{(2)}$	113.4(13)
$N^{(1)}-C^{(1)}$	131.8(3)	$O^{(1)}-C^{(2)}-O^{(2)}$	127.2(2)
$N^{(2)}-C^{(1)}$	132.9(2)	$O^{(1)}-C^{(2)}-C^{(3)}$	118.0(2)
$N^{(3)}-C^{(2)}$	131.6(3)	$O^{(2)}-C^{(2)}-C^{(3)}$	114.7(2)
$N^{(1)}-H^{(N(1),1)}$	91.3(20)	$N^{(1)}-C^{(1)}-N^{(2)}$	119.0(2)
$N^{(1)}-H^{(N(1),2)}$	77.8(20)	$N^{(1)}-C^{(1)}-N^{(3)}$	121.0(2)
$N^{(2)}-H^{(N(2),1)}$	99.3(20)	$N^{(2)}-C^{(1)}-N^{(3)}$	120.0(2)
$N^{(2)}-H^{(N(2),2)}$	79.8(21)		
$N^{(3)}-H^{(N(3),1)}$	91.0(20)		
$N^{(3)}-H^{(N(3),2)}$	81.3(21)		
Intermolecular:			
$O^{(1)}\cdots N^{(1)}$	287.3(2)	$N^{(1)}-H^{(N(1),1)}\cdots O^{(1)}$	170.1(19)
$O^{(1)}\cdots N^{(2)}$ (i)	314.8(2)	$N^{(2)}-H^{(N(2),2)}\cdots O^{(1)}$	149.2(21)
$O^{(1)}\cdots N^{(3)}$ (i)	299.6(3)	$N^{(3)}-H^{(N(3),1)}\cdots O^{(1)}$	151.5(18)
$O^{(1)}\cdots H^{(N(1),1)}$	197.0(21)		
$O^{(1)}\cdots H^{(N(2),2)}$ (i)	243.6(22)		
$O^{(1)}\cdots H^{(N(3),1)}$ (i)	216.3(21)		
$O^{(2)}\cdots N^{(1)}$ (ii)	298.1(2)	$N^{(1)}-H^{(N(1),2)}\cdots O^{(2)}$	148.8(23)
$O^{(2)}\cdots N^{(2)}$	288.6(2)	$N^{(2)}-H^{(N(2),1)}\cdots O^{(2)}$	173.3(17)
$O^{(2)}\cdots N^{(3)}$ (ii)	304.8(2)	$N^{(3)}-H^{(N(3),2)}\cdots O^{(2)}$	145.1(20)
$O^{(2)}\cdots H^{(N(1),2)}$ (ii)	228.9(21)	(i): $x,\ \frac{1}{2}-y,\ -\frac{1}{2}+z,$	
$O^{(2)}\cdots H^{(N(2),1)}$	189.7(21)	(ii): $1+x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$	
$O^{(2)}\cdots H^{(N(3),2)}$	234.5(21)		

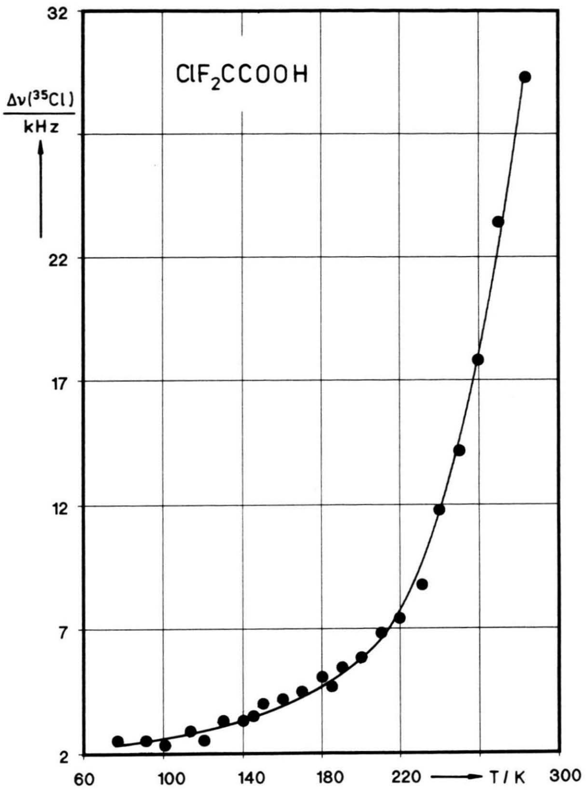


Fig. 4. Temperature dependence of the ^{35}Cl NQR line width (half width) $\Delta\nu$, in chlorodifluoroacetic acid.

Guanidinium chlorodifluoroacetate, $C(NH_2)_3^{\oplus}\cdot ClF_2CCOO^{\ominus}$

The ^{35}Cl NQR spectrum of GuClF$_2$A, shown in Fig. 6, is a single line spectrum for both solid phases of the compound, the low temperature phase II and the high temperature phase I. For phase II, both the line width $\Delta\nu(^{35}Cl)$ and the relaxation time $T_1(^{35}Cl)$ have been followed up from 77 K to the phase transition temperature $T_{I,II} = 296$ K $\cdots$ 303 K. The results are graphically shown in Figs. 7 and 8, respectively. A single ^{35}Cl NQR line for GuClF$_2$A is in agreement with the crystal structure determined at room temperature.

$NH_4^{\oplus}\cdot ClF_2CCOO^{\ominus}$, $4\text{-}(CH_3)C_6H_4NH_3^{\oplus}\cdot ClF_2CCOO^{\ominus}$

The ^{35}Cl NQR spectrum, a single line, of ammonium chlorodifluoroacetate was studied in the range $77 \leq T/K \leq$ fade out temperature (T_b). Also para-methylanilinium chlorodifluoroacetate shows a single line

Table 5. Power series expansion of $\nu(^{35}\mathrm{Cl}) = f(T)$ for the investigated compounds: $f(T) = \sum_{i=-1}^{3} a_i T^i$; ΔT: temperature range covered; z: number of data; σ: standard deviations.

Compound		ΔT / K	z	σ / kHz	a_{-1} / MHz · K	a_0 / MHz	$a_1 \cdot 10^3$ / MHz · K^{-1}	$a_2 \cdot 10^6$ / MHz · K^{-2}	$a_2 \cdot 10^9$ / MHz · K^{-3}
X = $\mathrm{ClF_2CCOO}$									
$\mathrm{ClF_2CCOOH}$		77–291.1	32	4.3	−103.719	40.912	−36.752	146.058	−262.904
$\mathrm{C(NH_2)_3^{\oplus} \cdot X^{\ominus}}$	phase II	77–296.2	16	8.7	−70.915	38.522	−50.338	216.090	−617.529
	phase I	303.3–423.5	29	0.8	5044.981	−40.637	243.913	−453.438	313.760
$\mathrm{NH_4^{\oplus} \cdot X^{\ominus}}$		77–200.9	28	2.4	−158.978	41.420	−57.274	240.292	−419.227
$\mathrm{4\text{-}(CH_3)C_6H_4NH_3^{\oplus} \cdot X^{\ominus}}$		77–118.2	12	2.2	101.303	33.071	229.198	−123.038	–
$\mathrm{KX} \cdot n\mathrm{HX}$		77–105.1	11	2.7	−0.813	37.415	−2.483	−43.502	–
		77–105.1	11	2.2	−218.923	43.808	−81.694	255.143	–
		77–105.1	11	2.2	−76.723	38.770	−27.034	61.903	–
		77–107.1	11	2.9	−137.085	40.674	−53.940	163.626	–
$\mathrm{RbX} \cdot n\mathrm{HX}$		77– 96.0	9	3.4	−998.028	69.262	−360.427	1240.215	–
		77–106.1	13	5.6	−496.338	51.691	−171.404	547.666	–
$\mathrm{TlX} \cdot n\mathrm{HX}$		77– 96.1	9	3.6	−1069.829	73.538	−413.998	1490.040	–
		77–100.3	11	2.5	−129.523	40.121	−34.837	52.981	–
		77– 92.1	7	3.8	−665.026	59.236	−296.744	985.761	–
		77–100.3	11	3.6	−33.086	36.506	−0.274	−79.612	–
X = $\mathrm{Cl_2HCCOO}$									
$\mathrm{C(NH_2)_3^{\oplus} \cdot X^{\ominus}}$		77–404.7	18	6.5	−55.287	38.463	−16.170	46.554	−70.000
		77–404.7	19	8.5	−54.424	38.312	−16.016	47.080	−72.409

Table 6. Some ^{35}Cl frequencies at selected temperature and signal to noise ratio, S/N (lock in technique; time constant 10 s). ν_b: bleaching out frequency; T_b: bleaching out temperature.

Compound (X = $\mathrm{ClF_2CCOO}$)	$\nu(^{35}\mathrm{Cl})$ / MHz $\left(\frac{T}{\mathrm{K}}\right)$	S / N	$\nu_b(^{35}\mathrm{Cl})$ / MHz $\left(\frac{T_b}{\mathrm{K}}\right)$	S / N
$\mathrm{ClF_2CCOOH}$	37.486 (77)	134	35.751 (291.2) [a]	2
$\mathrm{C(NH_2)_3^{\oplus} \cdot X^{\ominus}}$				
phase II	34.989 (77)	85	30.244 (296.2)	2
phase I	17.018 (303.3)	4	17.080 (423.5)	2
$\mathrm{NH_4^{\oplus} \cdot X^{\ominus}}$	36.178 (77)	34	35.420 (200.9)	2
$\mathrm{4\text{-}(CH_3)C_6H_4NH_3^{\oplus} \cdot X^{\ominus}}$	35.422 (77)	30	34.919 (118.2)	2
$\mathrm{KX} \cdot n\mathrm{HX}$	36.956 (77)	6	36.666 (105.1)	2
	36.187 (77)	7	35.957 (105.1)	<2
	36.060 (77)	7	35.883 (105.1)	<2
	35.711 (77)	8	35.510 (105.1)	<2
$\mathrm{RbX} \cdot n\mathrm{HX}$	35.901 (77)	6	35.693 (96.0)	<2
	35.291 (77)	5	34.992 (106.1)	<2
$\mathrm{CsX} \cdot n\mathrm{HX}$	36.060 (77)	3	–	–
	35.729 (77)	4	–	–
$\mathrm{TlX} \cdot n\mathrm{HX}$	36.601 (77)	8	36.383 (96.1)	2
	36.070 (77)	18	35.868 (100.3)	<3
	35.674 (77)	19	35.534 (92.1)	2
	35.583 (77)	19	35.346 (100.3)	2
$\mathrm{Cl_2HCCOOH}$ [b]	38.807 (77)			
	37.729 (77)			
$\mathrm{C(NH_2)_3^{\oplus} \cdot Cl_2HCCOO^{\ominus}}$				
	36.746 (77)	70	34.762 (404.7)	<2
	36.621 (77)	44	34.598 (404.7)	<2

[a] 6 K below the melting point. – [b] lit. [14].

^{35}Cl NQR spectrum. For these two compounds $\nu(^{35}\mathrm{Cl}) = f(T)$ is shown in Figure 9; frequencies and parameterization of $\nu(^{35}\mathrm{Cl}) = f(T)$ are found in Tables 5 and 6. DTA experiments have shown that $\mathrm{4\text{-}(CH_3)C_6H_4NH_3^{\oplus} \cdot ClF_2CCOO^{\ominus}}$ undergoes a phase transition solid ↔ solid at $T = 295$ K. Since the fade out temperature T_b of the ^{35}Cl NQR line is near 120 K, it was not our aim to study the crystal structure of this compound.

$\mathrm{M^{\oplus} ClF_2CCOO^{\ominus} \cdot nClF_2CCOOH}$

We have tried, see Table 1, to synthesize acid salts of the chlorodifluoroacetic acid. The results of the chemical analysis, preliminary X-ray diffraction studies, and the ^{35}Cl NQR results are not concordant. We report here the temperature dependence of the ^{35}Cl NQR spectra for the salts with M = K, Rb, Cs, and Tl; n is unknown, ≥ 1. Figure 10 shows $\nu(^{35}\mathrm{Cl}) = f(T)$; frequencies etc. are given in Tables 5 and 6.

Guanidinium dichloroacetate,
$\mathrm{C(NH_2)_3^{\oplus} \cdot Cl_2HCCOO^{\ominus}}$

GuDCA reveals a two line ^{35}Cl NQR spectrum, smoothly following the Bayer model [13]. $\nu(^{35}\mathrm{Cl}) = f(T)$ is shown in Figure 11. The two line spectrum

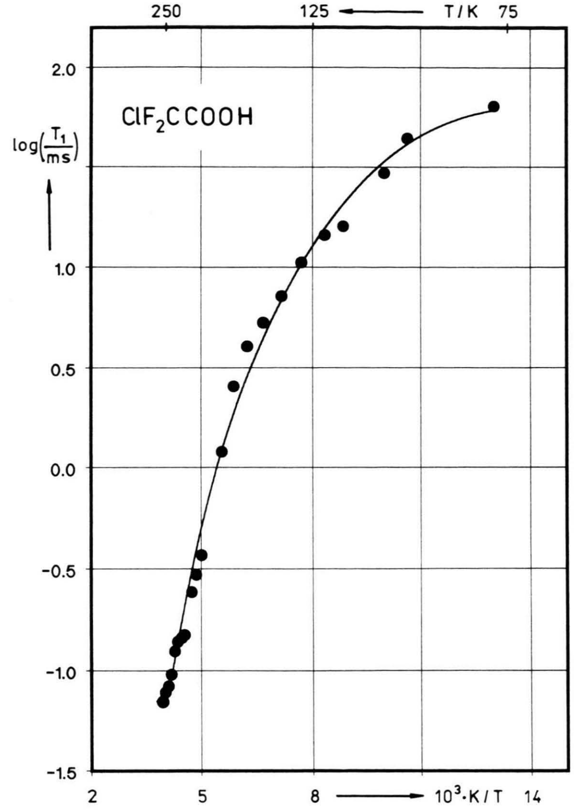


Fig. 5. Logarithm ($\log_{10}$) of the spin lattice relaxation time $T_1(^{35}Cl)$ as a function of the reciprocal temperature, $1/T$, in chlorodifluoroacetic acid.

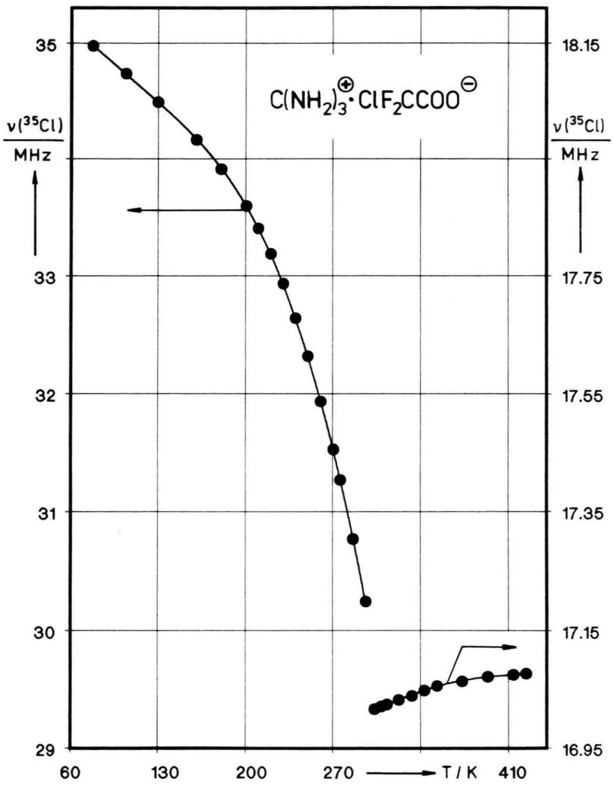


Fig. 6. Temperature dependence of $\nu(^{35}Cl)$ in guanidinium chlorodifluoroacetate, $C(NH_2)_3^{\oplus} \cdot ClF_2CCOO^{\ominus}$.

shows no sign for as phase transition over the whole temperature range studied. Bleaching out (fade out) of the chlorine NQR resonances was observed; the signals disappear at 405 K (30° below the melting point). For ^{35}Cl NQR frequencies etc. see Tables 5 and 6

Discussion

The crystal structures of the two guanidinium salts, guanidinium chlorodifluoroacetate and guanidinium dichloroacetate, are determined by a network of the hydrogen bonds $N-H \cdots O$ one finds in both crystalline compounds. The guanidinium ion can form six bonds $N-H \cdots O$. There are, however, only two oxygen per anion. Therefore one expects at most three bonds $N-H \cdots O$ for each oxygen, which is quite unlikely and, to our knowledge, never reported in literature.

Let as first consider the intraionic structure of the guanidinium ion in both compounds. The best plane through the carbon atom and the three nitrogen atoms is, for $GuClF_2A$:

$$0.7400\,x - 0.6726\,z = 4.0343$$

and for GuDCA:

$$0.5043\,x + 0.6671\,y - 0.5477\,z = 15.0014\,.$$

The deviations of the atoms from these planes are very small (in pm): $+0.32$(C), $-0.11\,(N^{(1),(2)})$ in $GuClF_2A$; 1.07(C), -0.35, $-0.36(N^{(1,2,3)})$ in GuDCA. This proves: The carbon-nitrogen frame in the guanidinium ion is essentially planar with a very slight deformation to a trigonal pyramid. The hydrogens of the guanidinium ion are in both compounds out of plane, but we shall not discuss this in detail because of the uncertainties of the hydrogen positions.

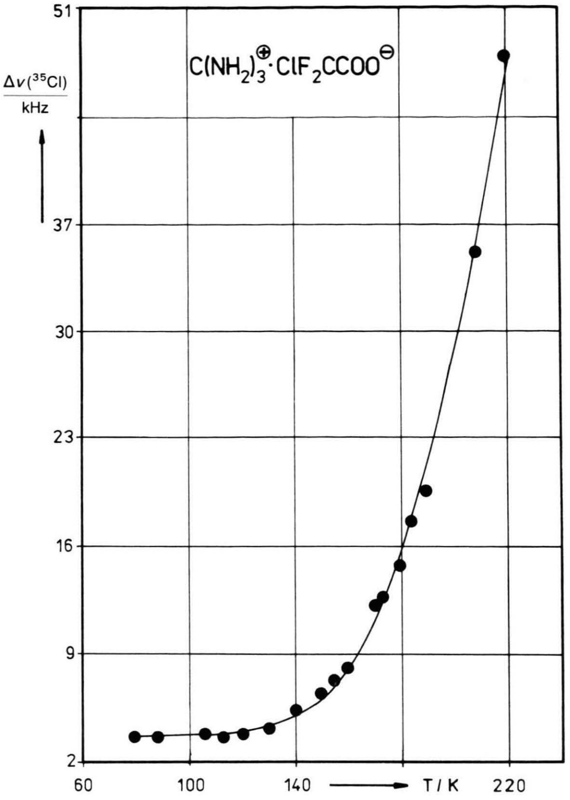


Fig. 7. Line width (half width) $\Delta\nu$ of the ^{35}Cl NQR line of guanidinium chlorodifluoroacetate, $C(NH_2)_3^{\oplus} \cdot ClF_2CCOO^{\ominus}$, phase II.

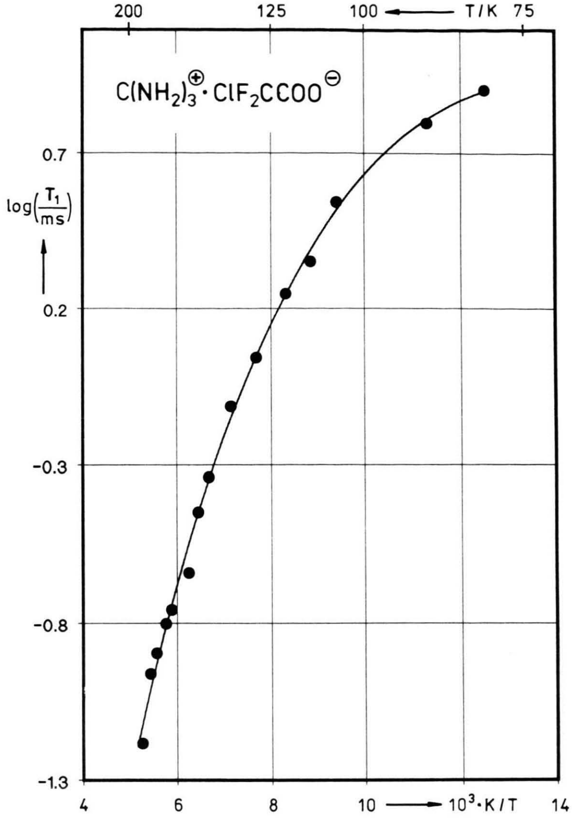


Fig. 8. $\log_{10}[T_1(^{35}Cl)] = f(1/T)$ of guanidinium chlorodifluoroacetate, phase II.

As mentioned above, the crystal structure of $GuClF_2A$ can be described in the centrosymmetric space group Pnma and in the acentric space group $Pna2_1$. In both descriptions, the ^{35}Cl NQR single line spectrum of $GuClF_2A$ is in accordance with the crystal structure. A deciding experiment would be provided by ^{14}N NQR, which in the case of centrosymmetry would show two different ^{14}N nuclear quadrupole coupling constants (for $N^{(1)}$ and $N^{(2)}$), and in the case of noncentrosymmetry three coupling constants of ^{14}N ($N^{(1)}$, $N^{(2)}$, $N^{(3)}$). A ^{14}N NQR experiment and crystal structure determination well above and below the phase transition point have to be done.

In agreement with the crystal structure, the ^{35}Cl NQR spectrum of GuDCA shows two lines. The splitting is small, 120 kHz at 77 K, 160 kHz at 405 K, not matching the fairly large difference in the bond distances C–Cl (178 and 176 pm).

The distances C–Cl are in the range reported in literature. In GuDCA the mean distance C–Cl is 177 pm; in 4-methylanilinium dichloroacetate it is 176.5 pm for both formula units in the asymmetric unit of the elementary cell, and in 3,4-dimethylanilinium dichloroacetate the mean is 175.7 pm [7]. There is a shortening of the C–Cl bond length in the group ClF_2C – compared to the dichloro- and trichloromethyl group. The bond length C–Cl in $GuClF_2A$ is 171 pm. One should not overestimate such a comparison of bond distances, since the ^{35}Cl NQR experiments show that in many cases the C–Cl bond may by dynamically shortened due to the motion of the halogenomethyl group.

The hydrogen bond system in the title compounds of which the crystal structures are reported here is not a strong one. The bond scheme can be seen in Figs. 1 and 2. The interionic bond distances (Table 4)

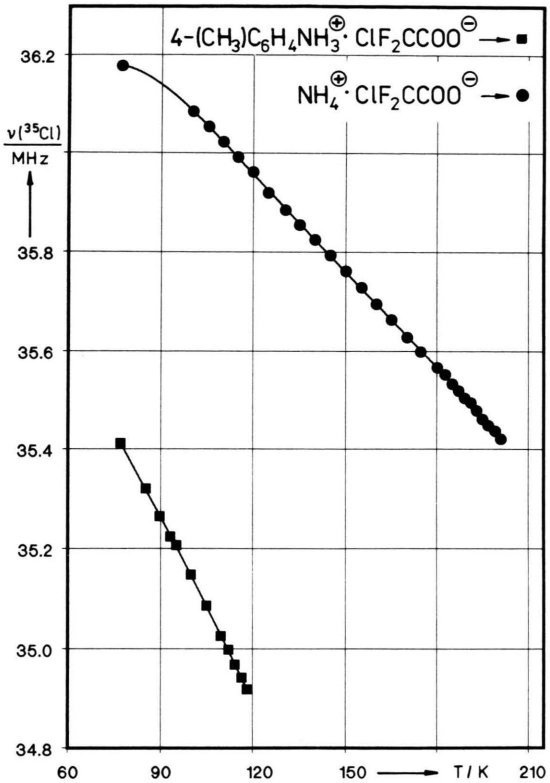


Fig. 9. Temperature dependence of $\nu(^{35}Cl)$ in ammonium chlorodifluoroacetate and in para-methylanilinium chlorodifluoroacetate.

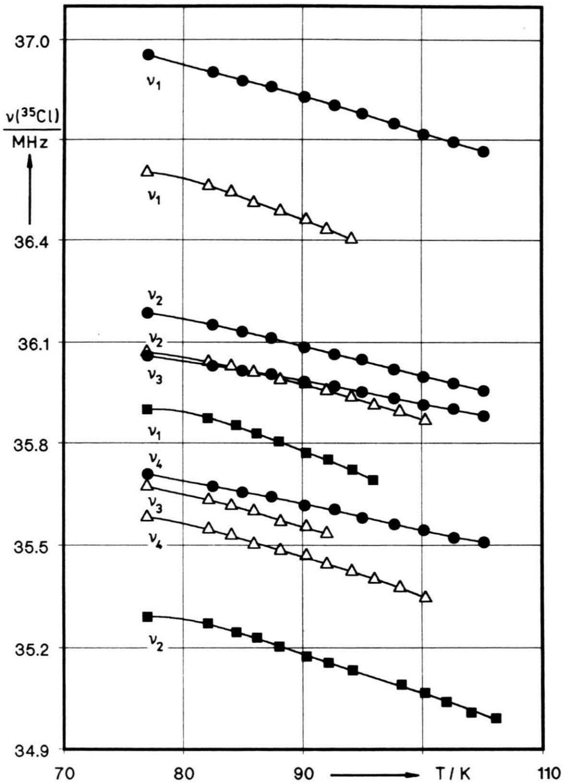


Fig. 10. Temperature dependence of $\nu(^{35}Cl)$ for several acid chlorodifluoroacetates;
●: $K^{\oplus}ClF_2CCOO^{\ominus}\cdot nClF_2CCOOH$,
■: $Rb^{\oplus}ClF_2CCOO^{\ominus}\cdot nClF_2CCOOH$, and
△: $Tl^{\oplus}ClF_2CCOO^{\ominus}\cdot nClF_2CCOOH$; $n \geq 1$.

$N-H\cdots O$ are in the range $292 \leq d(N\cdots O)/pm \leq 328$ for $GuClF_2A$ and $287 \leq d(N\cdots O)/pm \leq 314$ for GuDCA, rather long for $N-H\cdots O$ bond [15]. It is a weak hydrogen bond network in the two compounds; but at least two bonds connect each oxygen of the cation with the nitrogen of the anions in both compounds.

In Figs. 4 and 5 we have shown the line width and the reciprocal spin lattice relaxation time of the ^{35}Cl NQR in chlorodifluoroacetic acid. In Figs. 7 and 8 these properties are given for guanidinium chlorodifluoroacetate, phase II. Therefrom the activation energy of the reorientational motion of the group $-CF_2Cl$ can be calculated. T_1 is determined by the

Table 7. The activation energies and parameters (see (2)–(4)) obtained from spin-lattice relaxation and $\Delta\nu$ line width measurements of ^{35}Cl NQR of ClF_2CCOOH, and $[C(NH_2)_3^{\oplus}][ClF_2CCOO^{\ominus}]$.

Compound ($X = ClF_2CCOO$)		$\frac{a}{s^{-1}\cdot K^{-n}}$	n	$\frac{b}{s^{-1}}$	$\frac{E_a}{kJ\cdot mol^{-1}}$	$\frac{c}{s^{-1}}$	$\frac{E_a}{kJ\cdot mol^{-1}}$
ClF_2CCOOH		$0.13\cdot 10^{-6}$	2.7	$0.11\cdot 10^{5}$	14.0	$0.6\cdot 10^{4}$	12.5
$C(NH_2)_3^{\oplus}\cdot X^{\ominus}$	phase II	$2.85\cdot 10^{-6}$	2.4	$0.04\cdot 10^{5}$	9.2	$0.5\cdot 10^{4}$	8.8
$4\text{-}ClC_6H_4NHCOF_2Cl$ [a]		$4.00\cdot 10^{-4}$	2.3	$18.67\cdot 10^{5}$	13.0	–	–
$Cl_3P{=}NCCl(CF_3)_2$ [b]		–	–	–	10.0	–	–

[a] Lit. [18]. [b] Lit. [19].

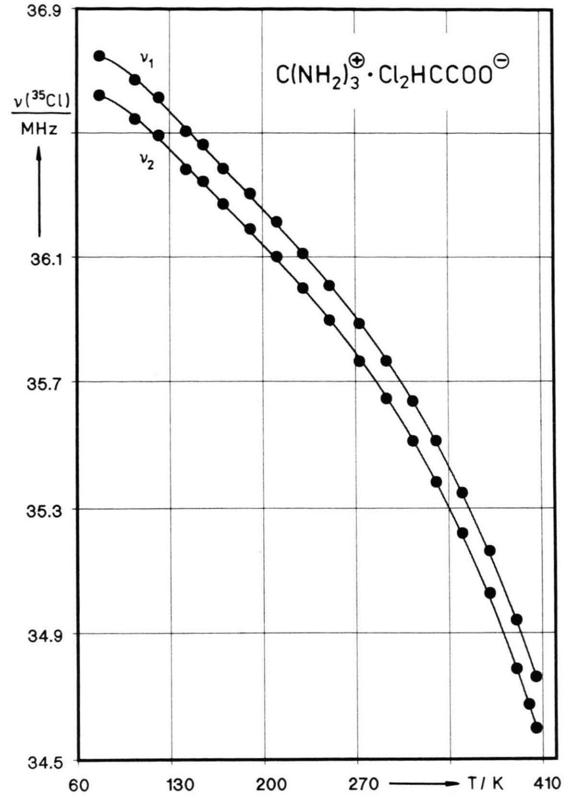


Fig. 11. Temperature dependence of $\nu(^{35}Cl)$ in guanidinium dichloroacetate, $C(NH_2)_3^{\oplus} \cdot Cl_2HCCOO^{\ominus}$.

librations and the reorientations of the group as follows [16, 17]:

$$T_1^{-1} = (T_1^{-1})_{\text{lib}} + (T_1^{-1})_{\text{reor}} \tag{2}$$

and

$$T_1^{-1} = a\,T^n + b\exp(-E_a/RT)\,. \tag{3}$$

From the line width as a function of temperature, the activation energy can be found, too [6]:

$$\Delta\nu = c\exp(-E_a/RT)\,. \tag{4}$$

In Table 7 we report the results for the reorientational motion we found for chlorodifluoroacetic acid and for $GuClF_2A$. Also some literature data for the reorientational motion of the $-CF_2Cl$ group are given for comparison. Determinations of the activation energy E_a for the reorientation of the group $-CCl_3$ in trichloroacetates can be found in literature [6, 20, 21].

Our ^{35}Cl NQR results on the acid salts $M^{\oplus}ClF_2CCOO^{\ominus} \cdot nClF_2CCOOH$ we shall not discuss here in detail because today there are discrepancies between the chemical analysis, the X-ray diffraction results, and the ^{35}Cl NQR spectra.

Acknowledgement

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