Tetraalkylammonium Tetrachlorothallates(III); X-Ray, ^{35}Cl-NQR, and ^{1}H-NMR Studies

Marco Lenck *, Shi-qi Dou, and Alarich Weiss
Institut für Physikalische Chemie, Physikalische Chemie III,
Technische Hochschule Darmstadt, Darmstadt, Germany

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The crystal structure of $(CH_3)_4NTlCl_4$ and $(C_2H_5)_4NTlCl_4$ was determined at room temperature by single crystal technique. $(CH_3)_4NTlCl_4$: D_{2h}^{17}-Cmmm; $Z=2$; $a=913.2$ pm, $b=894.6$ pm, $c=752.5$ pm; $(C_2H_5)_4NTlCl_4$: C_{6v}^{4}-$P6_3mc$; $Z=2$; $a=827.9$ pm, $c=1329.8$ pm. $(C_2H_5)_4NTlCl_4$ is isomorphous with $(C_2H_5)_4NInCl_4$. The compounds undergoe a phase transition at 239 K and 222 K, respectively. For both compounds no ^{35}Cl NQR signal was observable in the high temperature phase I due to the dynamics of the anion. The ^{35}Cl NQR was studied in the low temperature phase II of both compounds as a function of temperature. $(CH_3)_4NTlCl_4$ shows a two line, $(C_2H_5)_4NTlCl_4$ a four line spectrum. The possible phase II structures and the dynamics of the cation, studied by ^{1}H-NMR, are discussed.

I. Introduction

Thallium(III) undergoes a variety of coordinations with halogens, as reported in literature [1–7]. Out of these coordinations, a tetrahedral one represented by the ions $[TlX_4]^-$, X = Cl, Br, I. Cotton et al. [1] found that $[TlCl_4]^-$ is a tetrahedron in the crystalline state of $[As(C_6H_5)_4]TlCl_4$, isomorphous to $[As(C_6H_5)_4] \cdot FeCl_4$. The crystal structure of the latter one has been determined by Zaslow and Rundle [2]. Scaife et al. [3] determined the ^{35}Cl NQR frequencies of the tetraphenylphosphonium- and tetraphenylarsonium-tetrachlorothallates(III). Recently the room temperature crystal structure of pyridiniumtetrachlorothallate(III) was published by Millikan et al. [4]. They found also a phase transition between 237 K and 172 K. Another example of a tetrachlorothallate(III) ion with tetrahedral structure is $[Co(en)_2Cl_2]$ $TlCl_4$ [5]. The compounds $M^+[TlCl_4]$, where M^+ is K^+, Rb^+, NH_4^+, or Tl^+, have been studied by Thiele et al. [6, 7]. Whereas the tetrachlorothallates(III) are formed easily with large cations [1], the stability range of Tl(III) salts with alkali metal ions in solution is quite small, and for the crystal structure studies of $MTlCl_4$, M = K, NH_4, Rb, Tl, single crystals had to be selected from the bulk of a chemically inhomogenous precipitate [6, 7]. The authors have shown that the structures of the tetrachlorothallates(III) with alkali metal ions (K, Rb, NH_4) as cations are of Scheelite type [7], as is the compound $Tl[TlCl_4]$ [6]. According to Pratt [8], $CsTlCl_4$ cannot be prepared from solution because of the wide stability range of $Cs_3Tl_2Cl_9$. ^{35,37}Cl NQR is a rather sensitive spectroscopic method in determining symmetry elements in crystals and the ionicity of bonds halogen-X [9]. We found it interesting to study both ^{35}Cl NQR and the crystal structure of salts $M[TlCl_4]$. Because of the easy access of pure material the compounds tetramethylammonium-tetrachlorothallate(III) ((TMA)$TlCl_4$), tetraethylammonium-tetrachlorothallate(III) ((TEA)$TlCl_4$), and tetrapropylammonium-tetrachlorothallate(III) ((TPA)$TlCl_4$) were chosen for this study.

^{35}Cl NQR experiments on (TPA)$TlCl_4$ were without success, probably due to order-disorder phenomena within the partially flexible cation. We shall not report on this compound further in this paper. Since ^{1}H-NMR is sensitive to molecular dynamics in solids, the ^{1}H-NMR spectrum of (TMA)$TlCl_4$ was studied, too.

II. Experimental

Preparation

In their study of Tl(III)-halogene complexes, Cotton et al. [1] prepared the compounds from acetonitrile solution. It turned out that the compounds we

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* Part of the Dr. Ing. Dissertation of Marco Lenck, D17, Technische Hochschule Darmstadt.

Reprint requests to Prof. Dr. Al. Weiss, Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstr. 20, D-6100 Darmstadt.

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Table 1. Experimental conditions for the structure determination of (TMA) $TlCl_4$ and (TEA) $TlCl_4$ and crystal structure data.

	(TNA) $TlCl_4$	(TEA) $TlCl_4$
Formula	$[(CH_3)_4N]TlCl_4$	$[(C_2H_5)_4N]TlCl_4$
Molar mass/(g · mol^{-1})	420.33	476.43
Crystal habitus	prism, colourless	flat needle, colourless
Diffractometer	STOE Stadi 4	
Wavelength/pm	MoKα 71.069	
Monochromator	Graphite (002)	
T/K	301	297
Absorption coefficient/m^{-1}	140.26	109.30
Scan	$2\Theta/\omega$	
Scan range	$3 < 2\Theta < 55$	$3 < 2\Theta < 60$
F (000)	384	448
Reflexion, measured, number of	1294	4902
symmetry independent	431	918
considered	431	876
Number of free parameters	23	16
$R(F)$	0.0410	0.1092
$R_w(F)$	0.0425	0.0860
Lattice constants		
a/pm	913.2 (4)	827.9 (3)
b/pm	894.6 (4)	—
c/pm	752.5 (3)	1329.8 (4)
Volume of the unit cell		
$V \cdot 10^{-6}$/pm^3	614.7 (7)	789.4 (8)
Space group	D_{2h}^{19}-Cmmm	C_{6v}^{4}-$P6_3mc$
Formular units/cell	2	2
$\varrho_{calc}/10^3$ kg m^{-3}	2.271 (3) (301 K)	2.004 (2) (297 K)
$\varrho_{exp}/10^3$ kg m^{-3}	2.15 (297 K)	1.92 (295 K)
Point positions (0, 0, 0; 1/2, 1/2, 0) +		
Tl in 2a	$0, 0, 0.$	Tl, Cl(1) in 2*a* $0, 0, z; \quad 0, 0, 1/2+z.$
Cl(1) in 8o	$x, 0, z; \quad \bar{x}, 0, \bar{z};$ $\bar{x}, 0, z; \quad x, 0, \bar{z}.$	Cl(2) in 6c $x, \bar{x}, z; \quad x, 2x, z;$ $2\bar{x}, \bar{x}, z; \quad \bar{x}, x, 1/2+z;$ $\bar{x}, 2\bar{x}, 1/2+z; \quad 2x, x, 1/2+z.$
Cl(2) in 8p	$x, y, 0; \quad \bar{x}, \bar{y}, 0;$ $\bar{x}, y, 0; \quad x, \bar{y}, 0.$	N in 2b $1/3, 2/3, z; \quad 2/3, 1/3, 1/2+z.$
N in 4 h	$x, 0, 1/2; \bar{x}, 0, 1/2.$	

report on here are easily prepared from aqueous solution.

a) (TMA) $TlCl_4$ was prepared from a solution of 8.80 g $TlCl_3 \cdot 4H_2O$ (Alfa Products) in 200 ml water, acidified with 2 ml 2 n hydrochloric acid. Under heating and stirring, a solution of 2.79 g $(CH_3)_4NCl$ in 50 ml water was added. To gain a well crystallized solid for the NQR measurements and for the crystal structure investigation it was necessary to cool the solution slowly over six weeks down to room temperature. The white crystals obtained have the composition Tl 49.3% (48.6%), C 11.47% (11.43%), H 2.79% (2.88%), and N 3.40% (3.33%); calculated values given in brackets. The compound decomposes at 285 °C.

b) $((C_2H_5)_4N)TlCl_4$ was prepared in the same way, but instead of crystallizing from water, a 1:1 mixture of water and ethanol was used. The elemental analysis (C, H, N) shows the following results: C 20.17% (20.16%), H 4.23% (4.24%), and N 2.94% (2.97%). The compound melts at 244 °C under decomposition.

c) Also $(n\text{-}(C_3H_7)_4N)TlCl_4$ was prepared as described above a), b), but pure ethanol was used for crystallisation. The elemental analysis gave: C 26.76% (27.07%), H 5.09% (5.30%), and N 2.70% (2.63%). The compound melts at 128 °C.

X-Ray Investigation

The crystal structures of (TMA) $TlCl_4$ and (TEA) · $TlCl_4$ were determined by single crystal X-ray technique at room temperature using a four circle X-ray diffractometer with MoKα radiation. The experimental conditions and crystallographic data are listed in Table 1.

Table 2. Positional and thermal parameters of (TMA)$TlCl_4$ and (TEA)$TlCl_4$. 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 the isotropic mean for the nitrogen atom. K is the occupation factor.

Atom	x/a	y/b	z/c	K	U_{11}, U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
(TMA)$TlCl_4$										
Tl	0	0	0	1	897 (9)	816 (9)	478 (7)	0	0	0
Cl (1)	0.1289 (13)	0	0.2752 (12)	0.5	1549 (99)	1290 (82)	573 (50)	291 (147)	−197 (64)	−488 (186)
Cl (2)	0.1480 (15)	0.2149 (16)	0	0.5	1664 (123)	1540 (121)	1487 (115)	229 (361)	−645 (225)	−628 (156)
N	0.4273 (59)	0	0.5	0.5	1657 (257)					
(TEA)$TlCl_4$										
Tl	0	0	0.0000 (0)	1	703 (8)	703 (8)	691 (11)	0	0	351 (4)
Cl (1)	0	0	0.1796 (14)	1	1223 (99)	1223 (19)	749 (104)	0	0	611 (49)
Cl (2)	−0.1595 (5)	0.1595 (5)	−0.0548 (11)	1	1143 (50)	1143 (50)	1069 (62)	54 (37)	−54 (37)	728 (57)
N	0.3333	0.6667	0.1883 (46)	1	1863 (509)					

^{35,37}*Cl NQR and* ^{1}*H-NMR*

To study the ^{35,37}Cl NQR spectra of (TMA)$TlCl_4$ and (TEA)$TlCl_4$ a superregenerative NQR spectrometer has been used. The temperature dependence of the resonance lines was measured over a temperature range from 100 K to 400 K with a temperature controlled N_2-gas stream. The accuracy in measuring the temperature at the sample site is about 0.2 K. For the measurement at 77 K the sample holder was placed directly in the liquid nitrogen. The frequencies given are accurate to ±5 kHz; the accuracy being determined by the line width of ^{35}Cl NQR.

The ^{1}H-NMR second moment studies of (TMA) $TlCl_4$ were done with a broadband regenerative oscillator at a frequency of about 8.100 MHz in a field of 0.1900 Tesla. The temperature at the sample was controlled by a regulated stream of nitrogen gas with an accuracy of ±1 K.

III. Results

Crystal Structure

From the X-ray diffraction intensity data and the systematic extinctions it was found that (TMA)$TlCl_4$ crystallizes in the orthorhombic space group D_{2h}^{19}-Cmmm. (TEA)$TlCl_4$ belongs to the hexagonal space group C_{6v}^4-$P6_3mc$. The position of the thallium and chlorine atoms was determined by the Patterson method (SHELX-86). The nitrogen position was taken from a difference Fourier map. The carbon atoms could not be fixed because of the tumbling motion of the tetraalkylammonium ions at room temperature. The structures were refined by means of the full matrix least squares method. In Table 1 the space group and the lattice constants are given. Table 2 contains the positional and thermal parameters. Table 3 shows bond lengths, intermolecular distances, and angles within the $TlCl_4$-tetrahedron.

Table 3. Bond lengths in pm and bond angles in degrees.

(TMA)$TlCl_4$				
Tl−Cl 1	238.2 (9)		Cl 1−Tl−Cl 2	106.5 (2)
Tl−Cl 2	245.0 (13)		Cl 1−Tl−Cl 1	120.8 (6)
			Cl 2−Tl−Cl 2	109.8 (7)
N−N′	132.8 (107)			
N Cl 1	320.7	2*x*		
N Cl 1	439.2	2*x*		
N Cl 2	459.7	2*x*		
N Cl 1	481.0	4*x*		
(TEA)$TlCl_4$				
Tl−Cl 1	238.8 (18)		Cl 1−Tl−Cl 2	107.7 (3)
Tl−Cl 2	240.1 (8)	3*x*	Cl 2−Tl−Cl 2	111.2 (3)
N Cl 2	422.9	3*x*		
N Cl 1	478.1	3*x*		
N Cl 2	525.3	6*x*		

^{35}*Cl Nuclear Quadrupole Resonance and DTA Measurements*

Figure 1 shows the temperature dependence of the ^{35}Cl NQR frequencies of (TMA)$TlCl_4$ and (TEA) · $TlCl_4$. The corresponding ^{37}Cl NQR frequencies have been detected, too. The two resonance lines of (TMA)$TlCl_4$ vanish due to a first order phase transition at $T_{tr}=239$ K (DTA: $T_{tr}=243$ K). Above T_{tr} no ^{35}Cl NQR signal could be detected.

The four resonance lines of (TEA)$TlCl_4$ also disappear as consequence of a first order phase transition at $T_{tr}=222$ K (DTA: $T_{tr}=217$ K). The four line ^{35}Cl NQR spectrum of (TEA)$TlCl_4$, low temperature phase II, is split into two groups of lines, a three line group at about 19.9 MHz and an 'isolated' line at about 21 MHz ($T=77$ K).

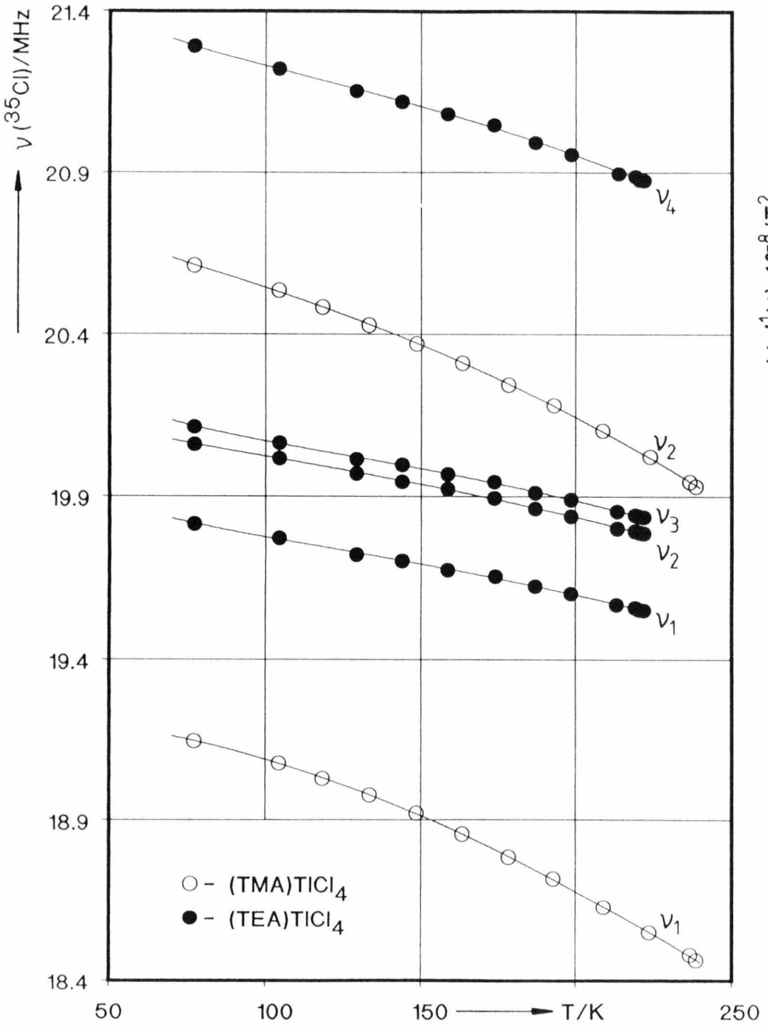

Fig. 1. ^{35}Cl-NQR frequencies of tetramethylammonium-tetrachlorothallate(III) (TMA)TlCl$_4$ and tetraethylammonium-tetrachlorothallate(III) (TEA)TlCl$_4$ as functions of temperature.

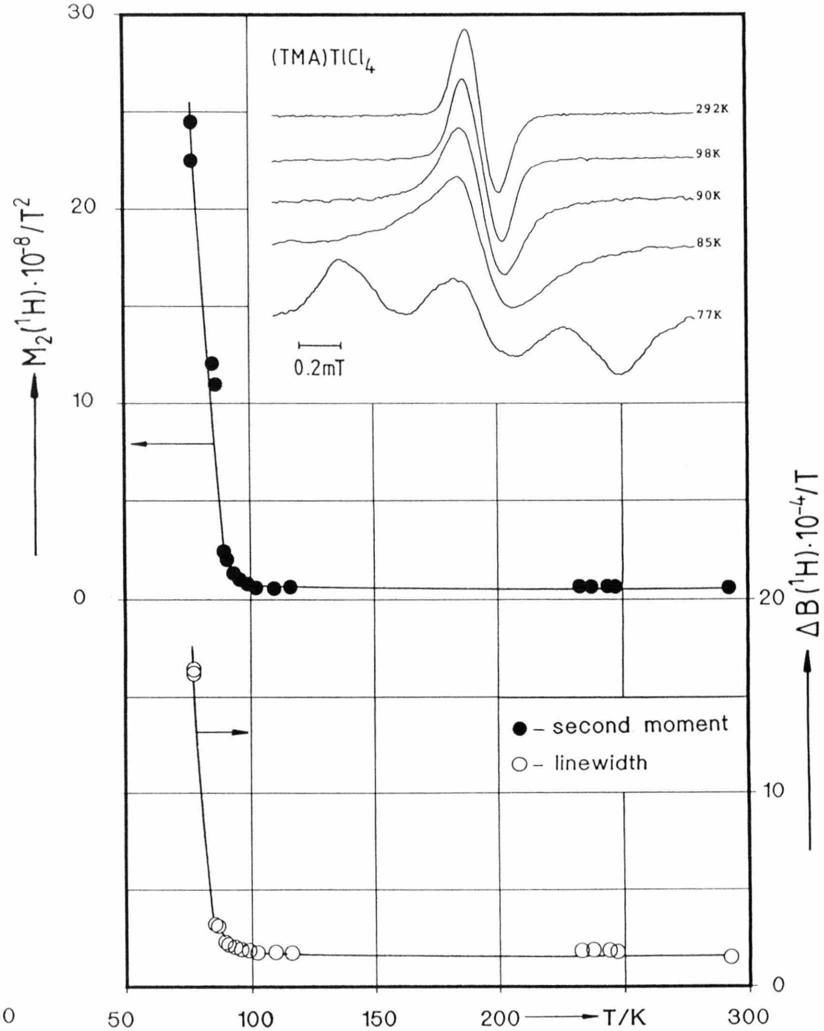

Fig. 2. ^{1}H-NMR linewidth ΔB and second moment $M_2(^1H)$ of tetramethylammonium-tetrachlorothallate(III). The change of the ^{1}H-NMR spectrum with temperature is shown, too.

Table 4. ^{35}Cl-NQR frequencies and polynomial parameters, $\nu(T) = a_0 + a_1 T + a_{-1} T^{-1} + a_2 T^2$. σ is the mean deviation of the calculated frequencies. The signal to noise ratio, S/N, was measured with lock in technique, time constant 10 s. n is the number of data points. The power series development is valid in the range $77 \leqq T/\mathrm{K} \leqq T_{tr}$; ($T_{tr}$ (TMA)TlCl$_4$ = 239 K; T_{tr} (TEA)TlCl$_4$ = 222 K).

Substance	ν/MHz	n	S/N	σ/kHz	a_0/MHz	$a_1 \cdot 10^3$/MHz K^{-1}	a_{-1}/MHz K	$a_2 \cdot 10^6$/MHz K^{-2}
(TMA)TlCl$_4$	19.149	12	10	2	19.359	−1.2933	−3.9718	− 9.9918
	20.610	12	10	4	20.593	0.0107	6.8737	12.095
(TEA)TlCl$_4$	19.817	12	6	3	19.693	0.4696	9.4433	− 5.8271
	20.062	12	6	3	20.045	−0.2562	4.9181	− 4.5059
	20.117	12	6	3	19.931	0.7903	12.700	− 6.6056
	21.292	12	6	5	21.051	1.3131	15.816	−10.986

For both compounds, $\nu(^{35}\mathrm{Cl}) = f(T)$ was fitted with a polynom of the form

$$\nu(T) = \sum_{i=-1}^{2} a_i \cdot T^i. \tag{1}$$

The resonance frequencies at 77 K and the coefficients a_i are given in Table 4.

^{1}*H-NMR; Line Width and Second Moment*

The ^{1}H-NMR linewidth and the second moment $M_2(^1H)$ of the TMA protons were studied as functions of temperature. Figure 2 shows the broadening of the resonance line with decreasing temperature. In the range $100 \leqq T/\mathrm{K} \leqq 300$, both the linewidth and $M_2(^1H)$ are independent of T. In the range $77 \leqq T/\mathrm{K} \leqq 100$ the line is broadened and at 77 K the line shape becomes strongly structurized. The second moment rises from a plateau at $0.67 \cdot 10^{-8}$ T^2 up to more than $24 \cdot 10^{-8}$ T^2. The interesting fact is a constant $M_2(^1H)$ during the phase transition.

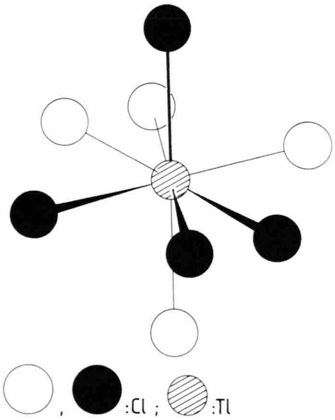

Fig. 3. The two possible tetrahedral positions of chlorine around the thallium in (TMA)TlCl$_4$.

IV. Discussion

Tetramethylammonium-tetrachlorothallate(III) (TMA) TlCl$_4$

(TMA)TlCl$_4$, phase I, stable at room temperature, crystallizes in the orthorhombic space group Cmmm with two formula units in the unit cell. The arrangement of the chlorines around the thallium is quite interesting. They form a distorted cube, with the Tl^{3+} ion in the center. Each corner of the cube is occupied with only half a chlorine atom. Each thallium is surrounded by four chlorine atoms, but there are two orientations of the TlCl$_4$ tetrahedron possible. Statistically each one is occupied with the weight factor K = 1/2. Together they give a distorted cube, as seen in Figure 3. The tetrahedral surrounding of the Tl^{3+} in tetrahalogenothallates(III) is also proved by Raman and infrared vibrational measurements [10–13]. In all tetrachlorothallates(III) the symmetric stretching vibration (A$_1$) occurs at frequencies above $\nu_1 = 300$ cm^{-1}. Other coordinations around the thallium like (TlCl$_5$)$^{2-}$, (TlCl$_6$)$^{3-}$, or (Tl$_2$Cl$_9$)$^{3-}$ would exhibit an intensive Raman (IR) band below 300 cm^{-1} [10, 13]. The asymmetric stretching vibration (F$_2$; $\nu_3 \approx 290$ cm^{-1}) and two bending vibrations (E, F$_2$; $\nu_{2,4} \approx 100$ cm^{-1}) are related to the tetrahedral coordination. For (TMA)TlCl$_4$ [11], the Raman spectrum shows the following frequencies: $\nu_1 = 303$, $\nu_2 = 88$, $\nu_3 = 293$, and $\nu_4 = 104$ cm^{-1}. This indicates the tetrahedral structure of the TlCl$_4$ ion.

The bond length of the Tl–Cl bond is dynamically shortened by the motion of the tetrahedron. The average value for the Tl–Cl bond in (TMA)TlCl$_4$ is 236.6 pm, while the typical bond length, for example in NH$_4$TlCl$_4$, is 241.8 pm.

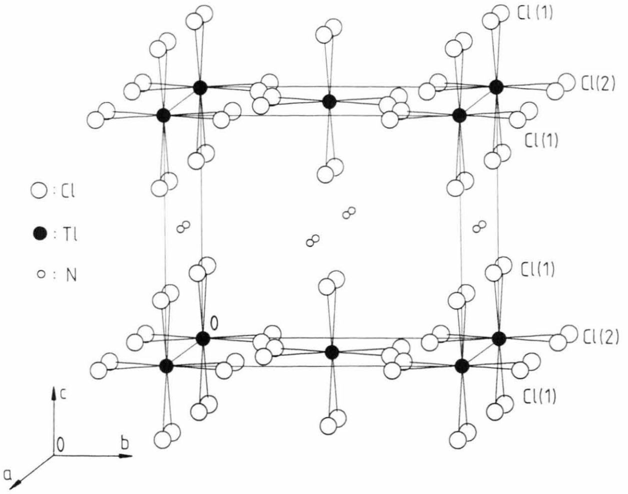

Fig. 4. The unit cell of (TMA)$TlCl_4$.

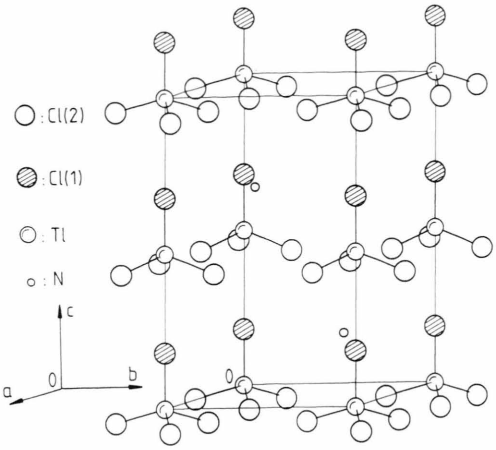

Fig. 5. Projection of the unit cell of (TEA)$TlCl_4$, phase I, along [100] onto the plane (100).

Figure 4 shows the unit cell of (TMA)$TlCl_4$. There are two locations of the $TlCl_4$ tetrahedron. The first unit lays at the corners of the unit cell, the second one is face centered, on the (001) plane.

The centers of gravity of the TMA groups, the nitrogen atoms, are located near the planes (100) and (010). However, the positions are not exactly in plane. One position is slightly behind and one is in front of the mirror plane. The occupancy factor K for each of the two positions is 0.5. Between these two locations, which have a distance of 132.8 pm, the nitrogen atom and therefore the whole TMA group oscillates.

The ^{35}Cl-NQR data and the crystal structure analysis are not directly comparable because of the different temperature ranges of observation. The crystal structure was determined at room temperature and the ^{35}Cl-NQR measurements were taken between 77 K and 240 K. From the phase transition observed at ~240 K we know that the crystal structures at 77 K and room temperature are different. This is in accordance with the DTA results and the observation that the crystals crack when they are cooled down through T_{tr}. The ^{35}Cl-NQR measurements show two resonance lines up to the point of the phase transition. From this one concludes that phase II has like phase I two crystallographically independent chlorine atoms. The chlorine atoms in phase II, however, cannot be statistically disordered. A disorder would disturb the electrical field gradient and no ^{35}Cl-NQR signal could be detected. We therefore conclude that the phase transition is connected with an order/disorder effect in the anion sublattice, and the ^{35}Cl nuclear quadrupol resonances bleach out at the phase transition temperature, becoming unobservable above T_{tr}.

Another problem is the behaviour of the TMA cation. To study it, ^{1}H-NMR experiments were done. The linewidth $\Delta B(^1H)$ and also the second moment $M_2(^1H)$ are both constant in the range from $100 \leqq T/K \leqq 300$. There from it follows that the phase transition does not have any effect on the overall tumbling motion of the TMA group. The low value of the second moment $M_2(^1H) = 0.67 \cdot 10^{-8}$ T^2 compared e.g. with the $M_2(^1H)$ of tetramethylammoniumchloride ($1.5 \cdot 10^{-8}$ T^2) [14] indicates the flipping of the nitrogen atoms between their two positions connected with the tumbling motion of the whole cation (see Table 5). At $T \leqq 100$ K both the tumbling motion of the ion $(CH_3)_4N^+$ and the individual methyl group reorientations are partially frozen in and the $M_2(^1H)$ is increased to a value above $24 \cdot 10^{-8}$ T^2. At 77 K this process is not completed and the TMA group is not totally rigid. $M_2(^1H)$ does not reach its plateau, and for that reason no limiting value for (TMA)$TlCl_4$ can be given. This compound has no temperature range where only the methyl group reorientation takes place like in (TMA)Cl or (TMA)Br. The motion is frozen in one step.

Tetraethylammonium-tetrachlorothallate (III) (TEA) $TlCl_4$

(TEA)$TlCl_4$ belongs to the space group $P6_3mc$. The $TlCl_4^-$ ion is a slightly distorted tetrahedron. It has a threefold axis (oriented along the crystallographic *c*-axis, see Figure 5). This leads to three crystallographically equivalent chlorine atoms. The fourth chlorine is located on the threefold axis with a slightly shortened bond d(Tl–Cl) = 240.1 pm and d(Tl–Cl) = 238.8 pm, respectively, see Table 3. The chlorine coordination of the TEA group is derived from a tetrahedron, the corners of which are cut-off, leading to a polyhedron with twelve coordinating corners, consisting of four triangles and four hexagons (Figure 6).

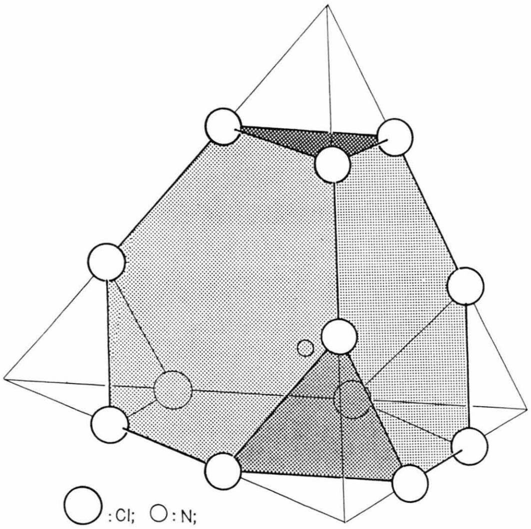

Fig. 6. The coordination of chlorine around the TEA group.

Table 5. Comparison of the second moment $M_2(^1H)$ in 10^{-8} T^2 of the TMA group.

	(TMA)Cl	(TMA)Br	(TMA)$TlCl_4$
Rigid	33.6	30	> 24
Methyl reorientation	11.6	10	–
Isotropic reorientation	1.5	1.6	0.67
Reference	[14]	[17]	this work

(TEA)$TlCl_4$ is isostructural with the corresponding indium salt, whose crystal structure was investigated by Trotter [15]. For comparison see Table 6.

The Raman and IR investigations of Millikan [13] support the tetrahedral coordination of the $TlCl_4$ ion. The symmetric stretching vibration was found at $\nu_1 = 304\ \text{cm}^{-1}$, the anti-symmetric stretching vibration at $292\ \text{cm}^{-1}$, and the bending vibrations at $90\ \text{cm}^{-1}$ with Raman scattering techniques. We remark that the unit cell of the indium salt ($794 \cdot 10^{-6}\ \text{pm}^3$) is within the error of the same size as that of the thallium compound ($789.4 \cdot 10^{-6}\ \text{pm}^3$), although the In–Cl bond (230 pm, respectively 236 pm) is shorter than the Tl–Cl bond (238.8 pm, respectively 240.1 pm). This means that not the anion but the cation size determines the structure. The temperature dependent NQR measurements of (TEA)$TlCl_4$ show four ^{35}Cl NQR lines in the range $77 \leqq T/\text{K} \leqq T_{\text{tr}}$. Above T_{tr} no signal could be detected. From the crystal structure determination at room temperature we know that there are two crystallographically independent chlorine atoms. At the phase transition the chlorine atoms at the point position 6c, connected by the C_3-axis, must split with lowering the symmetry into three independent positions. This leads to the three observed lower NQR frequencies. According to the equation

$$\text{EFG} = \int \varrho \left(\frac{3\cos^2\Theta - 1}{r^3} \right) \mathrm{d}\tau \qquad (2)$$

with ϱ = charge density,
Θ = angle with the z-axis,
r = distance of the volume element $\mathrm{d}\tau$ from the quadrupolar nucleus,

the longer Tl–Cl(2) bonds belong to the lower ^{35}Cl-NQR frequencies, whereas the upper line at ~21

Table 6. Comparison of the isotopic compounds (TEA)$TlCl_4$ and (TEA)$InCl_4$ (space group $P6_3mc$ [15]).

	(TEA)$TlCl_4$			(TEA)$InCl_4$		
	x/a	y/b	z/c	x/a	y/b	z/c
Tl/In	0	0	0	0	0	0
Cl (1)	0	0	0.1796	0	0	0.1775
Cl (2)	−0.1595	0.1595	−0.0548	−0.1527	0.1527	−0.0511
N	0.3333	0.6667	0.6883	0.3333	0.6667	0.7367
a/pm	827.9			830		
c/pm	1329.8			1331		
c/a	1.606			1.604		

MHz belongs to the shorter Tl–Cl(1) bond; parallel to the *c*-axis. However, the ^{35}Cl NQR frequency is not only determined by the Tl–Cl bond. Also the lattice contributes to the electric field gradient. The contribution is proportional to the reciprocal volume of a formula unit V_f in the elementary cell [16] and lowers the EFG.

$$\mathrm{EFG} = e\,q_{\mathrm{bond}} - C\,1/V_f; \tag{3}$$

C is a constant which contains the positional parameters of the atoms and the Sternheimer antishielding factor of chlorine.

This means, the larger the volume of one formula unit the smaller the lattice contribution. Therefore the average ^{35}Cl NQR frequency of $\mathrm{TMATlCl_4}$ (ν_{av} = 19.880 MHz; $V_f = 307.4 \cdot 10^{-6}$ pm^3/mol) is lower than the one of $\mathrm{TEATlCl_4}$ (ν_{av} = 20.322 MHz; $V_f = 394.7 \cdot 10^{-6}$ pm^3/mol).

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