An NQR Study of Tetrachloride Complexes of Group IVA Elements*

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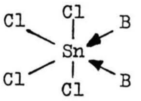
The results of an NQR study on the MCl_4 complexes (M = Si, Ge, Sn) with organic heteroatom ligands (including those containing several coordination centers) are summarized: chloroanhydrides of unsaturated, aromatic and heteroaromatic carboxylic acids; alkylarylethers, ketones, aryldichlorophosphates, nitrogen-containing compounds, etc. The octahedral or trigonal-bipyramidal structure of these complexes has been established, and the factors influencing the formation and structure of such complexes (component ratio, character of ligand and M atom) have been analyzed. The structure of several complexes may vary with time or depend on the crystallization condition of the system. Some of these results indicate coordination isomerism. The quantitative ratios between the ^{35}Cl NQR frequency shifts of ligand and axial Sn–Cl bonds in trigonal-bipyramidal $RCOCl \cdot SnCl_4$ complexes relative to the initial component frequencies have been found.

Introduction

Until recently information on the structure of tetrahalide complexes of group IVA elements (M = Si, Ge, Sn) has been limited. Of the available data on their composition and structure, the overwhelming majority was related to the octahedral complexes of tin tetrachloride $2B \cdot SnCl_4$ (see e.g. [1, 2]). This led some investigators to the erroneous conclusion that usually $SnCl_4$ forms complexes with organic ligands octahedral in which the Sn atom is hexacoordinated (I) and (II) [1]. The ratio of the electron density of axial and equatorial Cl atoms in cis-octahedral $2B \cdot SnCl_4$ complexes was debatable (see e.g. [3]). Data on the spatial distribution of the halogen atoms in octahedral complexes were practically absent, and such evidence was completely absent for trigonal-bipyramidal tetrahalide complexes of group IVA elements (III), etc.



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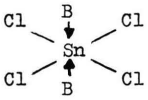

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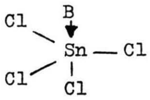

(III)

In the present work we summarize our results obtained in ^{35}Cl NQR studies of tetrachloride complexes of group IVA elements with various organic heteroatom ligands: chloranhydrides of unsaturated, aromatic and heteroaromatic carboxylic acids, alkylaryl ethers, ketones, aryldichlorophosphates, nitrogen-containing organic compounds, etc. Table 1 shows only a small part of the obtained data.

Results and Discussion

We suppose that analogously to MCl_n (M = Al, Ga, Sb; n = valency of M) tetrachlorostannane may react with carboxylic acid chloranhydrides to give $RCOCl \cdot SnCl_4$ complexes [4]. Indeed, such complexes were obtained [4–7], and their structure was established using the ^{35}Cl NQR technique. The formation of these complexes is indicated by large NQR frequency shifts of the system $RCOCl \cdot SnCl_4$ (1:1) compared to the frequencies of the initial components. For example, the ^{35}Cl NQR frequency of the C–Cl bond in $C_6H_5COCl \cdot SnCl_4$ (Table 1) is 2.127 MHz higher than that of C_6H_5COCl. The Cl atoms of the Sn–Cl bonds possess three lines in the complex, two of which with an intensity ratio of 2:1 are close in frequency, and the third line is shifted to low frequency by 3.116 MHz [4]. This spectrum suggests that the coordination polyhedron of the Sn atom in the $C_6H_5COCl \cdot SnCl_4$ complex has the structure of a trigonal bipyramid. In the axial positions there are the ligand and one Cl atom which possesses the lowest frequency line in the spectrum. The other three Cl

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Table 1. ^{35}Cl NQR frequencies at 77 K of $B \cdot MCl_4$, $2B \cdot MCl_4$ complexes (M = Si, Sn, B = ligand) as well as the signal/noise ratio (s/n) in their spectra.

Compound	ν^{77} (MHz)	s/n
C_6H_5COCl	29.920	50
$C_6H_5COCl \cdot SnCl_4$	32.047	23
	24.382	40
	24.220	20
	21.104	18
4-$(CH_3)_3SiC_6H_4COCl$	30.062	4
	29.953	4
4-$(CH_3)_3SiC_6H_4COCl \cdot SnCl_4$	31.301	18
	24.539	40
	21.848	13
4-$CH_3SC_6H_4COCl$	30.077	30
2-(4-$CH_3SC_6H_4COCl) \cdot SnCl_4$	30.318	18
	19.476	4
3-$ClCOC_5H_4N$	29.919	20
2-(3-$ClCOC_5H_4N) \cdot SnCl_4$	31.228	10
	18.196	2
	17.828	2
2-$CH_3OC_6H_4COCl$	29.944	–
2-$CH_3OC_6H_4COCl \cdot SnCl_4$	32.590	2
	23.305	6
Immediately after preparation	19.994	2
After 3 days	34.415	30
	21.420	12
	20.788	12
	19.893	10
	19.662	15
2-$(ClCH_2COOCH_3) \cdot SnCl_4$	37.756	8
	21.913	5
	19.593	15
	18.566	6
$[(CH_3)_2N]_2CO \cdot SiCl_4$	21.653	15
	21.155	15
	18.448	8
	17.343	4
$(CH_3)_3N \cdot SiCl_4$	21.502	10
	21.296	24
	18.857	11

atoms bonded with the Sn atom occupy the equatorial positions, two of them having the same electron distribution. Their ^{35}Cl NQR frequency ($\nu^{77} = 24.382$ MHz) is somewhat higher than that of $SnCl_4$ (24.296, 24.226, 24.140 and 23.720 MHz). The NQR spectrum of $C_6H_5COCl \cdot SnCl_4$ implies that it has a symmetry plane passing through the ligand, the axial and one equatorial Sn–Cl bond. Besides the spectrum of $C_6H_5COCl \cdot SnCl_4$, the ^{35}Cl NQR spectrum of the mixture of $SnCl_4$ with C_6H_5COCl (1:2) contains one line from the initial C_6H_5COCl. This indicates that $SnCl_4$ and C_6H_5COCl form only the complex 1:1 [4].

In the NQR spectra of 4-$(CH_3)_3SiC_6H_4COCl \cdot SnCl_4$ the electron acceptor possesses two low frequency lines (Table 1), the lower frequency one being shifted by 2.691 MHz with respect to the neighbouring line, which is approximately 3 times more intense. This spectrum indicates a trigonal-bipyramidal structure for the complex. The lower frequency line here belongs to the axial Cl atom, and the neighbouring more intense lines to the three equatorial atoms whose electron distributions are identical. This implies that the coordination polyhedron of the Sn atom in this complex has a 3-fold symmetry axis which coincides with the axial bonds of this atom.

Analogously to the $XC_6H_4COCl \cdot MCl_n$ complexes (M = Al, Sb), whose structure was established using X-ray analysis [8–10], it may be assumed that M = Sn complex formation also occurs via the carbonyl oxygen atom of the ligand, but not involving its chlorine atom. If the latter is involved in complex formation, its frequency would be lowered relative to the initial chloranhydride, as for bridging halogen atoms in $C_6H_5TeCl_3$ [11] dimers $(AlHal_3)_2$, $(GaCl_3)_2$, etc. (see e.g. [12]).

ROC_6H_4COCl contains two electron donor centers: carbonyl and ether oxygen atoms. One of these oxygen atoms or both atoms simultaneously may participate in complex formation with $SnCl_4$. Accordingly, the formation of complexes of various structure and composition is possible. However, from the ^{35}Cl NQR spectra, $SnCl_4$ with ROC_6H_4COCl usually forms 1:1 trigonal-bipyramidal complexes involving the carbonyl oxygen atom [4, 5]. The complex 2-$CH_3OC_6H_4COCl \cdot SnCl_4$ has such a structure and composition immediately after being formed and crystallized [13], this being shown by its NQR spectrum (Table 1). The high frequency line in this spectrum belongs to the Cl atom of the COCl group. Its frequency is 3.646 MHz higher than that of 2-$CH_3OC_6H_4COCl$ (28.944 MHz). Two low frequency lines in the spectrum of intensity ratio 3:1 belong to Cl atoms bonded to the Sn atom. The line for the axial Cl atom is 3.311 MHz lower than that for the three equatorial atoms. The coordination polyhedron of the Sn atom in this complex has a 3-fold symmetry axis as in the $C_6H_4COCl \cdot SnCl_4$ complex (see above). Storage of the 2-$CH_3OC_6H_4COCl \cdot SnCl_4$ complex changes significantly its NQR spectrum. For example, 5 hours after its formation and crystallization, the spectrum shows 5 additional lines besides the 3 lines of the trigonal-bipyramidal complex. After 3 days, the spectrum contains only these 5 additional lines (Table 1). They belong to the cis-octahedral 2-$CH_3OC_6H_4COCl \cdot SnCl_4$ complex (1:1), whose axial positions are occupied by two Cl atoms of the acceptor, and the equatorial positions by its other two Cl atoms, as well as carbonyl and ether O atoms of the donor. The formation of a 1:1 octahedral complex rather than 2:1 is confirmed by the absence of individual $SnCl_4$ lines in the NQR spectrum as well as a much higher NQR frequency of the electron donor in the octahedral complex as compared to the trigonal-bipyramidal one [13].

Therefore, the $2\text{-}CH_3OC_6H_4COCl \cdot SnCl_4$ complex in the solid state, having a trigonal-bipyramidal structure, converts into a cis-octahedral complex of the same composition. This transition was earlier unknown, and evidently the latter complex is energetically more favourable than the former. The ability of complexes to exist in different spatial forms (with different coordination numbers of the electron acceptor) was named by us "coordination isomerism" [13].

For the $2\text{-}CH_3O\text{-}4\text{-}CH_3C_6H_3COCl \cdot SnCl_4$ complex (1:1), coordination isomerism is not observed. This complex is cis-octahedral and both the carbonyl and ether oxygen atoms of the ligand are involved in its formation [14].

With $1,2\text{-}(CH_3O)_2C_6H_4$ the tetrachlorostannane also forms a 1:1 cis-octahedral complex involving both oxygen ligand atoms; with $1,3\text{-}(CH_3O)_2C_6H_4$ it forms a 1:1 complex involving only one oxygen atom [14, 15]. In the $1,4\text{-}(CH_3O)_2C_6H_4$ complex both oxygen atoms participate in complex formation with $SnCl_4$, but each of them interacts with a different $SnCl_4$ molecule. In the complex formed the coordination polyhedron of both Sn atoms is trigonal-bipyramidal [14]. The $4\text{-}CH_3SC_6H_4COCl$ has also some electron donor centers which may participate in complex formation with $SnCl_4$. The ^{35}Cl NQR spectrum of their 2:1 mixture is a doublet (Table 1). Its high frequency line belongs to the chlorine atom in the COCl group and is only slightly higher in frequency than that for $4\text{-}CH_3SC_6H_4COCl$. The other line of the doublet is significantly lower than the lines in the spectrum of $SnCl_4$. The spectrum obtained indicates the formation of a trans-octahedral complex involving the sulphur atom rather than the carbonyl oxygen atom. In the spectrum of an equimolar mixture of $4\text{-}CH_3SC_6H_4COCl$ and $SnCl_4$, in addition to the lines of the octahedral complex, lines from $SnCl_4$ are observed [5]. The trans-octahedral complex is also formed by interaction of $SnCl_4$ and the chloranhydride of pyridine-3-carboxylic acid, whose electron donor center is an N atom [6].

The ^{35}Cl NQR frequency shifts of the ligand Cl atom and the axial Sn–Cl bond in trigonal bipyramidal $RCOCl \cdot SnCl_4$ complexes relative to the mean values of the NQR frequencies of the corresponding initial components correlate well with each other [7]. This correlation may indicate the participation in complex formation of the same coordination ligand center.

As with the overwhelming majority of carboxylic acid chloranhydrides, $SnCl_4$ forms trigonal-bipyramidal complexes with alkylaryl ethers [15, 16].

The $SnCl_4$ complexes with $ClCH_2OR$ [3], $RR'CO$ [17, 18] and $RCOOR'$ [19–22] may have both octahedral and trigonal-bipyramidal structure at low temperature, according to the component ratio and ligand character. The $RR'CO \cdot SnCl_4$ or $RCOOR' \cdot SnCl_4$ system (1:1 or 2:1) often contains a mixture of complexes of different structure, and each system may have complexes containing both hexa- and pentacoordinated Sn atoms. In the course of time in the solid state one complex may be converted into another, including a change in coordination number of the Sn atom [17–22]. For example, the equimolar $(C_6H_5)_2CO \cdot SnCl_4$ system at first contains a mixture of trigonal-bipyramidal, and octahedral complexes. In the course of time in the solid state it converts into a mixture of two isomers of the trigonal-bipyramidal complex [17, 18].

The peculiarity of all trigonal-bipyramidal $SnCl_4$ complexes with ketones and esters is a significant change in the electron distribution of not only the axial Cl atoms but also the equatorial ones as compared to $SnCl_4$. Their NQR frequencies are much lower than those of $SnCl_4$. The electron density of the axial Cl atom in them, and thus its partial negative charge, is noticeably higher than that in complexes with carboxylic acid chloranhydrides or ethers [17–22].

The ^{35}Cl NQR technique was used to study $SnCl_4$ complexes with phosphorus compounds, but only of octahexdral structure (see e.g. [1]). This agrees with the opinion that $SnCl_4$ usually forms octahedral complexes [1]. However, the data reported above show that the formation of trigonal-bipyramidal $SnCl_4$ complexes is not less likely than that of octahedral ones. Thus it may be assumed that the $SnCl_4$ complexes with phosphorus compounds may also have various structures, which is confirmed by the ^{35}Cl NQR spectra of $SnCl_4$ complexes with aryldichlorophosphates [23–25]. The octahedral or trigonal-bipyramidal structure of these complexes as well as many other $SnCl_4$ complexes depends on the component ratio and ligand character. In general, equimolar amounts of $SnCl_4$ and $XOPOCl_2$ result in trigonal-bipyramidal complexes, and the ratio 1:2 in octahedral ones. The NQR frequency shift of Cl atoms of the $POCl_2$ group following formation of octahedral complexes is usually somewhat larger than that following trigonal-bipyramidal complex formation [23, 26].

The NQR technique was also used by us to study the tetrachloride complexes of group IVA elements (M = Si, Ge or Sn) with nitrogen-containing organic ligands [26]. These complexes have either trigonal-bipyramidal or octahedral structures. The NQR spectrum shows that the trigonal-bipyramidal structure of the $[(CH_3)_2N]_2CO \cdot SiCl_4$ complex differs from that of other trigonal-bipyramidal complexes studied before. Probably the ligand here does not occupy its usual axial position but an equatorial position, and both axial positions are occupied by Cl atoms [26].

The $SnCl_4$ molecule possesses a larger ability for complex formation than $SiCl_4$ and $GeCl_4$, which is also indicated by the fact that $SiCl_4$ and $GeCl_4$ do not form complexes with C_6H_5COCl, $C_6H_5OCH_3$, $CH_3COOC_2H_5$, etc., where $SnCl_4$ is involved in complex formation [26].

New possibilities in studying the electronic and spatial structure of compounds with a penta- or hexacoordinated atom of group IVA elements, including complex compounds, are offered by the EFG asymmetry parameters (η) at the halogen atom nuclei. Previously, these values were measured only for some octahedral complexes [27]. We supplemented these data [28] and measured the η values for trigonal-bipyramidal MCl_4 complexes (M = Si, Ge, Sn) [29, 30]. The η value makes it possible to estimate the interaction mechanism of the halogen atoms with other atoms, to distinguish more reliable than by the NQR frequency the cis- and trans-octahedral complexes, etc. In trigonal-bipyramidal and octahedral molecules the electron distribution of the axial Cl atoms is close to axiallly symmetric, while that of the equatorial atoms is not [28–32]. This deviation is due to the interaction of unshared electron pairs of halogen equatorial atoms with the central atom p-orbitals involved in the formation of the axial fragment of the molecule or the entire axial fragment. X-ray emission PK_β spectra of trigonal-bipyramidal chlorophosphoranes are consistent with such an interaction [32, 33]. The η values and thus the electron distribution deviation of the equatorial chlorine atoms in trigonal-bipyramidal $B \cdot MCl_4$ complexes increase significantly on going from M = Sn to M = Ge and Si [32]. Apparently this is also true with respect to the other structure containing an equatorial halogen atom. The great difference in electron distribution symmetry of axial and equatorial halogen atoms makes it possible to determine from the η values the position of the halogen atom in the coordination polyhedron of the central atom, thus establishing more accurately the structure of this polyhedron [29].

The η values of the trigonal-bipyramidal $SiCl_4$ complex with tetramethyl urea are in accordance with the conclusion drawn from the ^{35}Cl NQR spectrum [26] as to the unusual structure of this complex (see above) [30]. For the high frequency doublet in the NQR spectrum of the complex, these values are much larger (43.1 and 38.8%) than those for the low frequency doublet (7.5 and 1.7%), and they are close to the η values of the equatorial Cl atoms in the $(CH_3)_3N \cdot SiCl_4$ complex [30].

In the ^{35}Cl NQR spectrum of the octahedral $2\text{-}ClCH_2COOCH_3 \cdot SnCl_4$ the Cl atoms of the Sn–Cl bonds form a triplet with an intensity ratio of 1:2:1, and the line splitting is significant. Such an NQR spectrum does not allow the cis- or trans-octahedral structure to be assigned [21, 32]. However, the η values for this complex indicate that the two Cl atoms giving rise to the middle line of the triplet occupy equatorial positions of octahedron. The symmetry of their electron distribution differs much from the axial one ($\eta = 9.0\%$), and the electron distribution of the two other acceptor Cl atoms is close to axial symmetry (1.1 and 1.7%). These atoms occupy axial positions of the octahedron, and thus this complex is cis-octahedral. One of the axial Cl atoms has a higher NQR frequency and the other has a lower NQR frequency than the equatorial atoms [28]. These and similar data (see e.g. [21]) show that the ratio between the ^{35}Cl NQR frequencies of axial and equatorial Cl atoms in cis-octahedral complexes, the charges at these atoms, etc., do not follow any rules [3, 28] which several investigators have tried to find (see e.g. [12] and references in [28]).

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