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Review

NQR STUDIES OF INTRAMOLECULAR COMPLEXES IN ORGANIC COMPOUNDS OF METALS OF GROUP IVA

V.P. FESHIN* and G.A. Polygalova
Institute of Organic Chemistry, Ural Branch of USSR Academy of Sciences, 614600 Perm (USSR)

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SUMMARY

The results of nuclear quadrupole resonance (NQR) studies of intramolecular complexes in halogen-containing organic compounds of metals of Group IVA are reviewed. This method is very efficient for establishing the electronic and spacial structure of these compounds, and the peculiarities of their intramolecular interactions.

CONTENT

I. INTRODUCTION

In molecules of metals of Group IVA which contain in a substituent a heteroatom which carries unshared electron pairs, the M atoms of these elements may have an extended coordination number due to their interaction with the heteroatom. Such compounds are of great interest in the theory of chemical structure and for their practical use, for example, as biologically active compounds or their precursors (see, e.g., refs. 1-4). At the present, the organosilicon compounds, especially the silatranes, are the most studied species of this type (see, e.g., refs. 1,5-7). The intramolecular complexes of germanium and tin are much less studied. X-Ray diffraction analysis, IR, NMR and NQR spectroscopy serve as the main physical techniques for investigating these compounds. Unfortunately, X-ray studies have been carried out on only a limited number of compounds, and the other methods of research are reflected in the evidence they can provide. For example, ^{29}Si NMR is very productive in establishing the pentacoordination of silicon atom in its organic compounds (see, e.g., refs. 6,7). The IR spectra allow presence of the intramolecular interaction M←O to be deduced, e.g., by a decrease in the stretching vibration frequency of a C=O bond as compared to compounds where such interaction is absent (see, e.g., refs. 2-4). NQR spectroscopy is very effective in studying halogen-containing intramolecular complexes. It makes it possible to establish not only the presence of the intramolecular coordination, but also the features of polyhedral coordination, to estimate the lengths of some bonds in the molecule, etc. The results of NQR studies of intramolecular complexes in organic compounds of elements of Group IVA are analysed in this paper.

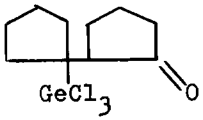
II. STRUCTURE DETERMINATION OF INTRAMOLECULAR COMPLEXES IN ORGANIC COMPOUNDS OF METALS OF GROUP IVA

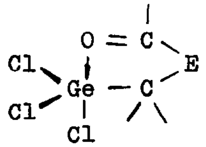
Of the intramolecularly complexed organosilicon compounds, only 1-substituted silatranes - 1-(chloroalkyl)- and 1-(chlorovinyl)-silatranes - have been studied by NQR (ref. 8). Their ^{35}Cl NQR spectra confirm the intramolecular interaction Si--N in these molecules, and indicate the strong electron donor properties of the silatranyl group.

The most interesting results were obtained in studying the organyltrihalogenogermanes and -stannanes (refs. 2,3,9-20). NQR is useful for studying these compounds because the electron distribution of all the halogen atoms in the Hal_3M group is practically equivalent 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 splitting of the lines in the NQR spectra of, for example, the chlorophosphoranes which have a trigonal-bipyramidal structure (ref. 21). The potential of NQR spectroscopy for studying organyltrihalogenogermanes and -stannanes was confirmed by comparison of the NQR spectra of these compounds with their X-ray data (Table 1).

The X-ray data (refs. 3,22) show that in molecules I and II (Table 1) the Ge atom is pentacoordinated by the intramolecular interaction Ge←O that forms the five-membered ring (1).

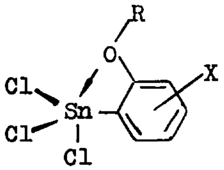
TABLE 1
^{35}Cl NQR frequencies at 77 K (ν^{77}) of organyltrichlorogermanes and stannanes Cl_3MX, the signal-to-noise ratio in their NQR spectra, the lengths of the bond M-Cl (r_{M-Cl}) and of the coordination bond (r) in these molecules

No.	Compound	ν^{77}(MHz)	s/n	r_{M-Cl}(Å)	r (Å)
I	$Cl_3GeCH_2CH_2CONH_2$	23.765	14	2.138	2.166
		23.245	12	2.156	
		15.344	5	2.253	
II	$Cl_3GeCH_2CHMeCONMe_2$	23.409	14	2.134	2.123
		23.286	12	2.144	
		16.483	6	2.264	
III	$Cl_3GeCMePhCH_2COPh$	24.040	20	2.138	2.507
		23.139	20	2.144	
		21.028	8	2.181	
IV		23.559	10	2.138	2.768
		23.451	10	2.148	
		20.671	10	2.169	
V	$Cl_3GeCH_2CH_2COOH$	23.550	23	2.121	3.228
		22.695	23	2.123	
		22.444	25	2.134	
VI	$Cl_3GeCH_2CHMeCOOH$	23.929	12	2.122	3.078
		22.870	10	2.127	
		22.078	9	2.141	
VII	$Cl_3GeCHMe\overline{NCO(CH_2)_2CH_2}$	23.688	7	2.134	2.140
		23.281	7	2.138	
		17.339	5	2.253	
VIII	$Cl_3GeCH_2\overline{NCO(CH_2)_4CH_2}$	23.630	7	2.140	2.120
		23.237	7	2.155	
		17.353	5	2.252	
IX	$Cl_3Sn(CH_2)_3Cl$	31.750	15	2.144	3.279
		20.352	12	2.320	
		20.160	15	2.336	
		19.668	6	2.314	
X	$Cl_3SnC_6H_3Me$-5-OMe-2	21.550	45	2.316	2.820
		19.497	18	2.276	



E = C, N

(1)



(2)

The length of the Ge←O bonds here is close to the sum of the covalent radii of Ge and O (1.92 Å). The bonds of the Ge atoms in these molecules are directed to the apexes of a distorted trigonal bipyramid with a carbon atom and two Cl atoms in equatorial positions, and the Cl and O atoms in axial positions. The axial Ge-Cl bond is significantly longer than the two equatorial ones. The ^{35}Cl NQR spectra of compounds I and II (Table I) agree with this structure of molecules. The low frequency line in these spectra related to axial Cl atom is markedly shifted with respect to the high frequency doublet ($\Delta\nu$ = 7.9 and 6.8 MHz) 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 forces (1.5 - 2.0% of frequency measured, ref. 23). The NQR frequencies of the equatorial Cl atoms of these compounds lie in the range characteristic of compounds Cl_3GeX of tetrahedral structure (see, e.g., ref. 23).

According to X-ray data, the Ge atom in molecules III and IV is also pentacoordinated by interaction with the carbonyl oxygen atom, the five-membered cycle closes up. However, the trigonal-bipyramidal structure of these molecules is noticeably more distorted than that of I and II. Thus, for instance, in molecule III the angles between the axial and equatorial Ge-Cl bonds are 101.73(8)° and 97.64(8)°, and the angle between the axial Ge-Cl bond and equatorial Ge-C bond is 105.8(1)°. Two of these angles are closer to tetrahedral ones than to the expected right angles. The distance Ge...O in molecules III and IV is accordingly larger than that in I and II. Nevertheless, it is much smaller than the sum of the Van der Waals radii of Ge and O atoms (~3.3 Å, ref. 2). The axial Ge-Cl bond in molecules III and IV is noticeably longer than the two equatorial bonds (ref. 8) (Table 1). The ^{35}Cl NQR spectra of these compounds are in agreement with their X-ray data. The low frequency line in them for the axial Cl atom is markedly shifted with respect to the high frequency doublet belonging to the equatorial Cl atoms, but this shift is much smaller than that in the spectra of compounds I and II (Table 1) (refs. 9,10). The NQR frequencies of the equatorial Cl atoms are close to that of the compounds Cl_3GeX that contain a tetracoordinated Ge atom.

The splitting pattern of the triplet in the ^{35}Cl NQR spectrum of compound V differs significantly from that considered above (refs. 9,10). The separation between the low frequency lines in the NQR spectrum of compound V ($\Delta\nu$ = 0.251 MHz) is now much less than that between the highest frequency and neighbouring low frequency lines ($\Delta\nu$ = 0.855 MHz). This indicates the similar electron distribution about two Cl atoms and the very different electron density distribution about the third Cl atom. In principle, this spectrum implies a relatively weak coordination interaction Ge←O and a trigonal-bipyramidal structure for molecule V. However, it implies also that the axial positions are occupied by two Cl atoms which show two low frequency signals in the spectrum, and the equatorial positions by carbon, oxygen and chlorine atoms. This does not agree with the experimentally observed rule that in a trigonal bipyramid the O atom being more electronegative than the Cl atom must occupy the axial position (see above and, e.g., ref. 24). An alternative explanation of the line splitting in the ^{35}Cl NQR spectrum is therefore called for. It may be due to the fact that one of the Ge-Cl bonds in V is somewhat longer than the other two (Table I), and one of the ClGeC angles (117.0°) differs significantly from tetrahedral, while the other ClGeC angles are close to tetrahedral (refs. 2, 22). The value of the longest Ge-Cl bond in V is close to the length of equatorial ones and is much less than that of the axial Ge-Cl bonds in molecules I-IV which have a trigonal-bipyramidal structure. The above data and the Ge...O distance in molecule V which is essentially equal to the sum of the van der Waals radii of Ge and O atoms (table 1) do not support a trigonal-bipyramidal structure (refs. 9,10).

The difference between the frequencies of these three lines in the NQR spectra of compound VI (Table 1) exceeds the ultimate crystal splitting and indicates the essential non-equivalence of all Ge-Cl bonds. This non-equivalence is characteristic neither of a tetrahedral nor pentacoordinated Ge atom. Apparently, it results from a state intermediate between four and five coordination. The X-ray data show that the lengths of two Ge-Cl bonds in VI are similar, and the third Ge-Cl bond is only slightly longer. The Ge...O distance is much larger than the sum of covalent radii, but somewhat smaller than the sum of the van der Waals radii (Table 1). These data do not support the pentacoordination of the Ge atom in molecule VI, but at the same time, it is also far from ideal tetracoordination, since one of the ClGeC angles is 120.1°, and one of ClGeCl angles is 102.6° (refs. 9,10).

The ^{35}Cl NQR spectra of compounds VII and VIII are analogous to those of I and II having a trigonal-bipyramidal structure. The low frequency lines in these spectra belong to axial Cl atoms, and two high frequency lines to two equatorial ones (ref. 11). The trigonal-bipyramidal structure of these molecules is confirmed by X-ray data. The Ge...O distance here is much smaller than the sum of the van der Waals radii. The length of the axial Ge-Cl bond is noticeably larger than that of the equatorial ones (Table 1). The $OGeCl_{ax}$ angle is close to 180° (ref. 25).

The quadruplet ^{35}Cl NQR spectrum of compound IX is also in agreement with a trigonal-bipyramidal structure for this molecule (ref. 10). The anomalously low NQR frequency of the Cl atom in the group $(CH_2)_3Cl$ of this compound (31.750 MHz) as compared with that in compounds $Cl(CH_2)_nX$ where $n \geqslant 3$ ($\sim$33.1 MHz, ref. 26) is due to the interaction of Cl with the Sn atom, to form a five-membered ring. The Cl atom in the Cl_3Sn group shows a low frequency triplet. Two of these Cl atoms occupy equatorial positions with a similar electron distribution, and their NQR frequencies differ only slightly. The axial Cl atom shows the lowest frequency line in the spectrum, and the separation between this line and the doublet that belongs to the equatorial Cl atoms exceeds the contribution of crystal effects. The trigonal-bipyramidal structure of this molecule is confirmed by X-ray data analysis (refs. 13,14).

Hence, the ^{35}Cl NQR spectra of the organyltrichloro-germanes and-stannanes Cl_3MX (M = Ge, Sn) which have been studied, where the low frequency line is significantly shifted with respect of the high frequency doublet, give evidence for the intramolecular interaction between M atom and the electronegative atom in the substituent X, and thus the trigonal-bipyramidal structure of molecule. The low frequency line belongs to the axial Cl atom, and high frequency ones to equatorial atoms. The NQR frequencies of the latter lie in the range characteristic for compounds Cl_3GeX of tetrahedral structure. The ^{35}Cl NQR method has been used for studying a large number of organyltrichlorogermanes containing the group $Cl_3Ge-\overset{|}{\underset{|}{C}}-E-C(O)R$ (E = C, N), for which the X-ray analysis turned out to be impossible (refs. 9,10,11).

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. The same shape of the ^{35}Cl NQR spectra and the same value of line separation in spectra of compounds that contain a fragment $Br_3Ge\text{-}\overset{|}{\underset{|}{C}}\text{-}E\text{-}C(O)R$ may imply the intramolecular interaction of Ge and O atoms (ref. 12). For example, in the ^{79}Br NQR spectrum of $(Br_3Ge)_2CHCH_2COOH$, this splitting has too small value (~ 3%) to allow the interaction $Ge \leftarrow O$ to be assumed in this molecule. Further, it is not confirmed either by X-ray data (ref. 7). At the same time, this interaction is unambiguously indicated by the triplet $^{79,81}Br$ NQR spectra of $Br_3GeCH_2\overline{NCO(CH_2)_2C}H_2$ and $Br_3GeCH_2\overline{NCO(CH_2)_3C}H_2$. The separation between the low frequency lines and the high frequency doublet is here ~26 and 28%, respectively (ref. 12). These values exceed the analogous ones for the corresponding organyltrichlorogermanes (24 and 25%) (refs. 9,10,12). This is probably due to the larger polarization ability of the axial Ge-Br bond as compared to the Ge-Cl bond, resulting from the intramolecular interaction $Ge \leftarrow O$ (ref. 12).

All the molecules discussed above undergo closing of a five-membered ring as a result of intramolecular interaction between M atoms of IVA group metals and the heteroatom in the ligand X (Table 1) (refs. 2-4,9-14, 18-20). The series of 2-alkoxyphenyltrichlorostannanes, where the pentacoordination of Sn atom is achieved by closing a four-membered ring (2), was also studied by ^{35}Cl NQR. These spectra also showed a low frequency line and a doublet that is rather distant, or a single line of double intensity (ref. 15). For example, in the doublet NQR spectrum of X the high frequency line is much more intense and is 2.53 MHz away from the low frequency one. Such a spectrum corresponds to a trigonal-bipyramidal structure of coordination polyhedra of Sn atoms. The electron density distribution of the two equatorial Cl atoms having the more intense low frequency line is the same, and the low frequency line corresponds to the axial Cl atom. This NQR spectrum shows that the electron distribution about the Sn atom in X has a symmetry plane passing through the aromatic ring, the Sn-C bond, the axial Sn-Cl bond and the oxygen atom (ref. 15). The intramolecular interaction $Sn \leftarrow O$ in this molecule is also confirmed by X-ray data. The distance between Sn and O atoms here is much less than the sum of their van der Waals radii (refs. 14,15). However, the coordination polyhedron of the Sn atom in this molecule differs significantly from that, where the 5-coordination of the Sn atom is achieved through the closing of a five-membered ring. The sum of the angles between the bonds at the central Sn atom in $2\text{-}CH_3O\text{-}5\text{-}CH_3C_6H_3SnCl_3$ is closer to the angle sum in the tetrahedron than in the trigonal bipyramid (refs. 14,15). It is probably also characteristic for other 2-alkoxyphenyltrichlorostannanes with the intramolecular interaction Sn←O (ref. 15). The similar structure is attributed to the coordination polyhedron of the Sn atom in the molecule $(CH_3)_2CHOC(S)SSn(C_6H_5)_3$, where the intramolecular interaction Sn←O leads also to closing a four-membered ring (ref. 28).

In the ^{35}Cl NQR spectra of 2-alkoxyphenyltrichlorostannanes (2) the lowest frequency line is lower, and the high frequency line is higher than those in the spectra of their para-isomers, where the intramolecular interaction Sn←O is impossible (refs. 14,15). Being in ortho-position to the $SnCl_3$ group, the alkoxy group (particularly its oxygen atom) lowers the NQR frequency of the most distant Cl atom and raises the frequency of the closest Cl atoms. This is due to the polarization of Sn-Cl bonds under the action of the partially negative charged oxygen atom of the alkoxy group directly through the field. The direction and value of this polarization depend on the distance and orientation of the Sn-Cl bonds with respect to the oxygen atom (see, e.g., refs. 29,30). The character of the intramolecular interaction between the OR and $SnCl_3$ groups in 2-alkoxyphenyltrichlorostannanes of badly distorted trigonal-bipyramidal structure gives rise to the significant difference in electron distribution of the Cl atoms, and between the ^{35}Cl NQR spectra of these compounds and the spectra of other compounds Cl_3MX.

For example, the separation between all three lines in the NQR spectrum of $2\text{-}CH_3O\text{-}3,5\text{-}(CH_3)_2C_6H_2SnCl_3$ is large (ref. 15). The low frequency line in this spectrum is even lower, and the high frequency lines are higher, than those in the NQR spectra of other 2-alkoxyphenyltrichlorostannanes studied, where intermolecular interaction between Sn and O atoms occurs. In the molecule $2\text{-}CH_3O\text{-}3,5\text{-}(CH_3)_2C_6H_2SnCl_3$, this interaction seems to be even stronger than in the other 2-alkoxyphenyltrichlorostannanes. The middle line in the NQR spectrum of this compound is closer to the low frequency line ($\Delta\nu$ = 1.128 MHz) than to the high frequency one ($\Delta\nu$ = 1.778 MHz). This is not characteristic of ^{35}Cl NQR spectra of other compounds Cl_3MX with pentacoordinated M atoms, the coordination polyhedra of which have a structure close to trigonal bipyramid (Table 1). Therefore, the structure of the coordination polyhedron of the Sn atom in this molecule differs significantly from the ideal trigonal bipyramid. The electron distribution of its Cl atoms differs significantly due to their different position with respect to the aromatic ring and oxygen atom (ref. 15).

The character of line splitting in the triplet ^{35}Cl NQR spectrum of 2,6-$(CH_3O)_2C_6H_3SnCl_3$ is the same (ref. 15) as in the previous case. However, the value of splitting is much smaller (0.602 and 0.40 MHz). The X-ray data show the close values of all Sn-Cl bonds lengths in this molecule. The coordination polyhedron of its Sn atom is close to tetrahedral. Nevertheless, the both Sn...O distances are much less than the sum of the van der Waals radii (ref. 31). Apparently, these atoms are noticeably interacting in the molecule, but their interaction does not lead to a significant change in bond angles at the central Sn atom and in the electron distribution of the Cl atoms in the $SnCl_3$ group. The ^{35}Cl NQR frequencies of two Cl atoms lie in the same range as in 4-$ROC_6H_4SnCl_3$, and that of the third is somewhat higher. It may be due to the fact that the interaction of the $SnCl_3$ group with one alkoxy group is compensated by its interaction with another alkoxy group (ref. 15).

Hence, on closing the strained four-membered ring, the coordination polyhedron of M usually differs significantly from the ideal trigonal bipyramid, and the electron distribution at the equatorial Cl atoms and their NQR frequencies may be quite different. Nevertheless, the differences in electron distribution of the Cl atom remain significant, and may provide rather reliable evidence of intramolecular interaction in molecules Cl_3MX.

III. ELECTRON DENSITY DISTRIBUTION OF CL ATOMS IN Hal_3MX MOLECULES OF TRIGONAL-BIPYRAMIDAL STRUCTURE

It may be assumed that in trigonal bipyramidal chlorophosphoranes (ref. 24) and B MCl_4 complexes of IV group elements tetrachlorides with organic ligands (refs. 20,32,33) the symmetry of the electron distribution of axial Cl atoms is similar to that of the axial atoms in molecules Hal_3MX, and that of the equatorial Cl atoms is very different (refs. 17,20). This is confirmed by the asymmetry parameters of the electric field gradient (η) for the ^{35}Cl nuclei in 3-chloropropyltrichlorostannane (ref. 13), the trigonal-bipyramidal structure of which is established by X-ray data analysis (ref. 14). The value of η for the two equatorial Cl atoms of this molecule is 6.4 and 10.7%, and for axial atom is 0.4% (ref. 13). The larger asymmetry of the electron distribution of the equatorial Cl atoms in trigonal-bipyramidal molecules is caused by the interaction of electron pair of these atoms with the p-orbital of central M atom (refs. 20,21,34). According to NQR theory (see, eg ., refs. 23,35), such interaction must lower the NQR frequency of these Cl atoms. Nevertheless, the NQR frequencies of the equatorial Cl atoms in all molecules of trigonal-bipyramidal structure are higher than those of the axial one. This reflects the much higher p_σ-electron density of the latter atom. The NQR frequencies of the equatorial Cl atoms for compounds Cl_3MX of trigonal-bipyramidal structure lie in the same range as NQR frequencies of these compounds with a pentacoordinated M atom, while the NQR frequencies of the axial atoms are lower. Therefore the intramolecular interaction in these molecules, as a result of which the M atom becomes pentacoordinated, does not practically influence the p_σ-electron density of the equatorial Cl atoms, but increases markedly the p_σ-electron density of the axial Cl atom. This increses makes the axial M-Cl bond much longer than the equatorial ones.

As the Ge-Cl bond length (r_{Ge-Cl}) in molecules $XGeCl_3$ increases, the NQR frequency of the corresponding Cl atom decreases (Tbale 1). A satisfactory linear correlation (refs. 9-11) is observed between the values r_{Ge-Cl} and ν^{77} of these compounds, which allows the Ge-Cl bond length to be determined from the ^{35}Cl NQR frequencies. The length of the axial Ge-Cl bond in molecules Cl_3GeX of trigonal-bipyramidal structure increases with decreasing Ge...O distance (Table 1). A satisfactory linear correlation is also observed between these values (ref. 10). However, the relationship between the values r_{Ge-Cl} and $r_{Ge\ldots O}$ in molecules with penta- and tetra-coordinated Ge atoms is better described by an exponential rather than a linear dependence (refs. 11,12):

$$r_{Ge-Cl} = 2.118 + 0.844 \exp(-0.394\, r^2_{Ge\ldots O}),\ S = 0.006,\ n = 8.$$

This is expected, because if Ge...O is very large the Ge-Cl bond length does not decrease proportionally, but tends to the value characteristic for molecules with a tetrahedral Ge atom. The decrease of the Ge...O distance is limited by the value of the covalent radii of Ge and O (ref. 11).

The ^{35}Cl NQR frequencies of compounds ClX (X = F, Cl, CRR'R'', SiRR'R'', etc) correlate well with the value of the charge on the Cl atom (q_{Cl}) that was found from quantum chemical calculations by the CNDO/2 method (ref. 35). It may be assumed that this correlation will hold for compounds Cl_3GeX, whose value q_{Cl} may be estimated from experimental ^{35}Cl NQR frequencies (ref. 11).

IV. CONDITIONS NECESSARY FOR PENTACOORDINATION OF METALS OF GROUP IVA

In molecules containing a fragment $Cl_3Ge-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow R}$, pentacoordination of the Ge atom may be attained by interaction with the carbonyl oxygen. In molecules containing a fragment $Cl_3Ge-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow NR_2}$, the Ge atom may interact in principle with oxygen or nitrogen atom, but in fact, it is coordinated by the more electronegative carbonyl oxygen atom which has the larger negative charge. This is confirmed by X-ray data (Table 1) (refs. 2,9, 10,22), which show that (ref. 36) in molecules $Cl_3SnCH_2CH_2COO-CH_3$, $Cl_2Sn[CH_2CH_2COOCH_3]_2$ and $Cl_2Sn[CH_2CH_2CONH_2]_2$, the carbonyl oxygen atom interacts also with the Sn atom, as it is more electronegative than the ether oxygen or the nitrogen atom. It is also possible that the interaction of only the carbonyl oxygen atom with the central Ge and Sn atom in these molecules is caused not only by its higher electronegativity, and thus higher negative charge, but also by its steric accessability.

In molecules containing a fragment $Hal_3M-\overset{|}{\underset{|}{C}}-E-C(O)R$, in substituted silatranes etc, intramolecular interaction between M atom and a heteroatom in the substituent closes a five-membered ring (or rings). However, this is not an obligatory condition for pentacoordination of the central atom, as we supposed previously (refs. 9,10). Such interaction may result also in closure of a four-membered ring (see above). Intracomplex silicon compounds are known, where the coordination bond $Si \leftarrow O$ closes up a six-membered ring (see, e.g., ref. 6).

The analysis of the data presented above and available in the literature allows the conditions necessary for pentacoordination of M (M = Si, Ge, Sn) to be postulated:

1. A large partial positive charge on the M atom and partial negative charge on the heteroatom of group X.
2. A molecular structure which allow these atoms to approach to a distance less than the sum of their van der Waals radii. This 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 system. For example, in molecules $Cl_3GeCH_2CH_2COOH$, $Cl_3GeCH_2CH(CH_3)COOH$ and $Cl_3GeCH(CH_3)CH_2COOH$, substantially the same probability may be assumed for formation of a five-membered ring that determines the pentacoordination of Ge atom. However, probably, due to steric factors, such a ring is energetically advantageous only in the last molecule (refs. 9,10). A significant influence of ste-

ric factors on the molecule structure is confirmed by different lengths of Ge–N (2.479–2.508 Å) and Ge–Cl (2.327–2.301 Å) bonds for two conformers of the molecule $C_6H_5(CH_3)Cl\overline{GeC_6H_4CH_2N}(CH_3)_2$-2 (ref. 37).

V.CONCLUSION

The above data show that the halogen NQR spectra of compounds Hal_3MX allow us to establish the type of coordination polyhedron of the central M atom, its symmetry elements, the Ge–Cl bond lengths and the Ge...O distance in molecules containing a fragment $Cl_3Ge{-}\overset{|}{\underset{|}{C}}{-}E{-}C(O)X$ (E = C, N). The ^{35}Cl NQR frequencies and EFG asymmetry parameters on the ^{35}Cl nuclei give information on spatial distribution of Cl atoms electron density, on the mechanism of their interaction with M atom, etc. This does not exhaust the potential of NQR. For example, valuable information on the structure of these compounds may be obtained from the Stark effect in the NQR spectra, but so far this effect was not been applied. In view of the absence of the need for any special preparation of the samples, the relative ease and speed with which the spectra of polycrystalline halogen-containing compounds can be recorded, the ease with which these spectra can be interpreted, and their high sensitivity to the small changes in electron distribution of the indicator atom, the NQR method may be considered to be an express-method for determining the electron and spatial structure of halogen-containing compounds.

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