^{35}Cl NQR Spectra of $SnCl_4$ Complexes with Methylaryl Ethers *

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$SnCl_4$ Complexes with methylaryl ethers and their ^{35}Cl NQR spectra have been obtained. All these complexes, except $SnCl_4 \cdot 1,2\text{-}(CH_3O)_2C_6H_4$, have a trigonal-bipyramidal structure. The latter compound has an essentially distorted octahedral structure. One of the ligand oxygen atoms takes part in the formation of the $SnCl_4$ complex with 1,3-, $1,4\text{-}(CH_3O)_2C_6H_4$ and RNO_2. These complexes have a trigonal-bipyramidal structure too.

Introduction

Usually complexes of $SnCl_4$ with organic ligands are octahedral with a hexacoordinated tin atom (see, for example [1–3]). Many complexes of $SnCl_4$ with chloroanhydrides of substituted benzoic acids, having a trigonal-bipyramidal structure, have been described by us previously [4]. They are formed by the interaction of the tin atom with the carbonyl oxygen of the ligand. For compounds with pentacoordinated Ge, Sn, P etc. atoms, a typical splittings in the low frequency region of their ^{35}Cl NQR spectra is observed, arising from the chlorine atoms of the acceptor: the axial chlorine line (or group of lines) is essentially lower in frequency than the equatorial ones. The NQR frequencies of the latter are close to that for $SnCl_4$ [5]. All the lines of the acceptor chlorine atoms in the ^{35}Cl NQR spectra of $SnCl_4 \cdot 2L$ complexes with an octahedral structure are in the low frequency region as compared with $SnCl_4$ and have a different pattern of splitting (see, for example [4–7]) compared to that in the ^{35}Cl NQR spectra of the trigonal-bipyramidal complexes. These distinctions permit us to establish reliably the structure of $SnCl_4$ complexes. We therefore use ^{35}Cl NQR technique for further investigation of $SnCl_4$ complexing with organic ligands.

Experimental

The complexes studied have been obtained by mixing (1 : 1, 1 : 2 or 2 : 1) of $SnCl_4$ with the corresponding ethers in the NQR tube. The NQR spectra at 77 K have been obtained by a pulsed IS-3 NQR spectrometer produced by SKB IRE AN SSSR.

Results and Discussion

The 1 : 1 mixtures (or, in a few cases, other component ratios) of $SnCl_4$ with methylaryl ethers and their ^{35}Cl NQR spectra are presented in Tables 1 and 2.

The quadruplet NQR spectrum of the 1 : 1 mixture of $SnCl_4$ with anisole indicates the formation of a trigonal-bipyramidal complex. One of the lines in this spectrum is lower (by approximately 3.2 MHz) than the three others. The latter ones split slightly. They belong to the three equatorial chlorine atoms, and the low frequency line belongs to the axial one. The same relation of the NQR frequencies for the axial and equatorial chlorine atoms is observed in the NQR spectra of chlorine-containing compounds of pentacoordinated Ge [8], Sn [4, 8] and P [9] atoms. The ^{35}Cl NQR spectrum of the 1 : 2 mixture of $SnCl_4$ with $C_6H_5OCH_3$ consists of 8 components (Table 2). Two lines in this spectrum have much lower frequencies than the rest. This spectrum corresponds to the trigonal-bipyramidal $SnCl_4 \cdot C_6H_5OCH_3$ complex with 2 molecules in the unit cell. Thus, the 1 : 1 and 1 : 2 mixtures of $SnCl_4$ with $C_6H_5OCH_3$ give complexes of the same structure.

The mixtures of $SnCl_4$ with $4\text{-}CH_3C_6H_4OCH_3$ and $3\text{-}(CH_3)_3SiC_6H_4OCH_3$ (Table 1) have the same spec-

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Table 1. The ^{35}Cl NQR spectra of $SnCl_4 \cdot L$* complexes at 77 K.

No.	Ligand	ν, MHz	S/N
1	$C_6H_5OCH_3$	23.851	23
		23.656	28
		23.391	28
		20.182	24
2	$2\text{-}CH_3C_6H_4OCH_3$	24.109	23
		23.210	21
		23.084	20
		20.243	15
3	$3\text{-}CH_3C_6H_4OCH_3$	24.507	4
		23.586	3
		23.384	3
		20.031	4
4	$4\text{-}CH_3C_6H_4OCH_3$	23.851	16
		23.568	16
		23.331	20
		20.147	20
5	$2\text{-}FC_6H_4OCH_3$	24.541	10
		23.577	15
		20.195	8
6	$2\text{-}NO_2C_6H_4OCH_3$	23.924	4
		23.483	4
		22.886	5
		20.101	6
7	$3\text{-}(CH_3)_3SiC_6H_4OCH_3$	23.618	23
		23.286	24
		23.059	24
		20.421	18

No.	Ligand	ν, MHz	S/N
8	$4\text{-}ClC_6H_4OCH_3$	35.597	11
		24.386	8
		23.564	8
		23.198	7
		20.252	12
9	$1,2\text{-}(CH_3O)_2C_6H_4$	21.131	8
		19.923	20
		19.692	8
10	$1,3\text{-}(CH_3O)_2C_6H_4$	24.435	23
		23.704	28
		23.096	29
		20.052	20
11	$1,4\text{-}(CH_3O)_2C_6H_4$	24.183	8
		23.890	9
		23.825	8
		23.636	7
		23.463	9
		23.303	8
		20.215	9
		19.881	9
12	$C_6H_5NO_2$	24.093	15
		23.960	16
		23.866	14
		23.336	35
		23.218	35
		23.158	35
		20.947	24
		20.835	14

* The ^{35}Cl NQR spectrum of $SnCl_4$ consists of 4 lines with equal intensities: 24.294; 24.226; 24.140 and 23.719 MHz [4, 5].

Table 2. The ^{35}Cl NQR spectra of $SnCl_4 + L$ mixtures at 77 K.

No.	$SnCl_4 + L$	ν, MHz (S/N)	
1	$SnCl_4 + 2\text{-}(C_6H_5OCH_3)$	24.556 (3)	23.356 (4)
		23.869 (6)	23.290 (5)
		23.666 (5)	20.312 (9)
		23.573 (4)	20.203 (7)
2	$SnCl_4 + 2\text{-}(4\text{-}ClC_6H_4OCH_3)$	35.604 (12)	23.563 (8)
		34.768 (7)	23.200 (7)
		24.386 (8)	20.257 (7)
3	$2\,SnCl_4 + 1,4\text{-}(CH_3O)_2C_6H_4$	24.186 (20)	23.464 (15)
		23.896 (20)	23.303 (16)
		23.824 (14)	20.212 (9)
		23.636 (12)	19.896 (8)
4	$3\,SnCl_4 + 1,4\text{-}(CH_3O)_2C_6H_4$	24.295 (14)	23.636 (10)
		24.196 (19)	23.463 (13)
		24.135 (12)	23.303 (14)
		23.889 (14)	20.212 (11)
		23.825 (12)	19.896 (9)
		23.716 (12)	
5	$2\,SnCl_4 + 1,3\text{-}(CH_3O)_2C_6H_4$	24.430 (5)	23.705 (15)
		24.291 (9)	23.091 (5)
		24.221 (9)	20.056 (5)
		24.126 (8)	

tra as the $SnCl_4 \cdot C_6H_5OCH_3$ (1 : 1) complex. Consequently, they have the same structure.

$SnCl_4$ with $2\text{-}CH_3C_6H_4OCH_3$, $3\text{-}CH_3C_6H_4OCH_3$, $2\text{-}NO_2C_6H_4OCH_3$, $4\text{-}ClC_6H_4OCH_3$, and $1,3\text{-}(CH_3O)_2C_6H_4$ forms complexes with more distorted trigonal-bipyramidal structures than in the previous cases. Their NQR spectra (Table 1) show a larger splitting of the lines (up to ~ 1 MHz) corresponding to the equatorial chlorine atoms, indicating some nonequivalent electron distribution in these atoms.

The high frequency line in the triplet NQR spectrum of the $SnCl_4$ complex with $2\text{-}FC_6H_4OCH_3$ (Table 1) is approximately twice as intense as the other one. The third line is considerably shifted to low frequency. This spectrum corresponds to an $SnCl_4 \cdot 2\text{-}FC_6H_4OCH_3$ complex with a trigonal-bipyramidal structure. Two equatorial chlorine atoms have an identical electronic distribution, noticeably different from that for the third equatorial chlorine atom. The two high frequency lines in the spectrum belong to the former. The low frequency line corresponds to the axial chlorine atom.

A line almost coincident in frequency with that of pure 4-$ClC_6H_4OCH_3$ (34.753 MHz) is observed in the NQR spectrum of the 1 : 2 mixture of $SnCl_4$ with 4-$ClC_6H_4OCH_3$ (Table 2) together with lines almost identical in frequency to those found in the 1 : 1 mixture (Table 1), demonstrating the formation of a single complex with a trigonal-bipyramidal structure in both cases.

It might be thought that both oxygen atoms of the corresponding ligands should participate in the formation of $SnCl_4$ complexes with 1,2-, 1,3-, and 1,4-$(CH_3O)_2C_6H_4$. However, according to the NQR spectra, this occurs only in the former case. The three lines in the NQR spectrum of the $SnCl_4 \cdot$ 1,2-$(CH_3O)_2C_6H_4$ complex are at a considerably lower frequency than in $SnCl_4$ (Table 1). The higher frequency line in the spectrum of this mixture is noticeably removed from the two low frequency ones, and the intensity of one of the latter is less than that of the other. This spectrum does not agree with the trigonal-bipyramidal structure of the complex. Obviously, this complex has a distorted octahedral structure.

The 1,3-$(CH_3O)_2C_6H_4 \cdot SnCl_4$ complex has a trigonal-bipyramidal structure (see above). Hence, one ligand oxygen atom participates in its formation. The spectrum of the 2 : 1 $SnCl_4 \cdot$ 1,3-$(CH_3O)_2C_6H_4$ mixture (with an excess of $SnCl_4$) consists of both lines from the complex and lines close to those found in the $SnCl_4$ spectrum (Table 2).

The frequencies in the ^{35}Cl NQR spectra of $SnCl_4 \cdot$ 1,4-$(CH_3O)_2C_6H_4$ 1 : 1 and 2 : 1 mixtures coincide, only their relative intensities differ. But the NQR spectrum of the 3 : 1 mixture contains lines for $SnCl_4$ with lines corresponding to the $SnCl_4 \cdot$ 1,4-$(CH_3O)_2C_6H_4$ complex (Tables 1 and 2). The NQR spectra of all these mixtures indicate the formation of a complex with a trigonal-bipyramidal structure, with two nonequivalent molecules in the unit cell. Consequently, only one oxygen atom of 1,4-$(CH_3O)_2C_6H_4$ takes part in the interaction with $SnCl_4$ in this case too.

The ^{35}Cl NQR spectra of all the trigonal-bipyramidal complexes examined are almost in the same frequency region. The NQR frequency of their axial chlorine atom changes insignificantly with variation of substituents and their position in the aromatic ring (19.9 – 20.5 MHz). In contrast, the *R* substituent influences essentially the electron density of the axial chlorine atom in $SnCl_4 \cdot RC_6H_4COCl$ complexes also having the trigonal-bipyramidal structure [4]. The variation in the NQR frequencies of the equatorial chlorine atoms of the complexes studied is greater than that of the axial ones (Table 1); however, the substituents in the aromatic ring of the methylaryl ethers have only a weak influence on this variation.

It is claimed [5] that a cis-octahedral complex is formed by interaction of $SnCl_4$ with $C_6H_5NO_2$. Both oxygen atoms take part in its formation. The NQR spectrum of this complex consists of 8 lines with different intensities, some of which belong to $SnCl_4$ [5]. The NQR spectrum of this complex as obtained by us differs only in the line intensities (Table 1). This difference is obviously due to the nonidentical conditions of sample crystallization. The NQR spectrum of this complex contains a low frequency doublet and a high frequency sextet. The doublet frequency is slightly higher than that for the axial chlorine atoms in $SnCl_4$ complexes with methylaryl ethers (Table 1). The high frequency lines of $SnCl_4 \cdot C_6H_5NO_2$ complex are in the same region as the NQR frequencies of the equatorial chlorine atoms in $SnCl_4 \cdot ArOCH_3$ complexes (Table 1). This gives rise to the conclusion that the $SnCl_4 \cdot C_6H_5NO_2$ complex has not a cis-octahedral structure but a trigonal-bipyramidal one. There are two (when the low frequency doublet intensities are equal) or three (when their intensity ratio is 1 : 2) $SnCl_4 \cdot C_6H_5NO_2$ molecules in the unit cell (Table 1). Obviously, the $SnCl_4 \cdot CH_3NO_2$ complex whose spectrum is also published in [5] has a trigonal-bipyramidal structure. This spectrum is identical with NQR spectra of $SnCl_4$ complexes with $C_6H_5OCH_3$, 2-NO_2-$C_6H_4OCH_3$, 4-$CH_3C_6H_4OCH_3$ etc. (Table 1) which have the trigonal-bipyramidal structure. Apparently, one oxygen atom of the nitro group takes part in an interaction with the acceptor in $SnCl_4 \cdot RNO_2$ complexes. This is confirmed by an X-ray structure analysis of the $TiCl_4 \cdot CH_3NO_2$ complex [10].

According to the NQR spectra, complexes are not formed when $SnCl_4$ is mixed with 2-$ClC_6H_4OCH_3$, 3,5-$Cl_2C_6H_3OCH_3$, 3- and 4-$BrC_6H_4OCH_3$, 2-Br-4-$ClC_6H_3OCH_3$, 1,3-$(CH_3O)_2$-4-Br-C_6H_3, 4-IC_6H_4-OCH_3, and methyl and ethyl ethers of β-naphthole. The ^{35}Cl NQR frequencies of these mixtures differ only slightly from those of the individual components.

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