^{35}Cl NQR Studies of Hexachlorometallates(IV) with Organic Cations, $A_2[MCl_6]$ and $A'[MCl_6]$, M = Sn, Te, Pb, and A^+, A'^{2+} = Organic Cation*

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^{35}Cl NQR spectra of eleven hexachlorometallates (IV) $A_2[MCl_6]$ and $A'[MCl_6]$, M = Sn, Te, Pb, and A^+ = ethylammonium, 4-picolinium, anilinium, triethylammonium, chinoxalinium, and piperidinium ions, and A'^{2+} = 1.3-propylenediammonium ion, have been observed as a function of temperature. The ethylammonium hexachlorometallates(IV) $(C_2H_5NH_3)_2[MCl_6]$, M = Sn, Te, show a phase transition at 128.8 K and 204 K, respectively. Both compounds yield a single resonance line in their high temperature phases. In case of the stannate this single ^{35}Cl resonance line splits up into two lines at $T_c = 128.8$ K, whereas for the tellurate no ^{35}Cl NQR signals could be found in the low temperature phase. A phase transition was also found for the 1.3-propylenediammonium hexachlorostannate(IV) at 287 K where the six line NQR spectrum of the low temperature phase changes into a four line spectrum. In contrast, the corresponding plumbate shows no transition. All other compounds studied contain distorted $[MCl_6]^{2-}$ octahedra, and therefore they yield more than one ^{35}Cl resonance line. The complexes have been investigated in the temperature range $77 \leqq T/K \leqq$ temperature where the lines fade out. In case of the hexachlorostannates(IV) with the ethylammonium, the 1.3-propylenediammonium and the triethylammonium ions, the crystal structures of the compounds are known and compared with the results of the ^{35}Cl NQR spectroscopy.

Introduction

^{35}Cl NQR spectroscopy is a valuable method to gain information about the symmetry of the hexachlorometallate(IV) complex anions $[MCl_6]^{2-}$. Each crystallographically different chlorine atom yields one ^{35}Cl NQR signal. From the frequency of these NQR lines one gains information about the nature of the chemical bond in these complexes, and from the numbers and the intensities of the resonances lines predictions about octahedral symmetry can be made. Therefore hexachlorometallates(IV) $A_2[MCl_6]$ and $A'[MCl_6]$, M = Sn, Te, Pb, Pt, and A^+, A'^{2+} = inorganic or organic cations, have been studied intensively within the last thirty years. For a review of literature see [1, 2]. The first compounds investigated by ^{35}Cl NQR spectroscopy were the hexachlorometallates(IV) with inorganic cations, like the alkali metal ions [3–7] or hexahydrated bivalent metal ions [5, 8–10], which all have highly symmetric crystal structures with regular or almost regular $[MCl_6]^{2-}$ octahedra.

In case of organic ammonium cations with lower symmetry two main effects have to be considered. First, the appearance of H-bonds N–H ... Cl between cations and anions leads to a decrease of octahedral $[MCl_6]^{2-}$ symmetry and mostly of the lattice symmetry, too. Furthermore, the symmetry of the $[MCl_6]^{2-}$ octahedra and of the crystal lattice will be decreased by the non sphericity of the organic cations. Examples are the ethylenediammonium (enH_2^{2+}) [11], the pyridinium (pyH^+) [12] and the piperazinium ($pipH^+$) ion [13].

Some approaches have been made to understand the nature of the chemical bond in such hexachlorometallate(IV) compounds [5, 14, 15]. We have recently shown that the ^{35}Cl NQR frequency and the electric field gradient (EFG) at the chlorine site in alkali hexachlorometallates(IV) can be well described using the "Multiple Scattering"-Xα-method (MS-Xα) and the point charge model [15]. A r^{-3} dependence is found for the ^{35}Cl NQR frequency, where r is the distance between the ions in the crystal lattice and the chlorine nucleus considered. We also have shown that this r^{-3} dependence is found for the averaged resonance frequency of the hexachlorometallate(IV) com-

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plexes with organic ammonium cations, too [16]. For the correlation $\langle \nu \rangle$ vs. r^{-3} we reported frequency data at room temperature of several hexachlorometallates(IV) with organic cations which shall be presented here in detail.

In the present paper ^{35}Cl NQR data of eleven hexachlorometallates with organic cations as a function of temperature are given, and in some cases a comparison with structural data is made.

Experimental

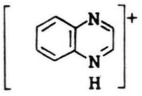
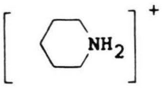
Preparation of the Compounds

The various title hexachlorostannate(IV) compounds were prepared by a general method: A solution of $SnCl_4$ in 2 n HCl was mixed with a stoichiometric amount of the organic amine in dilute hydrochloric acid. The white crystalline products formed were recrystallized from 2 n HCl. Similarly the tellurate compounds were synthesized: Tellurium dioxide TeO_2 was dissolved in conc. hydrochloric acid and mixed with a solution of the amine in conc. hydrochloric acid. The yellow precipitate was filtered off and recrystallized in conc. hydrochloric acid. In case of the lead compounds, $Pb(OOCCH_3)_4$ was dissolved in conc. hydrochloric acid. A stoichiometric amount of the corresponding organic amine hydrogenchloride was added. The yellow precipitate was filtered off immediately and redissolved in conc. hydrochloric acid. During this procedure and also during cooling, chlorine gas was passed through the solution to avoid reduction of the $[PbCl_6]^{2-}$ ion. The crystalline solid was filtered off and dried over $CaCl_2$ in a desiccator. The yields for all preparations were nearly quantitative. All chemicals were of commercial source and of laboratory grade. In Table 1 the chemical analysis, habitus of the crystalline solid, colour and the melting points are listed.

^{35}Cl NQR

All compounds were studied by ^{35}Cl NQR spectroscopy in the temperature range $77 \leqq T/\mathrm{K} \leqq$ temperature where the resonance lines fade out. For these investigations a superregenerative NQR spectrometer (DECCA-RADAR) was used. The experimental conditions were: magnetic modulation, sideband suppression (in most cases), and 10 s time constant. To get the wanted temperatures at the sample site, different methods were used (temperature range, method, estimated error in T): 77 K, liq. N_2 bath, ± 0.5 K; $100 \leqq T/\mathrm{K} \leqq 200$, N_2 gas stream, ± 0.8 K; $200 \leqq T/\mathrm{K} \leqq 300$, methanol bath, ± 0.1 K; $300 \leqq T/\mathrm{K} \leqq 450$, oil bath, ± 0.5 K. All temperatures were measured with copper-constantan thermocouples. The accuracy in determining the frequency is ± 0.005 MHz, and this limitation is due to the line width.

Table 1. Habitus, colour, decomposition temperature T_d, and chemical analysis (C, H, N) of various hexachlorometallates $A_2[MCl_6]$ and $A'[MCl_6]$, M = Sn, Te, Pb, and A^+, A'^{2+} = organic cations.

A^+, A'^{2+}	M	Colour	Habitus	T_d/K	Chemical analysis (% weight)					
					C_{calc}	C_{exp}	N_{calc}	N_{exp}	H_{calc}	H_{exp}
$C_2H_5NH_3^+$	Sn	white	plates	574	11.34	11.31	6.61	6.68	3.78	3.76
	Te	yellow	plates	415	11.10	10.92	6.48	6.40	3.70	3.76
$[H_3N(CH_2)_3NH_3]^{2+}$	Sn	white	plates	543	8.84	8.71	6.87	6.97	2.95	2.85
	Pb	yellow	prism	440	7.26	7.41	5.65	5.72	2.42	2.50
$[p\text{-}CH_3C_5H_4NH]^+$	Sn	white	plates	512	27.74	27.50	5.39	5.44	3.10	2.87
	Te	yellow	plates	469	27.27	27.17	5.30	5.35	3.05	2.97
	Pb	yellow	plates	385	23.70	23.70	4.61	4.63	2.65	2.54
$C_6H_5NH_3^+$	Sn	white	needles	420	27.70	27.70	5.40	5.38	3.08	3.09
$(C_2H_5)_3NH^+$	Sn	white	prism	464	26.90	26.61	5.23	5.19	6.02	5.92
	Sn	white	plates	549	32.26	32.20	9.44	9.42	2.36	2.32
	Sn	white	prism	501	23.84	24.02	5.56	5.53	4.77	4.75

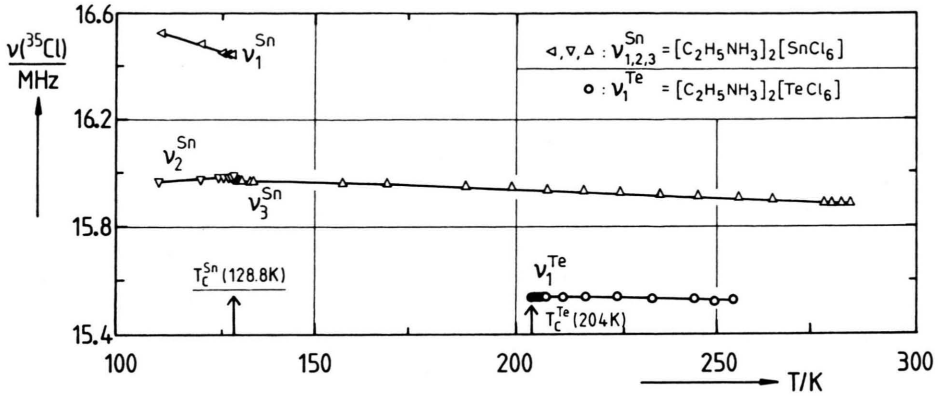


Fig. 1. ^{35}Cl NQR frequencies of ethylammonium hexachlorostannate(IV) $(C_2H_5NH_3)_2[SnCl_6]$ and of ethylammonium hexachlorotellurate(IV) $(C_2H_5NH_3)_2[TeCl_6]$ vs. temperature. T_c^{Sn} *and* T_c^{Te} are the temperatures of the phase transition I↔II of the tin and tellurium complexes, respectively.

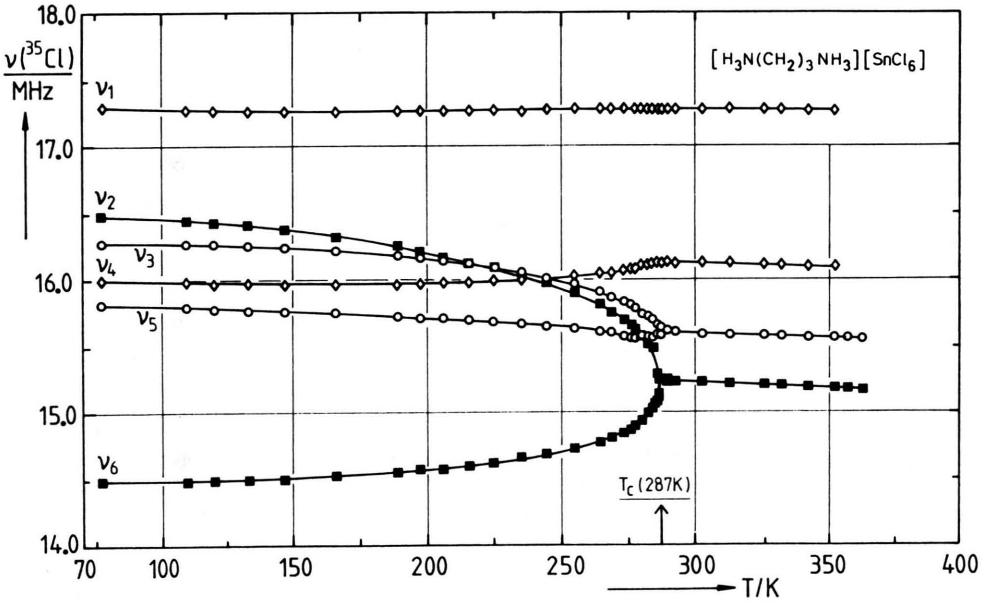


Fig. 2. ^{35}Cl NQR frequencies of 1.3-propylenediammonium hexachlorostannate(IV) $[H_3N(CH_2)_3NH_3]$ $[SnCl_6]$ vs. temperature. T_c is the temperature of the phase transition I↔II.

Results

In Fig. 1 the ^{35}Cl NQR frequencies of the ethylammonium hexachlorometallates(IV) $(EtNH_3)_2[MCl_6]$, M = Sn, Te are plotted vs. temperature. $(EtNH_3)_2SnCl_6$ shows two resonance lines of comparable intensities at 110 K. On decreasing the temperature, the lines become broad and intensities are decreasing, probably because of relaxation effects. At $T_c = 128.8$ K a phase transition occurs and the two line spectrum changes into a single line spectrum. The corresponding tellurate(IV) shows one ^{35}Cl NQR line in the temperature range $204 \leqq T/K \leqq 254$. At $T_c = 204$ K a phase transition, detected by the application of DTA, was observed for the tellurate(IV) too, but we were not able to observe any resonance lines below T_c, probably because of a disordered low temperature phase in $(EtNH_3)_2TeCl_6$.

In Fig. 2 the ^{35}Cl NQR frequencies of 1.3-propylendiammonium hexachlorostannate(IV), $[H_3N(CH_2)_3NH_3]SnCl_6$ are plotted vs. temperature. This compound also shows a phase transition at $T_c = 287$ K,

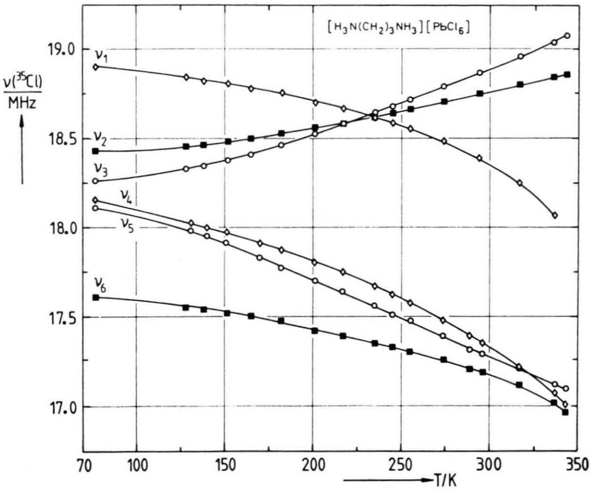


Fig. 3. ^{35}Cl NQR frequencies of 1.3-propylenediammonium hexachloroplumbate(IV) $[H_3N(CH_2)_3NH_3]$ $[PbCl_6]$ vs. temperature.

where the six line spectrum changes into a four line spectrum with an intensity ratio of 2:2:1:1 for the four resonance lines observed. The ^{35}Cl NQR spectrum of the corresponding plumbate(IV) shows six resonance lines (Fig. 3) in the temperature range $77 \leqq T/K \leqq 343$. No phase transition is observed.

Figures 4–6 include the temperature dependent ^{35}Cl NQR spectra of the 4-picolinium(4-picH) hexachlorometallates(IV) $(4\text{-}CH_3\text{-}C_5H_4NH)_2[MCl_6]$, M = Sn, Te, Pb. The NQR spectra of the tin and tellurium complexes are very similar; two resonance lines with the high frequency line of double intensity are observed. In case of the plumbate(IV) three resonance lines of comparable intensities are found in the temperature range $77 \leqq T/K \leqq 336$.

Figures 7–10 show the temperature dependent ^{35}Cl NQR spectra of four hexachlorostannates(IV) with different organic cations, i.e. the anilinium (anlH$^+$), Me_3NH^+, chinoxalinium (chinxlH$^+$), and piperidinium (pipH$^+$) ions.

To rationalize the ^{35}Cl NQR spectra of the various hexachlorometallates(IV), the experimental data were approximated by a power series

$$\nu(^{35}\mathrm{Cl}) = f(T) = \sum_{-1}^{4} a_i\, T^i. \tag{1}$$

The coefficients of this power series approximation are compiled in Table 2 and the resonance frequencies of these compounds at selected temperatures are given in Table 3. Additionally, in Table 3 the signal-to-noise ratios of the ^{35}Cl NQR lines are listed.

Discussion

The ^{35}Cl NQR spectrum of the high temperature phase of $(EtNH_3)_2SnCl_6$ shows a single resonance line which is in agreement with the crystal structure of this compound determined by Knop et al. [17]. The compound crystallizes in the hexagonal space group $P\bar{3}m1$ ($Z = 1$). The point symmetry of $[SnCl_6]^{2-}$ is $\bar{3}m$ and therefore all six chlorine atoms are crystallographically equal. $EtNH_3^+$ cations are disordered. The authors postulate a threefold rotational disorder of the ethylgroup around the N–C axis; from ^{35}Cl NQR we conclude that this is a dynamic disorder. At the phase transition point ($T_c = 128.8$ K) this rotation probably freezes in. The low temperature phase is ordered, containing distorted $[SnCl_6]^{2-}$ octahedra with, according to the two ^{35}Cl NQR lines, two crystallographically different chlorine atoms. In case of the corresponding tellurate(IV) no detailed crystal structure is known. Comparing the ^{35}Cl NQR spectra of both $EtNH_3^+$ salts one might conclude that both complexes are isostructural in their high temperature phase. $(EtNH_3)_2TeCl_6$ also shows a phase transition at $T_c = 204$ K. This transition was detected using DTA. In contrast to the stannate(IV) the low temperature phase of the tellurate(IV) must be statistically disordered because we were unable to detect ^{35}Cl resonance signals below T_c. At higher temperatures ($T > 250$ K) the resonance signals of both compounds broaden and fade out, probably because of relaxation phenomena.

Regarding the ^{35}Cl NQR spectrum of $[H_3N(CH_2)_3NH_3]SnCl_6$ one finds a phase transition at $T_c = 287$ K, where the symmery of $[SnCl_6]^{2-}$ is increased. The six line spectrum is changed, and in the high temperature phase four resonance lines are found with the intensity ratio of 2:2:1:1. This transition was confirmed by DTA experiments; we found a peak at 287.2 K. Abriel and Friedrich [18] have investigated the crystal structure of this compound by X-ray single crystal diffraction methods at room temperature, which means that they determined the structure of the high temperature phase. According to them, the $[H_3N(CH_2)_3NH_3]SnCl_6$ crystallizes in the orthorhombic space group Pnma with four formula units per unit cell. In agree-

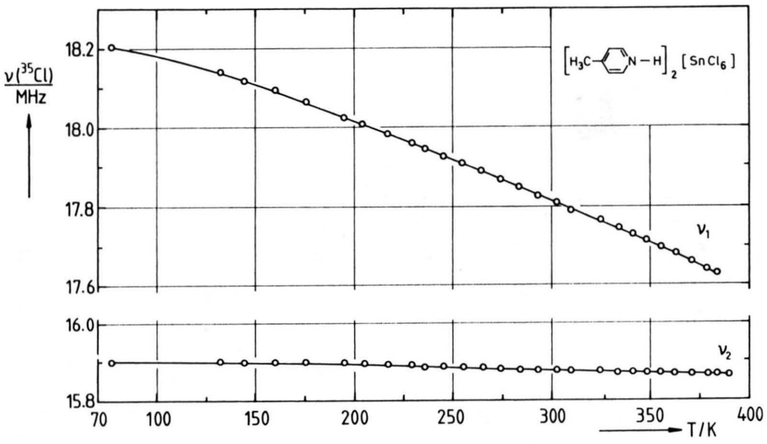


Fig. 4. ^{35}Cl NQR frequencies of 4-picolinium hexachlorostannate(IV) (4-CH_3-$C_5H_4NH)_2[SnCl_6]$ vs. temperature.

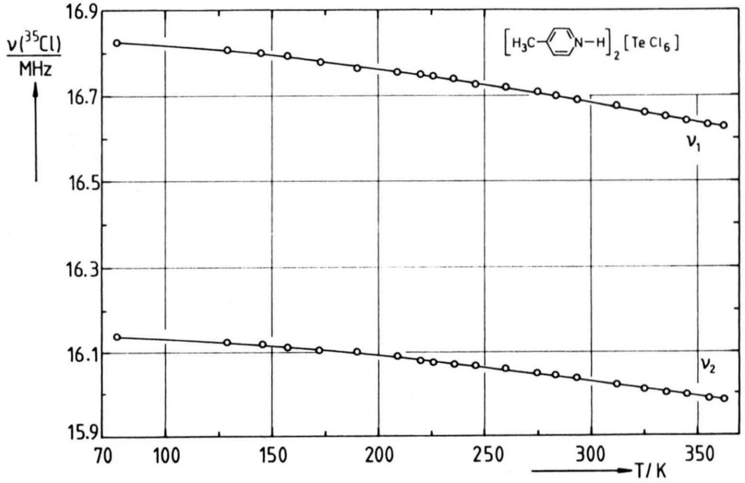


Fig. 5. ^{35}Cl NQR frequencies of 4-picolinium hexachlorotellurate(IV) (4-CH_3-$C_5H_4NH)_2[TeCl_6]$ vs. temperature.

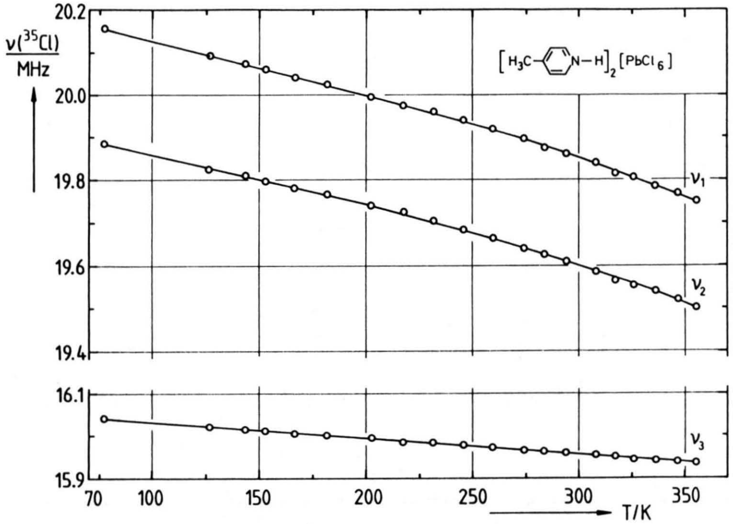


Fig. 6. ^{35}Cl NQR frequencies of 4-picolinium hexachloroplumbate(IV) (4-CH_3-$C_5H_4NH)_2[PbCl_6]$ vs. temperature.

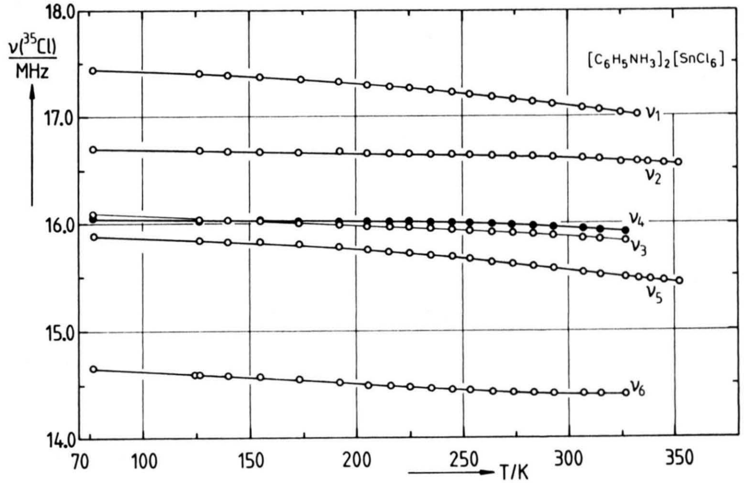


Fig. 7. ^{35}Cl NQR frequencies of anilinium hexachlorostannate(IV) $(C_6H_5NH_3)_2[SnCl_6]$ vs. temperature.

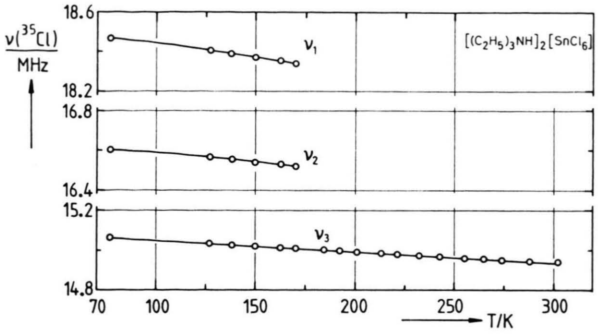


Fig. 8. ^{35}Cl NQR frequencies of triethylammonium hexachlorostannate(IV) $[(C_2H_5)_3NH]_2[SnCl_6]$ vs. temperature.

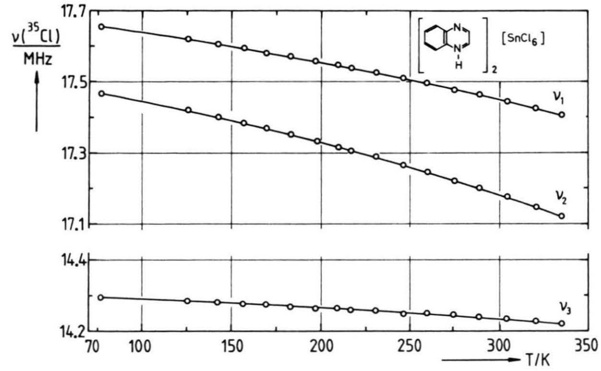


Fig. 9. ^{35}Cl NQR frequencies of chinoxalinium hexachlorostannate(IV) $(C_8H_7N_2)_2[SnCl_6]$ vs. temperature.

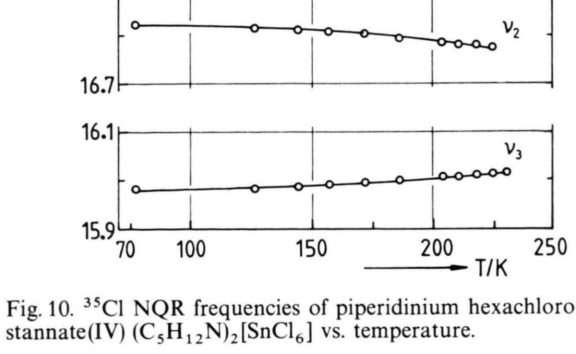
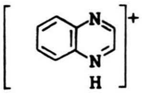
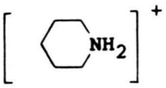


Fig. 10. ^{35}Cl NQR frequencies of piperidinium hexachlorostannate(IV) $(C_5H_{12}N)_2[SnCl_6]$ vs. temperature.

ment with our NQR data, the authors found four crystallographically different chlorine atoms. An interesting point considering this crystal structure is the disorder in the long cation. It is situated with its two nitrogen atoms and with two of the carbon atoms ($C^{(1)}$, $C^{(3)}$) on the mirror plane m at $y=1/4$. The carbon atom in the middle of the molecule ($C^{(2)}$) is disordered, lying off the mirror plane. On reflecting $C^{(2)}$ at the mirror plane two point positions will be generated for this atom. Another striking point are the bond angles within the cation: The N–C–C, C–C–C, and C–C–N angles are 123°, 124°, and 115° instead of about 109° for an ideal tetrahedron. Although the symmetry of the $[SnCl_6]^{2-}$ anion is well described by this space group, the unsolved problem how a disorder of the cation does affect the ^{35}Cl NQR spectrum is left. In case of the corresponding hexachloroplumbate(IV) no crystal structure data are available. The compound shows up six ^{35}Cl resonance lines in the temperature range $77 \leqq T/K \leqq 343$. Therefore one can conclude that the distortion of the $[PbCl_6]^{2-}$ octahedron is maximal. Furthermore, it is possible that the crystal lattices of the low temperature phase of $[H_3N(CH_2)_3NH_3]SnCl_6$ and the corresponding plumbate(IV) are isomorphous although no phase transition was observed for the plumbate(IV). Replacing the $[MCl_6]^{2-}$ anion by Br^- and I^-, respectively, the phase diagrams can be studied by NQR, too. Whereas the $[H_3N(CH_2)_3NH_3]Br_2$ does not experience a phase transition in the range $77 \leqq T/K \leqq 410$, a phase transition is observed for $[H_3N(CH_2)_3NH_3]I_2$ in the range $365 \leqq T/K \leqq 370$ showing hysteresis [19].

In Figs. 4–6 the ^{35}Cl NQR spectra of three $(4\text{-picH})_2[MCl_6]$, M = Sn, Te, Pb are plotted vs. temperature. The NQR spectra of the tin and tellurium complexes are very similar. Both yield two resonance lines with a higher frequency line of double intensity. The frequency of the second line is somewhat lower probably because of H-bonds N–H ... Cl. As we have shown recently [16], the M-Cl bond length of a H-bonded chlorine atom increases and therefore the EFG at the nucleus site decreases. The two 4-picolinium cations per formula unit have two acidic protons which are able to form H-bonds N–H ... Cl with two of the chlorine atoms of a $[MCl_6]^{2-}$ complex ion. Therefore the low frequency line of $(4\text{-picH})_2[MCl_6]$, M = Sn, Te, probably belongs to H-bonded chlorine atoms. Regarding the ^{35}Cl NQR spectrum of $(4\text{-picH})_2PbCl_6$ one finds three resonance lines of comparable intensity. In contrast to the stannate(IV)

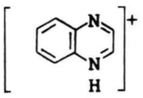
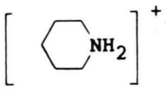
Table 2. Power series expansion $\nu(^{35}\text{Cl}) = f(T) = \Sigma\, a_i\, T^i$ for various hexachlorometallates $A_2[MCl_6]$ and $A'[MCl_6]$, M = Sn, Te, Pb and A^+, A'^{2+} = organic cation. Z is the number of experimental points used for the fitting. σ is the standard deviation and $\Delta T = T_1 \ldots T_2$ is the temperature range for which the polynomial $\Sigma\, a_i\, T^i$ was fitted to the experiment.

Cation	M	^{35}Cl NQR line	Z	$\frac{\sigma \cdot 10^3}{\text{MHz}}$	$\frac{a_{-1}}{\text{MHz K}}$	$\frac{a_0}{\text{MHz}}$	$\frac{a_1}{\text{MHz K}^{-1}}$	$\frac{a_2}{\text{MHz K}^{-2}}$	$\frac{\Delta T}{\text{K}}$
$C_2H_5NH_3^+$	Sn	ν_1	5	5.0	266.0207	10.1511	550.0752	−172.2438	111 ... 130
		ν_2	7	1.2	239.7649	9.8932	503.2356	−135.5900	111 ... 130
		ν_3	20	1.0	1.9590	15.9407	3.9882	−2.2393	130 ... 283
	Te	ν_1	14	2.0	296.0867	11.7223	167.8892	−25.3048	204 ... 254
$[H_3N(CH_2)_3NH_3]^{2+}$	Sn	ν_1	26	2.6	3.8468	17.2538	−2.9853	1.3701	77 ... 287
		ν_1	11	2.2	93.2698	15.7799	69.8580	−9.9358	287 ... 353
		ν_2	13	6.3	14.4111	16.0528	48.6810	−22.4280	77 ... 250
		ν_2	11	46	1597.80	−34.2030	3189.6	−577.057	250 ... 287
		$\nu_{2,6}$	13	1.6	499.7561	11.1300	118.00	12.2490	287 ... 363
		ν_3	13	2.9	17.9288	15.7570	50.846	−17.7220	77 ... 250
		ν_3	13	14	−91928.6	1023.00	−36654.0	4429.5	250 ... 287
		$\nu_{3,5}$	13	1.4	431.0953	12.2912	85.9648	−7.8759	287 ... 363
		ν_4	26	7.8	−28.3272	16.7724	−65.7890	16.2090	77 ... 287
		ν_4	13	1.4	−3189.65	45.9305	−920.0	93.7160	287 ... 353
		ν_5	30	8.8	−1.0758	15.8357	0.03857	−3.1138	77 ... 287
		ν_6	13	1.3	−13.6980	14.8955	−42.116	14.4980	77 ... 250
		ν_6	15	30	9783.87	−55.1410	1041.97	76.1706	250 ... 287
	Pb	ν_1	15	8.5	28.8654	18.2548	47.1452	−15.7163	77 ... 336
		ν_2	16	3.7	13.2136	18.1427	14.0023	1.6496	77 ... 343
		ν_3	16	4.6	26.2490	17.6627	32.5286	1.8344	77 ... 343
		ν_4	17	7.0	3.7167	18.1818	−3.4900	−8.1878	77 ... 343
		ν_5	17	8.6	−13.5782	18.5569	−32.7640	−3.0123	77 ... 343
		ν_6	17	12.8	15.5374	17.2852	23.1287	−9.6756	77 ... 343
$4CH_3\text{-}C_5H_4NH^+$	Sn	ν_1	28	2.7	−8.6395	18.4738	−19.9440	−0.3634	77 ... 389
		ν_2	27	1.6	−2.7243	15.9503	−2.3267	0.0674	77 ... 384
	Te	ν_1	21	3.0	−2.4517	16.8978	−4.5564	−0.7588	77 ... 363
		ν_2	21	2.0	−1.7181	16.1850	−2.5886	−0.8066	77 ... 363
	Pb	ν_1	20	2.2	5.0138	20.1222	−2.6778	−2.3138	77 ... 336
		ν_2	20	4.5	5.6339	19.8278	−0.3748	−2.6314	77 ... 336
		ν_3	20	1.6	0.8156	16.0521	−2.7743	−0.1795	77 ... 336
$C_6H_5NH_3^+$	Sn	ν_1	21	2.0	−2.8721	17.5147	−1.8602	−3.9144	77 ... 334
		ν_2	24	4.3	12.8730	16.4460	14.6450	−3.5827	77 ... 352
		ν_3	20	3.7	9.8696	15.9317	6.6243	−3.2480	77 ... 328
		ν_4	20	2.6	17.0349	15.6855	23.8150	−5.5863	77 ... 328
		ν_5	24	4.4	−11.2991	16.0856	−8.1147	−2.7676	77 ... 352
		ν_6	20	4.1	−14.4948	15.0858	−34.6130	4.5722	77 ... 328
$(C_2H_5)_3NH^+$	Sn	ν_1	6	1.1	6.8200	18.3338	11.3815	−7.9238	77 ... 170
		ν_2	6	1.4	−3.1420	16.7077	−7.7239	−1.2548	77 ... 170
		ν_3	14	2.0	−3.2312	15.1817	−10.7826	1.0032	77 ... 303
	Sn	ν_1	17	0.9	0.8720	17.6855	−4.3368	−1.2226	77 ... 335
		ν_2	17	1.0	−0.5549	17.5425	−7.5862	−1.4718	77 ... 335
		ν_3	17	1.5	−1.3749	14.8400	−3.4214	0.0026	77 ... 335
	Sn	ν_1	10	2.1	−9.2128	17.7426	−37.8317	2.2768	77 ... 225
		ν_2	10	1.1	−0.5543	16.8282	1.5772	−1.7150	77 ... 225
		ν_3	11	0.7	3.3768	15.9111	2.9572	0.3848	77 ... 225

or tellurate(IV) the high frequency line is split. From these results one can conclude that two of the six chlorine atoms of the $[MCl_6]^{2-}$ anion are involved in H-bonds N−H ... Cl between cation and anion. In case of the stannate(IV) and tellurate(IV) the remaining four chlorine atoms are crystallographically equivalent. In the plumbate(IV) the distortion of the complex anion is stronger, leading to three different kinds of chlorine atoms.

The first ^{35}Cl NQR data of $(4\text{-picH})_2[MCl_6]$, M = Sn, Te, Pb, were published by Brill and Welsh [7]. For the tin and tellurium complexes the authors reported

Table 3. ^{35}Cl NQR frequencies ν_i/MHz of various hexachlorometallates(IV) $A_2[MCl_6]$ and $A'[MCl_6]$, M = Sn, Te, Pb, and A^+, A'^{2+} = organic cations, at selected temperatures. The mean error of frequency is ±0.005 MHz. S/N is the signal-to-noise ratio at the given temperature.

Cation	M	^{35}Cl NQR line	77 K	S/N	200 K	S/N	300 K	S/N
$C_2H_5NH_3^+$	Sn	ν_1	–	–	15.941	20	15.875*	–
	Te	ν_2	–	–	15.543	40 (211 K)	15.520*	–
$[H_3N(CH_2)_3NH_3]^{2+}$	Sn	ν_1	17.287	3	17.266	4	17.293	4
		ν_2	16.482	3	16.195	4	15.230	8 (2,6)
		ν_3	16.275	3	16.155	4	15.595	8 (3,5)
		ν_4	15.998	3	15.972	4	16.132	4
		ν_5	15.804	3	15.708	4	–	–
		ν_6	14.480	3	14.566	4	–	–
	Pb	ν_1	18.899	3	18.713	4	18.350	5
		ν_2	18.431	3	18.554	4	18.755	5
		ν_3	18.264	3	18.517	4	18.891	5
		ν_4	18.154	3	17.803	4	17.352	5
		ν_5	18.110	3	17.713	4	17.257	5
		ν_6	17.607	3	17.438	4	17.160	5
$(4\text{-}CH_3\text{-}C_5H_4NH)^+$	Sn	ν_1	18.206	4	18.017	8	17.813	9
		ν_2	15.898	2	15.892	5	15.877	5
	Te	ν_1	16.826	6	16.764	6	16.684	12
		ν_2	16.138	3	16.092	3	16.029	6
	Pb	ν_1	20.155	2	20.001	4	19.850	7
		ν_2	19.882	2	15.743	4	15.598	7
		ν_3	16.040	2	15.993	4	15.955	7
$(C_6H_5NH_3)^+$	Sn	ν_1	17.440	4	17.310	5	17.092	4
		ν_2	16.702	4	16.656	5	16.610	4
		ν_3	16.092	4	15.983	5	15.872	4
		ν_4	16.056	4	16.021	5	15.954	4
		ν_5	15.862	4	15.761	5	15.551	4
		ν_6	14.660	4	14.512	5	14.411	4
$(C_2H_5)_3NH^+$	Sn	ν_1	18.463	20	–	–	–	–
		ν_2	16.600	15	–	–	–	–
		ν_3	15.063	15	14.990	10	14.937	10
	Sn	ν_1	17.656	3	17.554	5	17.448	5
		ν_2	17.468	3	17.329	5	17.180	5
		ν_3	14.796	4	14.765	5	14.735	6
	Sn	ν_1	17.345	9	17.030	3	–	–
		ν_2	16.823	9	16.788	3	–	–
		ν_3	15.980	9	16.000	3	–	–

* extrapolated value

only one resonance line at room temperature. From our results it can be concluded that they measured the high frequency lines, which have double intensity, for these two compounds. In case of the plumbate(IV) the authors mentioned three resonance lines, the two higher ones of which are identical with our data within the limits of error.

On comparing the 4-picolinium compounds with $(pyH)_2[MCl_6]$, M = Sn, Te, Pb, Pt [12] one finds out that in case of the 4-picolinium salts all ^{35}Cl NQR lines can be detected up to quite high temperatures (360–400 K). In contrast to $(pyH)_2[MCl_6]$, no rotational disorder of the cation is found here [20]. Probably because of the bulky methyl substituent in para position of the pyridinium ring such a rotational disorder of the cation around its pseudo-sixfold axis is impossible.

The ^{35}Cl NQR spectrum of $(anl\,H)_2SnCl_6$ shows six resonance lines, which indicates that the $[SnCl_6]^{2-}$ octahedron has maximum symmetry distortion. All resonance lines have been observed in the temperature range $77 \leqq T/K \leqq$ temperature where the lines fade out (≈ 350 K). The frequency of one of the ^{35}Cl resonance lines (ν_6) is below 15 MHz, which is a hint for a very strong H-bond N – H ... Cl. To confirm this supposition, IR spectroscopical experiments should be carried out.

$(Me_3NH)_2SnCl_6$ shows three resonance lines at 77 K. Heating up the sample, the two higher frequency lines broaden and fade out, whereas the lower frequency line can be observed up to room temperature. The structure of this compound, determined by Knop et al. [21], shows three crystallographically different chlorine atoms. The Me_3NH^+ cation is connected with the $[SnCl_6]^{2-}$ complex anion via a bifurcated H-bond having two different N – H ... Cl distances. The first N ... Cl contact is quite short (333 pm) whereas the second (346 pm) is relatively long for a N – H ... Cl H-bond in hexachlorometallates, see [11–13]. The first short H-bond is reflected in a low N – H stretching frequency (3110 cm^{-1}) at room temperature, which is about 110 cm^{-1} lower than in $(NH_4)_2SnCl_6$ [21]. According to Knop et al. the temperature dependence of the N – H and N – D stretching frequencies is "normal". Therefore the authors exclude a phase transition at lower temperatures. Our NQR experiments at low temperature confirm the results of the structure determination. The resonance frequencies of the three chlorine atoms are quite different, see Fig. 8 and Table 3. On comparing the Sn – Cl bond lengths and the ^{35}Cl NQR frequencies one can postulate an assignment $\nu_i \leftrightarrow Cl^{(i)}$. ν_3 is much lower than the other frequencies, therefore it should belong to the chlorine atom with the shortest N ... Cl contact (333 pm) and with the longest Sn – Cl distance (245.8 pm). ν_2 is not as low and should be assigned to the chlorine atom with the longer H-bond (N ... Cl = 346 pm) and the medium Sn – Cl bond length (242.7 pm). The third resonance line, ν_1, belongs to the chlorine atom with the shortest Sn – Cl bond (240.7 pm). The reason for the fade out of both higher frequency lines is not clear, probably relaxation phenomena are the reason. An onset of a rotational mode of the cation or other disorder effects are excluded because of the ordered crystal structure of this compound at room temperature. $(chinxlH)_2SnCl_6$ has been investigated by ^{35}Cl NQR spectroscopy in the temperature range $77 \leqq T/K \leqq 340$. The compound shows three resonance lines of equal intensity. The crystal structure of this complex has not been determined up to now, therefore the point symmetry of the $[SnCl_6]^{2-}$ octahedron is not known. From NQR spectroscopy one finds that the point symmetry must be at least $\bar{1}$. One of the three resonance lines representing two chlorine atoms is relatively low, probably because of hydrogen bonding. The two chinoxalinium cations per formula unit have two acidic protons which have to be distributed among the six chlorine atoms. Due to H-bonding, the splitting of the resonance frequencies is about 3.3 MHz, which is quite high.

Finally $(pipH)_2SnCl_6$ shows three resonance signals of the same intensity in the temperature range $77 \leqq T/K \leqq 230$. DTA experiments give no hint on a phase transition between 77 K and 360 K. Therefore the fade out of the lines is probably due to relaxation effects. No detailed crystal structure is known for this compound. Hjortdahl [22] has described crystals of $(pipH)_2SnCl_6$ as monoclinic prismatic. He determined the ratios of the lattice constants and the monoclinic angle $\beta = 90.29°$. The maximum splitting of the ^{35}Cl resonance lines of about 1.3 MHz in $(pipH)_2SnCl_6$ is much lower than in the corresponding chinoxalinium salt. Therefore the distortion of the $[SnCl_6]^{2-}$ octahedron due to H-bonding is lower.

All compounds investigated here include distorted $[MCl_6]^{2-}$ octahedra. The distortion is mainly caused by the appearance of H-bonds N – H ... Cl, which elongates the M – Cl distance of the H-bonded chlorine atom and decreases the EFG at the nucleus site and therefore the ^{35}Cl NQR frequency [16]. Additionally the non sphericity of the cations leads to a distortion of the $[MCl_6]^{2-}$ complex.

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