The Bond Sn–Cl in Sn^{IV} Complex Salts $A_2[(C_2H_5)SnCl_5]$. A Single Crystal ^{35}Cl NQR Study of Bis(methylammonium)-pentachloroethylstannate, $(CH_3NH_3)_2[(C_2H_5)SnCl_5]$ *

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Zeeman ^{35}Cl NQR spectroscopy has been applied to determine the magnitude and orientation of the EFG tensors at the chlorine sites in a single crystal of $(CH_3NH_3)_2[(C_2H_5)SnCl_5]$ at 293 K. The assignment of the NQR frequencies $\nu_i(^{35}Cl)$, the corresponding quadrupole coupling constants $eQ\Phi_{zz}^{(i)}h^{-1}$, and the asymmetry parameters $\eta_i(^{35}Cl)$ to certain $Cl^{(k)}$ atoms is discussed. The most probable assignment is (no. i of $\nu_i(^{35}Cl)$, $\nu_i(^{35}Cl)$/MHz, $eQ\Phi_{zz}^{(i)}h^{-1}$/MHz, $\eta_i(^{35}Cl)$, no. k of assigned $Cl^{(k)}$, d(Sn–$Cl^{(k)}$)/pm, $\sphericalangle(\Phi_{zz}^{(i)}$, d(Sn–$Cl^{(k)}$))): $i=1$, 17.032, 34.046, 0.056, $k=1$, 242.6, 3.1°; $i=2$, 12.072, 24.089, 0.117, $k=3$, 250.7, 1.9°; $i=3$, 11.537, 22.992, 0.146, $k=2$, 253.1, 2.8°; $i=4$, 10.770, 21.455, 0.154, $k=4$, 249.7, 2.9°; $i=5$, 9.969, 19.842, 0.171, $k=5$, 254.9, 1.7°. The orientation of the tensor axes $\Phi_{jj}^{(i)}$, $j=x, y, z$, $i=1-5$, in space is mainly determined by the geometry of the $[(C_2H_5)SnCl_5]^{2\ominus}$ anion. The $\Phi_{zz}^{(i)}$ are nearly parallel to the assigned bond directions Sn–$Cl^{(k)}$. $\eta(^{35}Cl)$ is low, increasing with decreasing $\nu(^{35}Cl)$. The reason for the asymmetry seems not to be a π-character in the Sn–Cl bond, but the charge distribution within the anion. The rule that a longer bond corresponds to a lower NQR frequency is valid as a general tendency, but not strict.

I. Introduction

The rearrangement of molecules SnX_4 (X = Cl, Br, I), particularly of $SnCl_4$, to an octahedral coordination by the addition of Lewis bases, $SnCl_4 + 2L \rightarrow SnCl_4 \cdot 2L$, and the formation of complex salts $A_2^{\oplus}[SnCl_6]^{2\ominus}$ ($A^{\oplus}$ = univalent cation) is known for a long time [1]. The ^{35}Cl nuclear quadrupole resonance, NQR, is an interesting method to study the change of the bonds Sn–Cl by the formation of $SnCl_4 \cdot 2L$ or $A_2^{\oplus}[SnCl_6]^{2\ominus}$, see e.g. [2, 3].

In the hexacoordinated complex salts of tin, $A_2^{\oplus}[(C_2H_5)SnCl_5]^{2\ominus}$, the influence of the ligand $C_2H_5^{\ominus}$ on the strength of the Sn–Cl bonds had been studied by ^{35}Cl NQR and X-ray analysis [4]. $C_2H_5^{\ominus}$ is the stronger electron donor compared to $Cl^{\ominus}$, and the Sn–Cl bond in trans position to the ethyl group is strengthened, while the four cis Sn–Cl bonds are weakened. This trans strengthening is opposite to the trans influence known for transition metal complexes.

$(CH_3NH_3)_2[(C_2H_5)SnCl_5]$ crystallizes with the space group C_i^1-$P\bar{1}$, $Z=2$ [4]. The $[(C_2H_5)SnCl_5]^{2\ominus}$ anion forms a distorted octahedron, and eight methylammonium cations are found in the environment of the anion (Figure 1).

$(CH_3NH_3)_2[(C_2H_5)SnCl_5]$ represents a connection between compounds with predominantly covalent bonds and pure ionic salts containing the $Cl^{\ominus}$ ion. By the influence of $C_2H_5^{\ominus}$ within the $[(C_2H_5)SnCl_5]^{2\ominus}$ anion a wide range for $\nu(^{35}Cl)$ appears. The highest frequency corresponds to mainly covalent structures. The lowest one is below 10 MHz in the range of pronounced ionic bonds Sn^{IV}–Cl. The lattice effect may be large because the crystal is composed of molecular cations and anions and its symmetry is low. Zeeman NQR studies on molecular complexes, $SnCl_4 \cdot 2L$, (L = $POCl_3$, $SeOCl_2$), with $\nu(^{35}Cl)$ as low as 17 MHz showed no lattice effects [5]. Graybeal studied the EFG tensor of the NQR signal, $\nu(^{35}Cl) = 15.5$ MHz at room temperature, in $(CH_3)_2SnCl_2$ [6] and found $\Phi_{zz}(^{35}Cl)$ parallel to the Sn–Cl bond direction and $\eta(^{35}Cl) = 0.32$, an extraordinary high value. $Ca(H_2O)_6SnCl_6$, an ionic compound, had been subject to a Zeeman NQR study, too. The single ^{35}Cl NQR is at $\nu(^{35}Cl) = 15.90$ MHz (room temperature) while $\eta(^{35}Cl) = 0.035$ [7].

The question arises to what extend the rule that $\nu(^{35}Cl)$ decreases with increasing ionic character of

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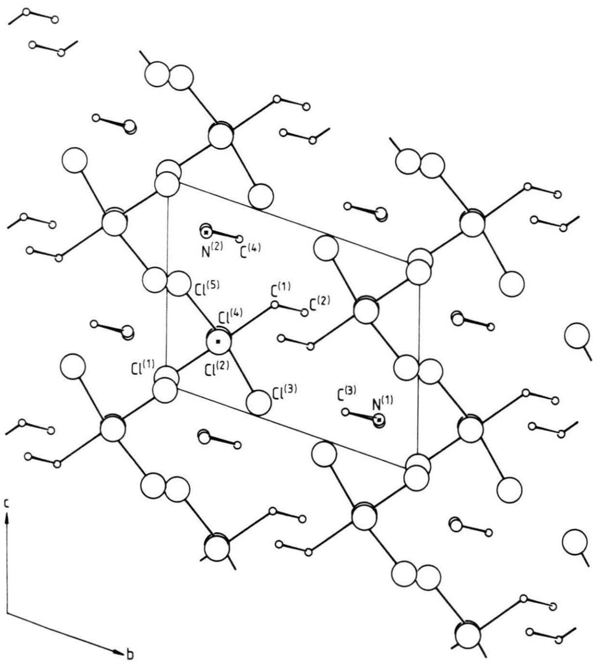

Fig. 1. View along the *a* axis onto the (*bc*) plane of the unit cell of $(CH_3NH_3)_2[(C_2H_5)SnCl_5]$, space group C_i^1-P$\bar{1}$, $Z = 2$. The numbering of the atoms is as follows: $Cl^{(1)}$ is Cl trans to the ethyl group $C^{(1)}-C^{(2)}$. The cis Cl atoms, $Cl^{(k)}$, $k = 2-5$, are numbered anticlockwise looking along $C^{(1)}-Sn-Cl^{(1)}$. The two crystallographically inequivalent methylammonium cations are $N^{(1)}-C^{(3)}$ and $N^{(2)}-C^{(4)}$.

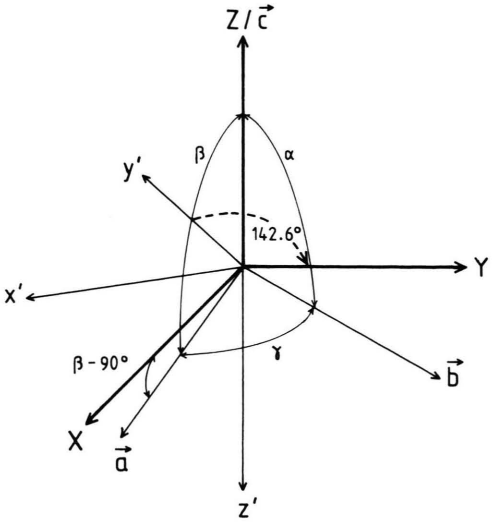

Fig. 2. Orientation of the coordinate system used in this paper. *X*, *Y*, *Z* is the Cartesian coordinate system to which all directions cosines given in this paper refer. ***a***, ***b***, ***c*** ($\alpha = 108.4°$, $\beta = 90.8°$, $\gamma = 93.9°$) represent the tricline crystal axes. ***c*** is parallel to *Z* and ***a*** is located in the plane of *X* and *Z*. *x'*, *y'*, *z'* are the axes of the laboratory system which coincides with the axes of the mutually perpendicular Helmholtz coils of the 4π Zeeman goniometer. The ***c*** axis of the single crystal had been parallel to the $\bar{z}'$ direction while the normal to the crystal face ($\bar{1}\,\bar{1}\,0$) had been parallel to *y'*. Therefore an angle of 142.6° between *y'* and *Y* results. The angles φ and ϑ of the Figs 3a and 3b refer to the laboratory system.

the bond (a factor of −0.4 MHz/pm had been deduced for Sn–Cl compounds from the study of a large number of compounds [8]) and that the orientation of the EFG tensor is determined solely by the valence electrons around Cl [9, 10], remains valid for the Sn–Cl bonds in $(CH_3NH_3)_2[(C_2H_5)SnCl_5]$. In this compound, the contributions of the lattice charges via their polarizing power (Sternheimer effect [11]) may play a more important role when the covalency of the Sn–Cl bond decreases. A straight forward way to improve the qualitative assignment of $\nu(^{35}Cl)$ to a certain bond is a single crystal Zeeman NQR experiment, whereby the EFG tensor in magnitude, orientation with respect to the crystal lattice, and the asymmetry parameter can be determined. Such a determination of the EFG tensors at the Cl sites in $(CH_3NH_3)_2[(C_2H_5)SnCl_5]$ is reported here.

II. Experimental

A single crystal of $(CH_3NH_3)_2[(C_2H_5)SnCl_5]$ (size 16 × 9 × 5 mm) has been grown by slow evaporation of a stoichiometric, aqueous solution of $(C_2H_5)SnCl_3$ and CH_3NH_3Cl. The crystal faces were indexed by X-ray diffraction. The crystal was fixed in the centre of a 4π Zeeman goniometer [12] with the ***c*** axis of the crystal parallel to the $\bar{z}'$-direction of the goniometer system and the normal to the plane ($\bar{1}\,\bar{1}\,0$) parallel to the *y'* direction, using the reflection of a laser beam for the orientation (see Figure 2). The accuracy of the orientation of the ***c*** axis is ±0.5° while the orientation in the *x'*, *y'* plane of the goniometer system is less accurate (±2°).

The Zeeman ^{35}Cl NQR spectra were measured at 293 K with a pulsed Fourier transform spectrometer. The zero splitting positions were determined to ±0.5°.

III. Results

From the space group and *Z*, the symmetry of the anion $[(C_2H_5)SnCl_5]^{2\ominus}$ is 1 and the point symmetry of the $Cl^{(k)}$, $k = 1-5$, is 1, too. Five ^{35}Cl EFG tensors had to be determined, $\Phi_{jj}^{(i)}$, $j = x, y, z$, $i = 1-5$. The EFG is

Table 1. Angles in degree between the *z*-components of the EFG tensor $\Phi_{zz}^{(i)}$ and the bond directions Sn–$Cl^{(k)}$ in $(CH_3NH_3)_2[(C_2H_5)SnCl_5]$.

	Sn–$Cl^{(1)}$	Sn–$Cl^{(2)}$	Sn–$Cl^{(3)}$	Sn–$Cl^{(4)}$	Sn–$Cl^{(5)}$	$\Phi_{zz}^{(1)}$	$\Phi_{zz}^{(2)}$	$\Phi_{zz}^{(3)}$	$\Phi_{zz}^{(4)}$
Sn–$Cl^{(2)}$	85.9								
Sn–$Cl^{(3)}$	85.7	92.1							
Sn–$Cl^{(4)}$	86.7	171.9	90.7						
Sn–$Cl^{(5)}$	85.2	88.6	170.8	87.4					
$\Phi_{zz}^{(1)}$	3.1	83.0	85.1	89.7	85.9				
$\Phi_{zz}^{(2)}$	85.7	90.2	1.9	92.6	170.9	85.0			
$\Phi_{zz}^{(3)}$	88.0	2.8	94.2	172.5	86.8	85.1	92.3		
$\Phi_{zz}^{(4)}$	83.8	169.2	90.4	2.9	87.3	86.8	92.2	170.3	
$\Phi_{zz}^{(5)}$	85.4	86.9	171.1	89.1	1.7	86.0	170.8	85.2	89.0

Table 2. ^{35}Cl NQR frequencies, $\nu_i(^{35}Cl)$, quadrupole coupling constants, $eQ\Phi_{zz}^{(i)}h^{-1}(^{35}Cl)$, and asymmetry parameters, $\eta_i(^{35}Cl)$, of $(CH_3NH_3)_2[(C_2H_5)SnCl_5]$ at 293 K. The errors are given in parentheses.

No. of ^{35}Cl NQR	$\nu(^{35}Cl)$ / MHz	$eQ\Phi_{zz}h^{-1}$ / MHz	$\eta(^{35}Cl)$
ν_1	17.032 (5)	34.046 (10)	0.056 (3)
ν_2	12.072 (5)	24.089 (10)	0.117 (3)
ν_3	11.537 (5)	22.992 (10)	0.146 (3)
ν_4	10.770 (5)	21.455 (10)	0.154 (3)
ν_5	9.969 (5)	19.842 (10)	0.171 (3)

a symmetric second rank tensor. It can be described as an ellipsoid with the principal axes Φ_{zz}, Φ_{yy}, and Φ_{xx}; $|\Phi_{zz}| \geqq |\Phi_{yy}| \geqq |\Phi_{xx}|$. The asymmetry parameter $\eta(^{35}Cl)$ is defined as $\eta = (\Phi_{xx} - \Phi_{yy})/\Phi_{zz}$. For ^{35}Cl with $I = 3/2$, the NQR frequency is $\nu = \frac{1}{2} eQ\Phi_{zz}h^{-1} \cdot (1+\eta^2/3)^{1/2}$ (*e*: electronic charge, *Q*: nuclear electric quadrupole moment, *h*: Planck constant).

By the second rank of the EFG tensor, two inverse zero splitting cones are present and can be observed easily with the 4π Zeeman goniometer.

The triclinic coordinate system of the crystal (***a***, ***b***, ***c***, α, β, γ) was transformed into a Cartesian system *X*, *Y*, *Z*. The ***c*** axis of the crystal is parallel to the *Z* axis of the reference coordinate system. The ***a*** axis lies in the plane of the axes *X* and *Z*. The orientation of the ***b*** axis follows therefrom (see Figure 2). We will use this Cartesian coordinate system throughout the paper. The direction cosines of the tensor axes and the bond directions of the five Sn–Cl bonds were transformed into the system *X*, *Y*, *Z*.

30 points (φ, ϑ) located at the zero splitting cones have been recorded for each of the five ^{35}Cl NQR frequencies. In Figs. 3 a and 3 b the zero splitting cones are shown (φ is the horizontal, ϑ the azimuthal angle of the magnetic field vector with respect to the orthogonal coordinate system of the 4π Zeeman goniometer.

Therefrom the principal axes of the ^{35}Cl EFG tensors, their direction cosines, and $\eta(^{35}Cl)$ were calculated. In Table 2 the $\nu_i(^{35}Cl)$, $eQ\Phi_{zz}^{(i)}h^{-1}(^{35}Cl)$, and $\eta_i(^{35}Cl)$, $i = 1-5$, are given for $T = 293$ K. The numbers *i* used to index the $\nu_i(^{35}Cl)$, $\Phi_{jj}^{(i)}$, and $\eta_i(^{35}Cl)$ are not identical with the numbers *k* of the $Cl^{(k)}$ atoms. The numbering of $Cl^{(k)}$ is the one given in the crystal structure determination [4]. $Cl^{(1)}$ corresponds to the Cl atom in trans position to the ethyl group, while the cis Cl atoms are numbered anticlockwise looking along the direction $C^{(1)}$–Sn–$Cl^{(1)}$. The ^{35}Cl NQR frequencies, $\nu_i(^{35}Cl)$, are numbered in the sequence of decreasing magnitude.

Table 3 lists the direction cosines of the principal tensor axes $\Phi_{jj}^{(i)}$, $j = x, y, z$, $i = 1-5$.

IV. Discussion

The first problem in the discussion of the experimental results is the assignment of the five ^{35}Cl NQR frequencies and the corresponding EFG tensors, including their orientations, to the five Cl atoms in the complex ion $[(C_2H_5)SnCl_5]^{2\ominus}$.

The assignment of the $\nu(^{35}Cl)$ can be a proof of the theoretically expected assignment only if the sequence of the values of the $\nu(^{35}Cl)$ and the d(Sn–Cl) is correct. Therefore, we consider the sequence of the five ^{35}Cl NQR frequencies and of the five d(Sn–Cl) first. The $\nu_i(^{35}Cl)$ measured at room temperature are listed in Table 2. Each of these values is motional averaged and therefore most probably lowered with respect to the resonance frequency at 4 K. Due to differences in

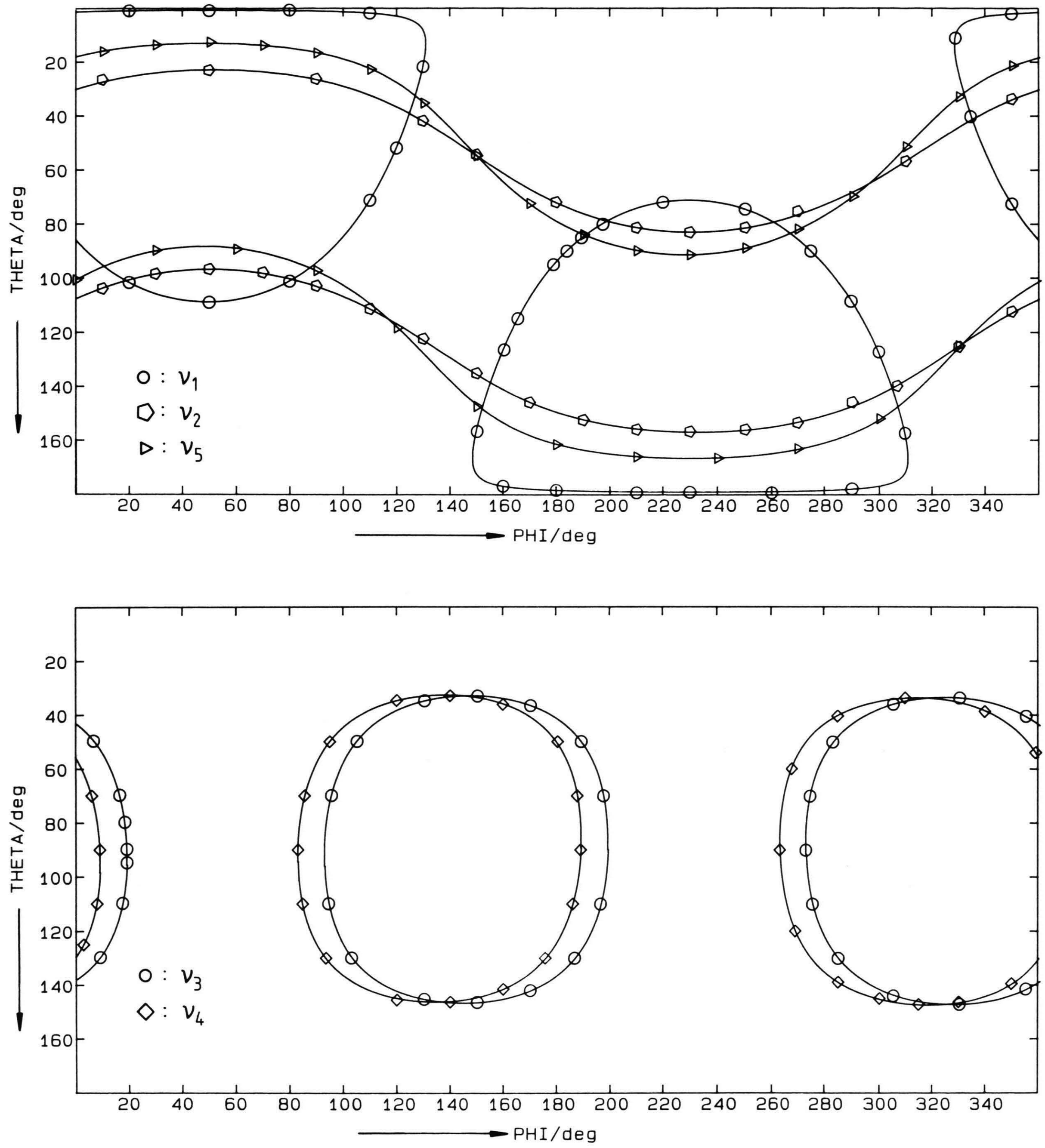

Fig. 3a and b. Representation of the zero splitting cones of the ^{35}Cl NQR frequencies ν_1, ν_2, and ν_5 (Fig. 3a) and ν_3 and ν_4 (Figure 3b). ϑ and φ are the angles of the Zeeman field with respect to the laboratory system of the 4π Zeeman goniometer (see caption of Figure 2). Each frequency shows two zero splitting cones connected by a centre of inversion which is a result of the properties of the EFG. The cones of ν_2/ν_5 and ν_3/ν_4, respectively, appear nearly at the same orientations of the Zeeman field ($\sphericalangle(\Phi_{zz}^{(2)}, \Phi_{zz}^{(5)}) = 170.8^{\circ}$; $\sphericalangle(\Phi_{zz}^{(3)}, \Phi_{zz}^{(4)}) = 170.3^{\circ}$; see Table 1).

Table 3. Direction cosines $\lambda^{(i)}$, $\mu^{(i)}$, $\nu^{(i)}$ of the components of the EFG tensors, $\Phi_{jj}^{(i)}$, and of the bonds Sn−Cl$^{(k)}$ of $(CH_3NH_3)_2[(C_2H_5)SnCl_5]$. The $\Phi_{jj}^{(i)}$ and the bond directions are symmetric with respect to an inversion. The numbering of Cl$^{(k)}$ corresponds to the crystal structure [4] and is different from that of the $\Phi_{jj}^{(i)}$.

	$\Phi_{zz}^{(i)}$			$\Phi_{yy}^{(i)}$			$\Phi_{xx}^{(i)}$		
	$\lambda^{(i)}$	$\mu^{(i)}$	$\nu^{(i)}$	$\lambda^{(i)}$	$\mu^{(i)}$	$\nu^{(i)}$	$\lambda^{(i)}$	$\mu^{(i)}$	$\nu^{(i)}$
$\Phi_{jj}^{(1)}$	0.04267	−0.81760	−0.57420	−0.02825	−0.57552	0.81730	0.99872	0.01858	0.04760
$\Phi_{jj}^{(2)}$	−0.01042	0.50058	−0.86563	−0.04162	−0.86515	−0.49979	0.99909	−0.03082	−0.02985
$\Phi_{jj}^{(3)}$	0.99850	−0.05476	0.00255	−0.05342	−0.98244	−0.17875	−0.01230	−0.17834	0.98389
$\Phi_{jj}^{(4)}$	−0.99347	−0.11380	−0.00861	0.11268	−0.96624	−0.23171	−0.01805	0.23116	−0.97275
$\Phi_{jj}^{(5)}$	0.04799	−0.62824	0.77655	0.04159	−0.77551	−0.62996	−0.99799	−0.06253	0.01108
Sn−Cl$^{(1)}$	−0.00916	−0.82564	−0.56412						
Sn−Cl$^{(2)}$	0.99681	−0.06563	−0.04550						
Sn−Cl$^{(3)}$	−0.04363	0.50024	−0.86479						
Sn−Cl$^{(4)}$	−0.99702	−0.07365	0.02273						
Sn−Cl$^{(5)}$	0.01846	−0.63148	0.77517						

Table 4. Sn−Cl bond lengths for $(CH_3NH_3)_2[(C_2H_5)SnCl_5]$. Standard deviations are given in parentheses.

Bond	d(Sn−Cl) pm	d(Sn−Cl) pm (corrected for libration)
Sn−Cl$^{(1)}$	242.7(1)	242.9
Sn−Cl$^{(2)}$	253.1(1)	253.4
Sn−Cl$^{(3)}$	250.8(1)	251.0
Sn−Cl$^{(4)}$	249.7(1)	250.0
Sn−Cl$^{(5)}$	254.9(1)	255.1

the temperature dependence of the $\nu_i(^{35}Cl)$, the sequence at 4 K may not be identical with that observed at room temperature. A look on $\nu_i(^{35}Cl) = f(T)$ in the range $77 \leqq T/K \leqq 300$ K shows that the gross pattern of one high resonance frequency and a group of four resonances at low frequencies will not change [4] and that the ^{35}Cl NQR frequencies at 12.072 MHz and at 9.969 MHz remain the highest and the lowest, respectively, of the low frequency group. Since the slopes of the NQR frequencies at 10.770 MHz and 11.537 MHz are opposite they may cross above 4 K. Also a temperature dependence of the bond length must be considered. A correction of the bond lengths in $(CH_3NH_3)_2[(C_2H_5)SnCl_5]$ refering to the librational motion of $[(C_2H_5)SnCl_5]^{2\ominus}$ according to the method of Shomaker and Trueblood [13] indicates that the bond lengths given in Table 4 are accurate.

Next we shall deal with the orientation of Φ_{zz}. If there is a significant contribution of the bonding electrons to the EFG at a Cl site, correlations between the orientation of the five $\Phi_{zz}^{(i)}$ and the geometry of the Sn−Cl$^{(k)}$ bonds should be observable.

The geometry of the 5 Sn−Cl$^{(k)}$ bonds is that of an umbrella slightly folded towards the direction Sn−Cl$^{(1)}$. The angles $\sphericalangle$(Cl$^{(1)}$−Sn−Cl$^{(k)}$), $k = 2-5$, given in the first number column of Table 1 are between 85.2° and 86.7°. The angles $\sphericalangle(\Phi_{zz}^{(1)}, \Phi_{zz}^{(i)})$, $i = 2-5$, listed in column 6 of Table 1 are nearly the same as given for the bond directions, i.e. the $\Phi_{zz}^{(i)}$ form an umbrella of the same shape as the bonds do, indicating a strong correlation between the $\Phi_{zz}^{(i)}$ and the bond directions Sn−Cl$^{(k)}$.

If we assume that the inverse tensor axes of $\Phi_{zz}^{(i)}$ are the correct ones, they form an umbrella turned up with respect to $\Phi_{zz}^{(1)}$ and folded with respect to the bond direction Sn−C$^{(1)}$. The $\sphericalangle(\Phi_{zz}^{(1)}, \Phi_{zz}^{(i)})$, $i = 2-5$, then change to values between 93° and 95°. The direction cosines of the $\Phi_{zz}^{(i)}$ given in Table 3 belong to the first version, $\sphericalangle(\Phi_{zz}^{(1)}, \Phi_{zz}^{(i)}) < 90°$, $i = 2-5$. How closely parallel are the directions of the $\Phi_{zz}^{(i)}$ (considered as vectors) to certain bond directions Sn−Cl$^{(k)}$? There is only one direction Sn−Cl$^{(k)}$ nearly parallel to $\Phi_{zz}^{(1)}$; *it is* $\boldsymbol{d}$(Sn−Cl$^{(1)}$), see Table 1. Within the error for the rotation of the crystal around Z, ±2°, $\Phi_{zz}^{(1)}$ is parallel to $\boldsymbol{d}$(Sn−Cl$^{(1)}$). The assignment of $\Phi_{zz}^{(1)}$ ($\nu_1(^{35}Cl)$ = 17.032 MHz) – highest frequency to the shortest bond – is unique and not unexpected.

The relation between the four $\Phi_{zz}^{(i)}$, $i = 2-5$, cis to $\Phi_{zz}^{(1)}$, and the four Cl atoms cis to Cl$^{(1)}$ is more complicated. In 4π Zeeman NQR we observe two pairs of $\Phi_{zz}^{(i)}$, one is $\Phi_{zz}^{(2)}$ and $\Phi_{zz}^{(5)}$, the other $\Phi_{zz}^{(3)}$ and $\Phi_{zz}^{(4)}$, where within one pair the directions of the axes $\Phi_{zz}^{(i)}$ are nearly parallel or antiparallel (170.8° and 170.3°, respectively, see Table 1). $\Phi_{zz}^{(2)}$, $\Phi_{zz}^{(5)}$ belong to Cl$^{(3)}$, Cl$^{(5)}$ and $\Phi_{zz}^{(3)}$, $\Phi_{zz}^{(4)}$ to Cl$^{(2)}$, Cl$^{(4)}$. However, there is an ambiguity: $\Phi^{(2)}_{zz} \leftrightarrow Cl^{(3)}$ or $\Phi^{(2)}_{zz} \leftrightarrow Cl^{(5)}$ and $\Phi^{(3)}_{zz} \leftrightarrow Cl^{(2)}$ or $\Phi^{(3)}_{zz} \leftrightarrow Cl^{(4)}$? The rule $\nu(^{35}Cl) \sim 1/d^n$, fails. It would lead to the assignment $\Phi^{(2)}_{zz}$ $(\nu_2(^{35}Cl) = 12.072$ MHz$)$ $\leftrightarrow Cl^{(4)}(d(Sn-Cl^{(4)}) = 249.7$ pm). This, however, is ruled out: $\measuredangle(\Phi^{(2)}_{zz}, \boldsymbol{d}(Sn-Cl^{(4)})) = 92.6°$. There are two possibilities (a) and (b) to assign $\Phi^{(2)}_{zz}$ and $\Phi^{(5)}_{zz}$ to $Cl^{(3)}$ and $Cl^{(5)}$:

	$d(Sn-Cl)$	$\nu(^{35}Cl)$	Angle $(\Phi_{zz}, \boldsymbol{d}(Sn-Cl))$
(a) $\Phi^{(2)}_{zz} \leftrightarrow Cl^{(3)}$	250.7 pm	12.072 MHz	1.9°
$\Phi^{(5)}_{zz} \leftrightarrow Cl^{(5)}$	254.9 pm	9.969 MHz	1.7°
(b) $\Phi^{(2)}_{zz} \leftrightarrow Cl^{(5)}$	254.9 pm	12.072 MHz	9.1°
$\Phi^{(5)}_{zz} \leftrightarrow Cl^{(3)}$	250.7 pm	9.969 MHz	8.9°

(b) assigns the longest bond to the highest frequency. Because $\Delta d(Sn-Cl)$ is 4 pm and $\Delta\nu(^{35}Cl)$ is 2.1 MHz for the frequencies and bond lengths in question, (b) is strongly against the correlation between NQR frequency and Sn–Cl bond length. Since, in addition, the deviations of Φ_{zz} from the bond direction are 9°, the assignment (b) has only a low probability compared with (a).

The two possible assignments of $\Phi^{(3)}_{zz}$ and $\Phi^{(4)}_{zz}$ to $Cl^{(2)}$ and $Cl^{(4)}$ are:

	$d(Sn-Cl)$	$\nu(^{35}Cl)$	Angle $(\Phi_{zz}, \boldsymbol{d}(Sn-Cl))$
(a) $\Phi^{(3)}_{zz} \leftrightarrow Cl^{(2)}$	253.1 pm	11.537 MHz	2.8°
$\Phi^{(4)}_{zz} \leftrightarrow Cl^{(4)}$	249.7 pm	10.770 MHz	2.9°
(b) $\Phi^{(3)}_{zz} \leftrightarrow Cl^{(4)}$	249.7 pm	11.537 MHz	7.5°
$\Phi^{(4)}_{zz} \leftrightarrow Cl^{(2)}$	253.1 pm	10.770 MHz	10.8°

Allowing a deviation from the correlation $\nu(^{35}Cl) \sim 1/d^n$, it is accompanied by small violations of the rule $\Phi_{zz} \parallel \boldsymbol{d}(Sn-Cl)$, while sticking to it causes fairly large deviations of Φ_{zz} from the rule $\Phi_{zz} \parallel \boldsymbol{d}$(bond). It is not possible to decide uniquely between assignment (a) and (b) for $(\Phi^{(3)}_{zz}, \Phi^{(4)}_{zz} \leftrightarrow Cl^{(2)}, Cl^{(4)})$.

In both cases, (b) leads to a turned up umbrella geometry and would be a violation of the correlation NQR frequency ↔ bond length and a mismatch of the Φ_{zz} of the cis Cl atoms and the bond directions by 10°. None of the four possibilities (umbrella like geometry, partly or fully turned up umbrella) can be ruled out, but the umbrella like geometry is most likely. The assignment for this geometry is given in (a) and Table 5. A graphical representation of the tensor axes $\Phi^{(i)}_{jj}$, $j = x, y, z$, $i = 1-5$, with respect to the bonds $Sn-Cl^{(k)}$, $k = 1-5$, is shown in Figure 4.

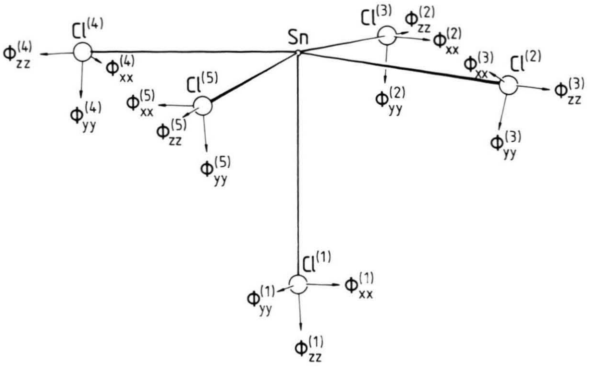

Fig. 4. Representation of the orientation of the tensor axes $\Phi^{(i)}_{zz}$, $\Phi^{(i)}_{yy}$, $\Phi^{(i)}_{xx}$, $i = 1-5$, with respect to the crystal geometry of the bonds $Sn-Cl^{(k)}$ of the $[(C_2H_5)SnCl_5]^{2\ominus}$ anion that follows from the assignment of the $\nu_i(^{35}Cl)$ to certain $Cl^{(k)}$ atoms given in Table 5. Note that the numbers i of the $\nu_i(^{35}Cl)$ and the $\Phi^{(i)}_{jj}$ are not identical with the numbers k of the $Cl^{(k)}$. The $Cl^{(k)}$ are numbered according to the crystal structure [4] while the numbers of the $\Phi^{(i)}_{jj}$ follows the sequence of the ^{35}Cl NQR frequencies $\nu(^{35}Cl)$. $\nu_1(^{35}Cl)$ is the highest NQR frequency and $\nu_5(^{35}Cl)$ the lowest one.

$\eta(^{35}Cl)$ increases with decreasing ^{35}Cl NQR frequency. $\eta(^{35}Cl) = 0.17$ for the lowest frequency, $\nu(^{35}Cl) = 9.97$ MHz, and $\eta(^{35}Cl) = 0.06$ for the highest one, $\nu(^{35}Cl) = 17.03$ MHz (Table 2); $\eta(^{35}Cl)$ increases with increasing ionicity of the Sn–Cl bond. This indicates that the π-character in the Sn–Cl bond – provided there is actually any – can not be significant. It is expected that a more covalent bond has a larger π-character than a more ionic bond; $\eta(^{35}Cl)$ would increase with increasing $\nu(^{35}Cl)$. The opposite sequence had been observed, however. Quite likely, the asymmetry of the EFG is a result of the imbalance of the charge distribution within the complex anion, especially between $C^{(1)}$ and $Cl^{(1)}$. The orientations of the $\Phi^{(i)}_{xx}$ and $\Phi^{(i)}_{yy}$, $i = 2-5$, support such a view. The axes $\Phi^{(i)}_{yy}$, $i = 2-5$, of the cis nuclei are nearly parallel to the direction of the bond $Sn-Cl^{(1)}$ and the $\Phi^{(i)}_{xx}$, $i = 2-5$, are perpendicular to that direction, being more or less in the sligthly distorted plane $(Cl^{(2)}, Cl^{(3)}, Cl^{(4)}, Cl^{(5)})$, see Tables 6 and 7.

The extraordinary high $\eta(^{35}Cl)$ measured by Graybeal for $(CH_3)_2SnCl_2$ [6], can not be explained by a π-character in the Sn–Cl bond. More likely, the reason for the high $\eta(^{35}Cl)$ value in $(CH_3)_2SnCl_2$ can be traced back to the coordination of Cl with Sn of the neighbouring $(CH_3)_2SnCl_2$ molecule. This would be

Table 5. Final assignment of ^{35}Cl NQR frequencies, $\nu_i(^{35}\mathrm{Cl})$, quadrupole coupling constants, $eQ\Phi_{zz}^{(i)}h^{-1}$, and asymmetry parameters, $\eta_i(^{35}\mathrm{Cl})$, $i = 1-5$, to certain $\mathrm{Cl}^{(k)}$ atoms, $k = 1-5$, in $\mathrm{(CH_3NH_3)_2[(C_2H_5)SnCl_5]}$. The Cl atoms are numbered according to the crystal structure [4] while the numbers i of the $\nu_i(^{35}\mathrm{Cl})$, the $eQ\Phi_{zz}^{(i)}h^{-1}$, and the $\eta_i(^{35}\mathrm{Cl})$ increase with decreasing NQR frequency. Errors are given in parentheses.

No. of ^{35}Cl NQR	$\mathrm{Cl}^{(k)}$	$\nu(^{35}\mathrm{Cl})$ / MHz	$eQ\Phi_{zz}^{(i)}h^{-1}(^{35}\mathrm{Cl})$ / MHz	$\eta(^{35}\mathrm{Cl})$	$d(\mathrm{Sn{-}Cl}^{(k)})$ / pm	$\sphericalangle(\Phi_{zz}^{(i)}, d(\mathrm{Sn{-}Cl}^{(k)}))$ / degree
ν_1	$\mathrm{Cl}^{(1)}$	17.032(5)	34.046(10)	0.056(3)	242.6(1)	3.1
ν_2	$\mathrm{Cl}^{(3)}$	12.072(5)	24.089(10)	0.117(3)	250.7(1)	1.9
ν_3	$\mathrm{Cl}^{(2)}$	11.537(5)	22.992(10)	0.146(3)	253.1(1)	2.8
ν_4	$\mathrm{Cl}^{(4)}$	10.770(5)	21.455(10)	0.154(3)	249.7(1)	2.9
ν_5	$\mathrm{Cl}^{(5)}$	9.969(5)	19.842(10)	0.171(3)	254.9(1)	1.7

Table 6. Angles in degree between the *x*-components of the EFG tensor $\Phi_{xx}^{(i)}$ and the bond directions $\mathrm{Sn{-}Cl}^{(k)}$ in $\mathrm{(CH_3NH_3)_2[(C_2H_5)SnCl_5]}$.

	$\mathrm{Sn{-}Cl}^{(1)}$	$\mathrm{Sn{-}Cl}^{(2)}$	$\mathrm{Sn{-}Cl}^{(3)}$	$\mathrm{Sn{-}Cl}^{(4)}$	$\mathrm{Sn{-}Cl}^{(5)}$	$\Phi_{xx}^{(1)}$	$\Phi_{xx}^{(2)}$	$\Phi_{xx}^{(3)}$	$\Phi_{xx}^{(4)}$
$\mathrm{Sn{-}Cl}^{(2)}$	85.9								
$\mathrm{Sn{-}Cl}^{(3)}$	85.7	92.1							
$\mathrm{Sn{-}Cl}^{(4)}$	86.7	171.9	90.7						
$\mathrm{Sn{-}Cl}^{(5)}$	85.2	88.6	170.8	87.4					
$\Phi_{xx}^{(1)}$	92.9	7.2	94.3	174.9	87.5				
$\Phi_{xx}^{(2)}$	88.1	2.2	91.9	174.0	89.2	5.3			
$\Phi_{xx}^{(3)}$	114.1	92.6	160.0	87.3	28.9	88.2	92.1		
$\Phi_{xx}^{(4)}$	69.0	89.4	16.7	91.2	154.2	93.4	89.8	176.4	
$\Phi_{xx}^{(5)}$	86.9	172.4	89.8	0.9	88.3	175.8	174.5	88.0	90.4

Table 7. Angles in degree between the *y*-components of the EFG tensor $\Phi_{yy}^{(i)}$ and the bond directions $\mathrm{Sn{-}Cl}^{(k)}$ in $\mathrm{(CH_3NH_3)_2[(C_2H_5)SnCl_5]}$.

	$\mathrm{Sn{-}Cl}^{(1)}$	$\mathrm{Sn{-}Cl}^{(2)}$	$\mathrm{Sn{-}Cl}^{(3)}$	$\mathrm{Sn{-}Cl}^{(4)}$	$\mathrm{Sn{-}Cl}^{(5)}$	$\Phi_{yy}^{(1)}$	$\Phi_{yy}^{(2)}$	$\Phi_{yy}^{(3)}$	$\Phi_{yy}^{(4)}$
$\mathrm{Sn{-}Cl}^{(2)}$	85.9								
$\mathrm{Sn{-}Cl}^{(3)}$	85.7	92.1							
$\mathrm{Sn{-}Cl}^{(4)}$	86.7	171.9	90.7						
$\mathrm{Sn{-}Cl}^{(5)}$	85.2	88.6	170.8	87.4					
$\Phi_{yy}^{(1)}$	89.2	91.6	173.4	84.9	4.8				
$\Phi_{yy}^{(2)}$	4.7	87.8	89.9	84.6	80.9	84.8			
$\Phi_{yy}^{(3)}$	24.1	88.9	109.5	83.0	61.3	65.1	19.7		
$\Phi_{yy}^{(4)}$	22.0	79.3	106.7	92.7	64.4	68.7	18.7	10.0	
$\Phi_{yy}^{(5)}$	5.6	83.0	81.1	89.9	89.9	94.0	10.3	29.3	25.8

similar to $\mathrm{SnCl_4 \cdot 2\,SeOCl_2}$, where the coordination Se ⋯ Cl rises $\eta(^{35}\mathrm{Cl})$ at one of the Cl sites of $\mathrm{SnCl_4}$ to 0.395 [5].

$\Phi_{yy}^{(1)}$ is almost parallel to the bond direction $\mathrm{Sn{-}Cl}^{(5)}$, $\sphericalangle(\Phi_{yy}^{(1)}, \boldsymbol{d}(\mathrm{Sn{-}Cl}^{(5)})) = 4.8°$. $\mathrm{Sn{-}Cl}^{(5)}$ is the most ionic bond of the anion. $\mathrm{Cl}^{(5)}$ is therefore the most negatively charged Cl. The asymmetry of the EFG of $\nu_1(^{35}\mathrm{Cl})$ seems to be orientated in direction of this charge.

$\Phi_{yy}^{(3)}$ and $\Phi_{yy}^{(4)}$ form an angle of 24.1° and 22.0° with the direction of $\mathrm{Sn{-}Cl}^{(1)}$. The belong to $\mathrm{Cl}^{(2)}$ and $\mathrm{Cl}^{(4)}$. If these angles are caused by the ethyl group orientation, $\mathrm{Cl}^{(3)}/\Phi_{yy}^{(2)}$ and $\mathrm{Cl}^{(5)}/\Phi_{yy}^{(5)}$ should be influenced, too, which is not the case. The observed angles of 24.1° and 22.0° are possibly a result of the lattice influence. The rotation of $\Phi_{yy}^{(3)}$ and $\Phi_{yy}^{(4)}$ is the only orientation of a tensor axis $\Phi_{jj}^{(i)}$, $j = x, y, z$, $i = 1-5$, that can not be explained by the intramolecular charge distribution.

The discussion can be summarized as follows: The Zeeman NQR study of $\mathrm{(CH_3NH_3)_2[(C_2H_5)SnCl_5]}$ shows that the strengthening of the trans Sn–Cl bond is mirrored by a high ^{35}Cl NQR frequency of 17.032 MHz. The assignment given in [4] was correct. Within the experimental error the direction of $\Phi_{zz}^{(1)}$ is parallel to the direction of the Sn–Cl$^{(1)}$ bond. η_1(^{35}Cl) is small and $\Phi_{yy}^{(1)}$ points in direction of the highest charge on Cl$^{(5)}$.

There are four possibilities to assign the 4 low resonance frequencies to certain cis Cl atoms. None of them fulfills the rule $\nu(^{35}\mathrm{Cl}) \sim 1/d^n$ strictly. For the most probable one (Table 5), the $\Phi_{zz}^{(i)}$ are parallel to the Sn–Cl$^{(k)}$ bond directions. The orientations of $\Phi_{xx}^{(i)}$ and $\Phi_{yy}^{(i)}$, $i = 1-5$, are mainly determined by the intramolecular charge distribution. The asymmetry parameter $\eta(^{35}\mathrm{Cl})$ is low. The only apparent influence of the lattice on the orientation of the EFG is the rotation of $\Phi_{yy}^{(3)}$ and $\Phi_{yy}^{(4)}$ by 20–25° away from the direction given by the molecular EFG.

There is an effect of the lattice charges on the magnitude of the z component of the EFG tensor. The ^{35}Cl NQR frequencies scatter by ± 1 MHz around the value expected from the correlation frequency ↔ bond length.

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[1] P. Pfeiffer, Organische Molekülverbindungen, 2. Aufl., Ferdinand Enke, Stuttgart 1927.

[2] L. Guibé and J. Jugie, Nuclear Quadrupole Resonance of Molecular Complexes, in: Molecular Interaction, Vol. 2, p. 343 (H. Rutajczak, W. J. Orville-Thomas, and M. Redshaw, eds.), John Wiley, New York 1981.

[3] D. Borchers and Al. Weiss, Ber. Bunsenges. Phys. Chem. **93,** 559 (1989).

[4] P. Storck and Al. Weiss, Ber. Bunsenges. Phys. Chem. **93,** 454 (1989).

[5] M. Mishima, J. Sci. Hiroshima Univ. Ser. A **46,** 41 (1982).

[6] J. D. Graybeal, J. Mol. Struct. **111,** 329 (1983).

[7] T. Kitazumo, M. Sekizaki, and M. Suhara, J. Mol. Struct. **58,** 161 (1980).

[8] P. Storck and Al. Weiss, Ber. Bunsenges. Phys. Chem. **94,** 179 (1990).

[9] E. A. C. Lucken, Nuclear Quadrupole Coupling Constants, Academic Press, New York 1969.

[10] V. Nagarajan, H. Paulus, N. Weiden, and Al. Weiss, J. Chem. Soc. Faraday Trans. **82,** 1499 (1986).

[11] R. M. Sternheimer, Z. Naturforsch. **41 a,** 24 (1986).

[12] V. Nagarajan, N. Weiden, R. Wendel, and Al. Weiss, J. Magn. Reson. **47,** 28 (1982).

[13] V. Shomaker and K. N. Trueblood, Acta Cryst. **B 24,** 63 (1968).