NQR Studies of Organic Compounds Containing Tetra- or Pentacoordinated Atoms of Elements of Groups IVA and VIA *

Valentin P. Feshin

Institute of Technical Chemistry, Ural Branch of USSR Academy of Sciences, Perm, USSR

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The ^{35}Cl and ^{79}Br NQR spectra of halogen-containing organic compounds of Si, Ge, Sn and Te, in which these atoms may be tetra- or pentacoordinated, have been compared to the results of their X-ray diffraction analysis. The NQR technique was also used to study a large number of such compounds for which X-ray investigations were found to be impossible. It has been shown that the NQR technique may be considered as a rapid method for the determination of the electronic and spatial structure of these compounds. The conditions for pentacoordination of atoms of IVA group elements have been also formulated.

Introduction

The ability of the atoms of group IVA and VIA elements to extend their coordination numbers causes a large diversity in possible intra- and intermolecular interactions as well as different structures of the coordination polyhedron of these atoms. The interaction of compounds of group IVA elements with organic ligands containing an electronegative heteroatom may lead to the formation of complexes of trigonal-bipyramidal or octahedral structure (see, e.g. [1, 2]). In such compounds with a heteroatom in a substituent, the atoms of these elements may have an extended coordination number due to their intramolecular interaction with the substituent heteroatom (see, e.g. [3–7]). The ability of the Te atom to exhibit both electron donor and electron acceptor properties causes much more diversity of possible intra- and intermolecular interactions and differences in the structure of its coordination polyhedron, as opposed to the compounds of group IVA elements [8, 9].

The NQR technique was found to be very efficient in studying these interactions and in establishing the structure of compounds which contain the atoms of the groups IVA and VIA. The present report summarizes the results of ^{35}Cl and ^{79}Br NQR studies at 77 K for halogen-containing compound of group IVA elements and some organotellurium compounds with various spatial structures.

Results and Discussion

Of the intramolecularly complexed organosilicon compounds, only substituted silatranes have been studied by NQR techniques [10]. Their ^{35}Cl NQR frequencies are much lower than those of the corresponding triethoxysilanes. This is consistent with the intramolecular interaction Si ← N in these molecules and indicates the strong electron donor properties of the silatranyl group. The most interesting results were obtained in studying the organyltrihalogeno-germanes and -stannanes (Table 1). The possibility of using NQR technique for studying these compounds is based on the fact that the electron distribution of all the halogen atoms in the Hal_3M group is similar when M is tetracoordinated, but the distribution is very different for axial and equatorial halogen atoms when M is pentacoordinated. This difference causes a large line splitting in the NQR spectra of the corresponding compounds, which is clearly manifested in the ^{35}Cl NQR spectra of chlorophosphoranes having a trigonal-bipyramidal structure. The NQR frequencies of axial Cl atoms are here markedly lower than those of equatorial ones [11]. The potential of NQR spectroscopy for studying organyltrihalogeno-germanes and -stannanes was confirmed by comparison of their NQR spectra with X-ray data.

The X-ray data [3, 4, 6, 7] show that in molecules I–III (Table 1) the Ge atom is pentacoordinated by

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Reprint requests to Dr. Valentin P. Feshin, Institute of Technical Chemistry, Ural Branch of USSR Academy of Sciences, 116 Bolshevistskaya st., Perm 614600, Russia.

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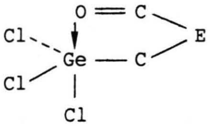
Table 1. ^{35}Cl NQR frequencies at 77 K of organyltrichloro-germanes and -stannanes Cl_3MX as well as telluranes Cl_2TeRR', the bond lengths M–Cl (r_{M-Cl}) and the distance $r_{M \cdots O}$.

No.	Compound	ν^{77} (MHz)	r_{M-Cl} (Å)	Assignment	$r_{M \cdots O}$ (Å)
I	$Cl_3GeCH_2CH_2CONH_2$	23.765	2.138	eq	2.166
		23.245	2.156	eq	
		15.344	2.253	ax	
II	$Cl_3GeCH_2CHMeCOMe_2$	23.409	2.134	eq	
		23.286	2.144	eq	2.123
		16.483	2.264	ax	
III	$Cl_3GeCHMeNCO(CH_2)_2CH_2$	23.686	2.134	eq	
		23.281	2.138	eq	2.140
		17.339	2.253	ax	
IV	$Cl_3Sn(CH_2)_3Cl$	31.750	2.144	C–Cl	
		20.352	2.314	eq	3.279
		20.160	2.320	eq	
		19.668	2.336	ax	
V	$Cl_3SnC_6H_3Me$-5-OMe-2	21.550 (45)	2.276	eq	
		19.497 (18)	2.316	ax	2.820
VI	$Cl_3SnC_6H_2Me_2$-3,5-OMe-2	23.119 (8)			
		20.341 (8)			
		19.213 (5)			
VII	$Cl_3SnC_6H_3(OMe)_2$-2,6	21.620 (12)	2.293		
		21.018 (11)	2.303		2.85
		20.617 (10)	2.311		3.20
VIII	Cl_3TePh	25.033 (10)			
		26.460 (3)			
		10.830 (3)			
		10.525 (3)			
IX	$Cl_2TePhC_6H_3(OMe)_2$-3,4	18.613 (2)			
		17.510 (2)			
X	$Cl_2Te[C_6H_3(OMe)_2\text{-}3,4]_2$	18.133 (2)			
		18.079 (3)			
		17.928 (2)			
		17.170 (2)			

the intramolecular interaction Ge ← O that forms the five-membered ring. The distance between these atoms is close to the sum of the covalent radii (1.92 Å). The coordination polyhedron of the Ge atom in these molecules represents a distorted trigonal bipyramid with a carbon atom and two chlorine atoms in equatorial positions, and the Cl and O atoms in axial positions. The axial Ge–Cl bond is much longer than the two equatorial ones. The ^{35}Cl NQR spectra of these molecules agree with such a structure [3–6] (Table 1). The low frequency line in these spectra related to the axial Cl atoms is markedly shifted with respect to the high frequency doublet that belongs to the two equatorial Cl atoms. This shift exceeds by more than one order of magnitude the maximum possible contribution to the ^{35}Cl NQR frequency of crystal effects (~1.5–2.0% of the measured frequency [12]). The NQR frequencies of the equatorial Cl atoms of these compounds lie in the range characteristic of the tetrahedral organyltrichloro-germanes. The quadruplet ^{35}Cl NQR spectrum of compound IV is also consistent with this structure (Table 1). The NQR frequency of the Cl atom of its chloropropyl group (31.750 MHz) is much lower than that of other compounds of the series $Cl(CH_2)_nX$ when $n \geqq 3$ (~ 33.1 MHz [13, 14]). The character of the line splitting in the low frequency triplet of the spectrum of compound IV, which belongs to the $SnCl_3$ group, is similar to the separation of the trigonal-bipyramidal compounds I–III. Such a structure of compound IV is confirmed by its X-ray data [15].



(E = C, N)

Hence, the ^{35}Cl NQR spectra of organyltrichloro-germanes and -stannates which have been studied, where the low frequency line is significantly shifted with respect to the high frequency doublet, give evidence for the intramolecular interaction between the M atom and the electronegative atom in the organic substituent X, and thus for the trigonal-bipyramidal structure of the molecule. The low frequency line belongs to the axial Cl atom, and the high frequency one to equatorial atoms. The NQR frequencies of the latter lie in the range characteristic of the tetrahedral organyltrichloro-germanes.

The separation between the low and high frequency lines in the ^{35}Cl NQR spectra of the organyltrichlorogermanes with pentacoordinated Ge atoms which have been studied is $\sim 7+35\%$ from the average value of the high frequency lines. Apparently, the same shape of the ^{79}Br NQR spectra and the same value of the line splitting in the spectra of analogous organyltribromogermanes may imply an intramolecular interaction of the Ge and O atoms in their molecules [5–7]. However, in the ^{79}Br NQR spectrum of $(Br_3Ge)_2CHCH_2COOH$ the splitting between the high frequency quadruplet and low frequency doublet is too small ($\sim$3%) [7] (Table 2) to allow the intramolecular interaction Ge ← 0 to be assumed in this molecule. Further, it is not confirmed by X-ray data [16]. At the same time, this interaction is unambiguously indicated by the triplet ^{79,81}Br NQR spectra of the compounds $BrGeCH_2\overline{NCO(CH_2)_2CH}_2$ and $Br_3GeCH_2\overline{NCO(CH_2)_3CH}_2$ (Table 2). The separation between the low frequency line and the high frequency doublet is here $\sim$26 and $\sim$28%, respectively. These values exceed the analogous ones for the corresponding organyltrichloro-germanes, which are 24 and 25% [3, 4].

All the molecules discussed above of the series Hal_3MX with a pentacoordinated M atom undergo closing of a five-membered ring. The series of 2-alkoxyphenyltrichlorostannanes, where the pentacoordinated of the Sn atom is achieved by closing a four-membered ring, was also studied by NQR. These spectra also show a low frequency line, and a doublet or a singlet of double intensity that are rather distant. For example, in the doublet NQR spectrum of compound *V* (Table 1), the high frequency line is much more intense than the low frequency line and is 2.053 MHz away from the latter. Such a spectrum corresponds to a trigonal bipyramidal structure of the coordination polyhedra of the Sn atom. The electron density distribution of the two equatorial Cl atoms having the most intense high frequency line is the same, and the low frequency line corresponds to the axial Cl atom. This NQR spectrum shows that the electron distribution of the Sn atom in this molecule has a symmetry plane passing through the aromatic ring, the axial Sn–Cl bond and oxygen atom [17]. The intramolecular interaction Sn ← O in this molecule is also confirmed by X-ray data. The distance between the Sn and O atoms here is much smaller than the sum of their van der Waals radii [17, 18].

The character of the intramolecular interaction between the OR and $SnCl_3$ group in 2-alkoxyphenyltrichlorostannanes of badly distorted trigonal-bipyramidal structure give rise to a significant difference in the electron distribution of the Cl atoms, and between the NQR spectra of these compounds and the distribution and spectra of organyltrichlorostannanes, where the coordination interaction forms a five-membered ring. For example, the separation between all three lines in the NQR spectra of compounds VI and VII is large [17]. The middle line of the triplet is closer to the low frequency line than to the high frequency one (Table 1). The X-ray data of the last molecule indicate similar values of all Sn–Cl bond lengths. The coordination polyhedron of its Sn atom is close to tetrahedral. Nevertheless, both Sn ··· O distances are here much smaller than the sum of the van der Waals radii of the Sn and O atoms [17, 19]. Apparently, these atoms in the molecule interact noticeably, but their interaction does not lead to significant changes in the angles between the bonds of the central Sn atom. Probably, on closing the stressed four-membered ring in organyltrihalogenostannanes, the coordination polyhedron of tin differs much from the ideal trigonal bipyramid, and the electron distribution of the equatorial Cl atoms and their NQR frequencies may be quite different. Nevertheless, the differences in electron distribution and NQR frequencies of axial and equatorial chlorine atoms remain significant and may

Table 2. ^{79}Br NQR frequencies of organotribromogermanes Br_3GeX [7].

X	ν^{77} (MHz)
$CH(GeBr_3)CH_2COOH$	200.268
	199.645
	198.500
	198.282
	193.776
	192.396
$CH_2\overline{NCO(CH_2)_2CH}_2$	198.060
	191.180
	144.030
$CH_2\overline{NCO(CH_2)_3CH}_2$	196.360
	189.780
	139.310

provide rather reliable evidence for an intramolecular interaction in organic compounds of IVA group elements.

The NQR technique was used to study the compounds of Si, Ge and Sn, in which the central atom is pentacoordinated as a result of closing the four- and five-membered ring. Some organosilicon compounds are known, where the intramolecular interaction of atoms closes up a six-membered ring (see, e.g., [19]). X-ray data of a large number of compound of IVA group elements, where an intramolecular interaction between non-bonded atoms occurs, show that the most negative charged heteroatom of the organic substituent is involved in this interaction with the central silicon, germanium of tin atom.

The analysis of the data presented above and available in the literature allows the following conditions necessary for pentacoordination of the M atom (M = S, Ge, Sn) to be postulated [6]:

1. A large partial positive charge on the M atom and partial negative charge on the heteroatom of the organic substituent.
2. A molecular structure which allows these atoms to approach to a distance less than the sum of their van der Waals radii.

The second condition involves not only the molecules' geometrical characteristics which allow the formation of an intramolecular cyclic system, but also the energetic advantage of such a molecule. For example, in $\mathrm{Cl_3GeCH_2CH_2COOH}$, $\mathrm{Cl_3GeCH_2CH(CH_3)COOH}$ and $\mathrm{Cl_3GeCH(CH_3)CH_2COOH}$ substantially the same probability may be assumed for the formation of a five-membered ring that determines the pentacoordination of the Ge atom. However, probably due to steric factors, such a ring is energetically advantageous only in the last molecule [6].

Analogously to the trigonal-bipyramidal chlorophosphoranes [11] and complexes of IVA group elements tetrachlorides with organic ligands [20–22], it may be assumed that the symmetry of the electron distribution of axial Cl atoms on molecules $\mathrm{Hal_3MX}$ of the same structure is similar to the axial, and that of the equatorial Cl atoms is very different. This is also confirmed by the asymmetry parameters for the $^{35}\mathrm{Cl}$ nuclei in $\mathrm{Cl_3Sn(CH_2)_3Cl}$ [14, 22], the trigonal-bipyramidal structure of which is established by X-ray data [15]. The large asymmetry of the electron distribution of the equatorial Cl atoms in such molecules is caused by the interaction of the unshared electron pair of these atoms with the p-orbital of the central M atom [11, 22]. Such an interaction must lower the NQR frequency of the corresponding Cl atom. Nevertheless, the NQR frequencies of equatorial Cl atoms in all trigonal-bipyramidal molecules are higher than those of axial ones, which is due to the much higher p_σ-electron density of the latter. The NQR frequencies of equatorial Cl atoms of trigonal-bipyramidal compounds $\mathrm{Cl_3MX}$ are in the same range as the NQR frequencies of these compounds with the tetracoordinated M atom, while the NQR frequencies of axial atoms are much lower. Therefore, in these molecules the intramolecular interaction, which causes the M atom to be pentacoordinated, does not practically influence the p_σ-electron density of equatorial Cl atoms, but significantly increases that of axial Cl atoms. A good linear correlations is observed between the $^{35}\mathrm{Cl}$ NQR frequencies of compounds $\mathrm{Cl_3GeX}$ and the corresponding Ge–Cl bond lengths [5]:

$$r(\mathrm{Ge{-}Cl}) = 2.519 - (0.016 \pm 0.0007)\,\nu^{77};$$
$$(r = 0.980,\ s = 0.009,\ n = 18).$$

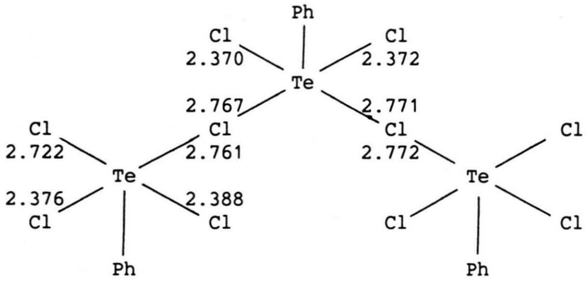
The axial Ge–Cl bond in organyltrichlorogermanes with a fragment $\mathrm{Cl_3Ge{-}\overset{|}{\underset{|}{C}}{-}E{-}C(O)R}$ correlates with the Ge ⋯ O distance with an exponential dependence [5]:

$$r(\mathrm{Ge{-}Cl}) = 2.118 + 0.844\exp[-0.394\,r^2(\mathrm{Ge}\cdots\mathrm{O})];$$
$$s = 0.006,\ n = 8.$$

The distance between the Ge and O atoms, and thus the axial Ge–Cl bond length may serve as a strength characteristic of the coordination bond Ge ← O. Taking into account the linear correlation between the Ge–Cl bond length and the $^{35}\mathrm{Cl}$ NQR frequency in such molecules, the strength characteristic of the coordination bond here may also be the NQR frequency of the axial chlorine atom.

The NQR technique was also used to study a large number of organyltrihalogeno-germanes and -stannanes [3–7, 17], as well as tetrachloride complexes of Si, Ge and Sn with organic ligands (see, e.g., [1, 2, 21, 22]), for which an X-ray analysis was found to be impossible. In order to elucidate the NQR possibilities for establishing the electronic and spatial structure of halogen-containing compounds, we have also studied some organotellurium compounds [9].

The X-ray analysis of $\mathrm{PhTeCl_3}$ [23, 24] incidates a polymeric structure for this compound with two non-equivalent molecules in the crystal unit cell. The coordination polyhedron of the Te atom represents a square pyramid, in the base of which there are four chlorine atoms, and in the apices a phenyl group. Two of the Cl atoms are bridges linking $PhTeCl_3$ molecules into a polymeric chain. Concerning the Te–Cl bond length, the electron distribution of the bridging chlorine atoms cannot be identical. Indeed, in the ^{35}Cl NQR spectrum, a low frequency doublet with little separation between the equally intense lines corresponds to these atoms (Table 1) [9]. Three of the four terminal Cl atoms of the two fragments $PhTeCl_3$ of the polymeric chain are essentially identical. Accordingly, in the NQR spectrum of this compound the terminal Cl atoms possess two lines with an intensity ratio 1:3, which are located over a much higher frequency range than the bridging Cl atoms.



The coordination polyhedron of the Te atom in Cl_2TeRR' has a trigonal-bipyramidal structure (see, for example, [8]). In axial positions it has two Cl atoms, and in equatorial ones there are substituents and an unshared electron pair of the Te atom. Such a structure is confirmed by X-ray data, for example, for Cl_2TeMe_2 [25]. The ^{35}Cl NQR spectrum of this compound [26] is consistent with this structure. Its NQR frequencies are close to those of dichlorotelluranes studied by us (Table 1).

The ^{35}Cl NQR frequencies of chlorine-containing compounds of Te correlate well with the length of the corresponding Te–Cl bonds, but the NQR frequencies and Te–Cl bond lengths of bridging Cl atoms and corresponding Te–Cl bond lengths in $PhTeCl_3$ do not obey this correlation [9].

The results of studying compound of group IVA elements and chlorine-containing tellurium compounds as well as many other similar data available in the literature show that the NQR technique allows us to establish the type of coordination polyhedron of the central atom, the symmetry elements of this polyhedron, to determine the lengths of some bonds in the molecules, and to evaluate the strength of the coordination bond. The ^{35}Cl NQR frequencies and asymmetry parameters of the electric field gradient at the ^{35}Cl nuclei give information on the spatial electron density distribution of the halogen atoms, on the mechanisms of their interaction with the central atom, etc. Taking into account the possibilities of the NQR technique for studying chemical compounds, the absence of special treatment of a substance for experiment, the relative ease and rapidity of recording NQR spectra of polycrystalline halogen-containing compounds, the simplicity of interpretation of these spectra, their high sensitivity to the smallest variations in electron distribution of the indicator atom and so on, the NQR technique may be considered as a rapid method for the determination of the electronic and spatial structure of halogen-containing compounds.

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