- 5. H. Stanley, Phase Transitions and Critical Phenomena [Russian translation], Mir, Moscow (1973), p. 419.
- 6. J. C. Bonner and M. E. Fisher, Phys. Rev., Ser. A, <u>135</u>, 640 (1964).
- M. I. Belinskii, B. S. Tsukerblat, and N. V. Gerbeleu, Fiz. Tverd. Tela, <u>25</u>, No. 8, 869 (1983).
- 8. M. I. Belinskii and B. S. Tsukerblat, Fiz. Tverd. Tela, <u>26</u>, No. 3, 758 (1984).
- 9. B. S. Tsukerblat and A. I. Belinskii, Fiz. Tverd. Tela, <u>25</u>, No. 11, 3512 (1983).
- Yu. V. Gagarinskii and L. A. Khripin, Uranium Tetrafluoride [in Russian], Atomizdat, Moscow (1966), p. 2316.

<sup>35</sup>C1 NQR SPECTRA OF COMPLEXES OF TETRACHLOROSTANNANE WITH SUBSTITUTED BENZOYL CHLORIDES

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UDC 548.58+546.814+541.6

 $^{35}$ Cl NQR spectra of mixtures of SnCl<sub>4</sub> with 2-, 3-, and  $4-XC_6H_4$ COCl were obtained. The electronic and steric structure of the complexes obtained was established. Their formation and structure depend on the nature of substituents X. Complexes with a trigonal-bipyramidal structure are formed with the participation of the carbonyl oxygen atom of the ligand as an electron-donor center, and complexes with trans-octahedral structure, with the participation of the sulfur atom of the X = CH\_3S substituent.

In the reaction of SnCl<sub>4</sub> with para-substituted benzoyl chlorides, complexes with a 1:1 composition are formed, in which the tin atom is pentacoordinated [1]. We obtained a crystalline complex with this structure in the reaction of ortho-methoxybenzoyl chloride with tetrachlorostannane [2]. In the course of time, it converts into a cis-octahedral complex [2]. In the continuation of a <sup>35</sup>Cl NQR study of complexes of tetrachlorostannane with organic ligands, we obtained <sup>35</sup>Cl NQR spectra of mixtures of SnCl<sub>4</sub> with 2-, 3-, or 4-substituted benzoyl chlorides (Tables 1 and 2).

The NQR spectra of equimolar mixtures of  $2-XC_6H_4COC1$  (X = F, C1CO) and  $3-XC_6H_4COC1$  (X =  $O_2N$ , C1CO) consist of the spectra of initial components (Table 1). The same NQR spectra were obtained for these values of X (except for X = F) for mixtures of SnCl<sub>4</sub> with  $4-XC_6H_4COC1$  [1]. This indicates the absence of complexation.

A  ${}^{35}$ Cl NQR spectrum of an equimolar mixture of SnCl<sub>4</sub> and 2-ClC<sub>6</sub>H<sub>4</sub>COCl consists of four lines with different width and intensity. The broad and intense lines in the spectrum are due to superposition of several closely positioned lines. Among these lines, the lowest frequency lies in the same region as most of the spectrum of individual SnCl<sub>4</sub>. The highfrequency broad and intense line in the spectrum belongs to the chlorine atom in the aromatic ring. The frequency of its maximum (36.88 MHz) practically coincides with that of the line of the same chlorine atom in the individual 2-ClC<sub>6</sub>H<sub>4</sub>COCl. In the NQR spectrum of a mixture of SnCl<sub>4</sub> with 2-ClC<sub>6</sub>H<sub>4</sub>COCl only one weak single line (29.666 MHz) is observed for the chlorine atom of the COCl grouping. Its frequency practically coincides with that of one of the lines for this chlorine atom in the spectrum of individual 2-ClC<sub>6</sub>H<sub>4</sub>COCl (see Table 1). The NQR spectrum obtained of a mixture of SnCl<sub>4</sub> and 2-ClC<sub>6</sub>H<sub>4</sub>COCl shows that no complexation took place.

In a quadruplet NQR spectrum of an equimolar mixture of  $SnCl_4$  with 2-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>COCl, the highest frequency line belongs to the chlorine atom in the COCl grouping, and the three low-

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Zhurnal Strukturnoi Khimii, Vol. 27, No. 6, pp. 68-72, November-December, 1986. Original article submitted July 30, 1985.

TABLE 1.  ${}^{35}$ Cl NQR Frequencies at 77°K ( $\nu^{77}$ ) of Mixtures of SnCl<sub>4</sub> with XC<sub>6</sub>H<sub>4</sub>COCl and Their Initial Components, and Also Their Signal/Noise Ratio (s/n) in the NQR Spectra

Compound	$\nu_{\tau}^{\pi}$ , MHz	s/n	Compound	ν <sup>77</sup> , MHz	s/n
SnCl <sub>4</sub> [7]	24,296 24,226 24,140 23,720	50 50 50 50	$2-\mathrm{ClC}_6\mathrm{H}_4\mathrm{COCl}+\mathrm{SnCl}_4$	36,52-37,00 29,666 24,80 24,0-24,5	6 2 2 6
2-Clocc <sub>6</sub> H <sub>4</sub> Cocl [8]	31,290 30,240	50 10	3-Clocc <sub>6</sub> H <sub>4</sub> CoCl [8]	$31,092 \\ 30,258$	50 50
$2\text{-Clocc}_6H_4\text{Cocl} + 6\text{nCl}_4$	31,230 30,220 24,290 24,229 24,140 23,720	4 15 18 21 18	$3-\text{ClOCC}_6\text{H}_4\text{COCl} + + \text{SnCl}_4$	31,065 30,256 24,298 24,219 24,130 23,719	9 13 26 25 23 23
$\begin{array}{l} 2\text{-FC}_{6}\text{H}_{4}\text{COCl} \\ 2\text{-FC}_{6}\text{H}_{4}\text{COCl} + \text{SnCl}_{4} \end{array}$	$\begin{array}{r} 30,380\\ 30,374\\ 24,290\\ 24,224\\ 24,126\\ 23,720 \end{array}$	35 8 36 32 24 45	$3-NO_{2}C_{6}H_{4}COCI [8]$ $3-NO_{2}C_{6}H_{4}COCI + SnCl_{4}$	31,404 31,200 31,409 31,199 24,292 24,220	10 10 11 12 11 11
2-ClC <sub>6</sub> H <sub>4</sub> COCl	36,828* 29,906 29,690	16 10 13		24,142 23,719	11 . 15

\*Unresolved doublet. Inappreciably differing NQR spectra are given for this compound in [8, 9].

frequency lines to chlorine atoms bound to the tin atom. The NQR frequency of the first line is appreciably higher than that of the individual  $2-CH_3C_6H_4COC1$  (see Table 2). This indicates the formation of a complex of  $2-CH_3C_6H_4COC1$  with tetrachlorostannane. In the low-frequency triplet spectrum, one line has an appreciably lower frequency than that of the two other lines. The ratio of intensities of the two latter lines is 1:2. A similar NQR spectrum corresponds to the complex with a trigonal-bipyramidal structure, in which the three chlorine atoms of the acceptor occupy the equatorial position, and the fourth chlorine atom and the ligand occupy an axial position. The axial chlorine atom has the lowest frequency line in the NQR spectrum, and the equatorial chlorine atom has two other lines of the low-frequency triplet. The electron distribution of the two equatorial chlorine atoms is the same, and that of the third only inappreciably differs from this distribution. Hence, the 2-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>COC1·SnCl<sub>4</sub> complex has a plane of symmetry passing through a ligand, the axial, and one equatorial Sn-C1 bond.

The highest frequency line in the triplet  ${}^{35}$ Cl NQR spectrum of a mixture of SnCl<sub>4</sub> with  $4-(CH_3)_3SiC_6H_4COCl$  belongs to a chlorine atom in the COCl grouping. It is appreciably shifted to the high-frequency region with respect to the individual  $4-(CH_3)_3SiC_6H_4COCl$ , which indicates complexation. The lowest frequency line in the NQR spectrum of this complex is much below the neighboring line with an NQR frequency that is close to the NQR frequencies of the individual SnCl<sub>4</sub>. Hence, the complex formed has a trigonal-bipyramidal structure. The electron distribution of its equatorial chlorine atoms, to which one, the most intense line of the triplet spectrum, belongs, is absolutely identical (naturally, within the resolving power of the spectrometer). This means that the electronic environment of the central tin atom has an axis of symmetry of the third order, coinciding with axial bonds of this atom. It is possible that there is practically no steric influence of the ligand on the equatorial chlorine atoms of the spectrum can be obtained that somewhat differs from the spectrum of the  $4-(CH_3)_3SiC_6H_4COCl\cdotSnCl_4$  complex, given in Table 2.

The highest frequency line in the NQR spectrum of the  $SnCl_4 + 3-ClC_6H_4COCl$  system belongs to the chlorine atom in the aromatic ring, and the neighboring high-frequency line to the chlorine atom in the COCl grouping. The first line is shifted inappreciably, and the second appreciably to the high-frequency region with respect to the corresponding lines in the NQR spectrum of the individual  $3-ClC_6H_4COCl$  (see Table 2). The line in the  ${}^{35}Cl$  NQR spectrum of the  $SnCl_4 + 3-BrC_6H_4COCl$  system, belonging to the chlorine atom in the COCl grouping, is also appreciably shifted to the high-frequency region with respect to the NQR TABLE 2.  ${}^{35}$ Cl NQR Frequencies at 77°K ( $\nu^{77}$ ) of Complexes XC<sub>6</sub>H<sub>4</sub>COC1·SnCl<sub>4</sub> and Individual XC<sub>6</sub>H<sub>4</sub>COC1 and Also Signal/Noise (s/n) Ratio in Their NQR Spectra

Compound	ν <sup>π</sup> , MHz	<b>s</b> / 1	Compound	ν <sup>77</sup> , MHz	s/n
2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> COCI 2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> COCI · SnCl <sub>4</sub>	29,242 33,040 24,384 23,858 20,254	10 14 10 20 11	$3-CH_3OC_6H_4COCl + 2SnCl_4.$	33,339 24,274 24,218 24,127 23,921 23,729	4 14 12 15 25
3-CIC <sub>6</sub> H <sub>4</sub> COCl [8]	35,532 30,250	5 5	4-C H-OC.H-COC)	20,525	12 16
3-CIC <sub>6</sub> H <sub>4</sub> COCl·SnCl <sub>4</sub>	35,646 31,307 25,399 24,286 23,808 22,690	26 27 15 15 18 18	4-C <sub>2</sub> H <sub>5</sub> OC <sub>6</sub> H <sub>4</sub> COCl·SnCl <sub>4</sub>	32,650 24,102 23,919 23,264 20,696	18 13 15 15
3-BrC <sub>6</sub> H <sub>4</sub> COCl	30,515	38	4-(CH <sub>3</sub> ) <sub>3</sub> SiC <sub>6</sub> H <sub>4</sub> COCI	30,062 29,953	4
3-BrC <sub>6</sub> H <sub>4</sub> COCl·SnCl <sub>4</sub>	31,365 25,541 24,287 23,909 22,620	25 20 20 23 18	4-(CH <sub>3</sub> ) <sub>3</sub> SiC <sub>6</sub> H <sub>4</sub> COCl·SnCl <sub>4</sub> 4-CH <sub>3</sub> SC <sub>8</sub> H <sub>4</sub> COCl	31,301* 24,539 21,848 30,077	18 40 13 30
3-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> COCl 3-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> COCl·SnCl <sub>4</sub>	30,273 33,345 23,931 23,736 20,527	45 15 60 30 25	$4-CH_3SC_6H_4COCl + SnCl_4$	30 315** 24,288 24,226 24,150 23,727 19,471	25 22 21 20 27 3
$2(3-CH_3OC_6H_4COCl) + SnCl_4$	33,345 30,271 23,931 23,740 20,527	58843	2(4-CH <sub>3</sub> SC <sub>6</sub> H <sub>4</sub> COCl) · SnCl <sub>4</sub>	30,318 19,476	18 4

 $\frac{1}{2}$   $\frac{1}$ 

spectrum of the individual 3-BrC<sub>6</sub>H<sub>4</sub>COC1. This indicates the formation of complexes of 3- $XC_6H_4COC1$  (X = C1, Br) with tetrachlorostannane. The complexation is also confirmed by an appreciable difference between the low-frequency quadruplet part of the NQR spectrum of these complexes, belonging to the electron-acceptor, and the spectrum of the individual SnCl4 (see Tables 1 and 2). It can be assumed that these complexes have a structure of an appreciably distorted trigonal bipyramid, since the low-frequency line in the quadruplet part of their NQR spectra is much lower than the three remaining lines. However, attention should be paid to the fact that, in this quadruplet part of the spectra, two terminal lines (high-frequency and low-frequency) are shifted by practically the same considerable value with respect to their central neighbors (1.115 ± 0.003 and 1.272 ± 0.018 MHz for X = C1 and Br, respectively). The splitting between these two central lines is appreciably smaller than this value (0.478 and 0.378 MHz, respectively). The terminal lines of the quadruplet are positioned relatively far behind the limits of the frequency range of the NQR spectrum of the individual SnCl<sub>4</sub>. The NQR frequencies of the two median lines (see Table 2) are also very close to the frequencies of the individual SnCl4 (see Table 1). The low-frequency lines in the NQR spectra of the  $3-XC_6H_4COC1\cdot SnCl_4$  complexes (X = C1, Br), which can be assigned to the axial chlorine atom of the electron-acceptor, are much higher than in the NQR spectra of other XC<sub>6</sub>H<sub>4</sub>COC1. SnCl, complexes with a trigonal-bipyramidal structure which have so far been investigated. The appreciable increase in the NQR frequency of one of the quadruplet lines in the NQR spectra of the 3-XC<sub>6</sub>H<sub>4</sub>COCl·SnCl<sub>4</sub> complexes (X = Cl, Br), compared with the individual SnCl<sub>4</sub>, and also the high symmetricity of this quadruplet, have been difficult to explain up to now.

By analogy with the  $XC_6H_4COC1$ ·MCl complexes (M = Al, Sb) with a structure established by x-ray diffraction analysis [3-5], it can be assumed that also, for M = Sn, complexation takes place at carbonyl oxygen atom of the ligand, and not with the participation of its chlorine atom. This is also indicated by increase in the <sup>35</sup>Cl NQR frequency in the COCl



Fig. 1. Correlation between shifts of  ${}^{35}$ Cl NQR frequencies of chlorine atoms of the 4-XC<sub>6</sub>H<sub>4</sub>COCl ligand ( $\Delta$ vC-Cl) and the axial Sn-Cl bond ( $\Delta$ vSn-Cl) in 4-XC<sub>6</sub>H<sub>4</sub>COCl·SnCl<sub>4</sub> complexes with respect to mean values of NQR frequencies of initial components, and also deviations from it of points corresponding to 2- and 3-XC<sub>6</sub>H<sub>4</sub>COCl·SnCl<sub>4</sub>. 4-X = CH<sub>3</sub> (1), Br (2), Cl (3), F (4), H (5), CH<sub>3</sub>O (6), (CH<sub>3</sub>)<sub>3</sub>Si (7), C<sub>2</sub>H<sub>5</sub>O (8); 2-X = CH<sub>3</sub> (9), CH<sub>3</sub>O (10); 3-X ~ CH<sub>3</sub> (11), CH<sub>3</sub>O (12), Cl (13), Br (14).

grouping of all the complexes studied of SnCl<sub>4</sub> with  $XC_6H_4COCl$ , compared with the corresponding individual acid chlorides ([1], see Table 2). In complexation with the participation of the chlorine atom of the COCl grouping of the ligand, its NQR frequency, in contrast, would decrease, as in the case of the bridging halogen atoms in dimers (AlX<sub>3</sub>)<sub>2</sub>, (GaCl<sub>3</sub>)<sub>2</sub>, etc. (see, for example, [6]).

The molecules of  $\text{ROC}_6\text{H}_4\text{COCl}$  contain two electron-donor centers: carbonyl and ether oxygen atoms. One of these oxygen atoms or two atoms can simultaneously participate in the formation of complexes with tetrachlorostannane. Thus, the formation of complexes with different composition and structure is possible. In the case of the participation of only the ether oxygen atom of the 3- or 4-ROC<sub>6</sub>H<sub>4</sub>COCl ligand in the complexation, the NQR frequency of its chlorine atom should change inappreciably compared with that of the individual  $\text{ROC}_6\text{H}_4$ -COCl, since the influence of the redistribution of the electron density in the meta- or parasubstituent on this chlorine atom is inappreciable. In fact, its NQR frequency in the 3-CH<sub>3</sub>-OC<sub>6</sub>H<sub>4</sub>COCl·SnCl<sub>4</sub> complex is much higher than that of the individual 3-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>COCl, and in the 4-CH<sub>3</sub>CH<sub>2</sub>OC<sub>6</sub>H<sub>4</sub>COCl·SnCl<sub>4</sub> complex it is much higher than in 4-CH<sub>3</sub>CH<sub>2</sub>OC<sub>6</sub>H<sub>4</sub>COCl (see Table 2). The value of this increase is approximately the same as on transition from 4-Cl- and 4-BrC<sub>6</sub>H<sub>4</sub>COCl to their corresponding complex with tetrachlorostannane, and much higher than on transition from C<sub>6</sub>H<sub>4</sub>COCl to its complex with SnCl<sub>4</sub> (see Table 2).

When two oxygen atoms of  $ROC_6H_4COC1$  participate in the complexation, the complex should have the composition of L·2SnCl<sub>4</sub>. However, the data obtained show that complexes of SnCl<sub>4</sub> with 3-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>COC1 and 4-CH<sub>3</sub>CH<sub>2</sub>OC<sub>6</sub>H<sub>4</sub>COC1 with a 1:1 composition are formed. In the case of a 1:2 or 2:1 ratio of the components, besides the lines belonging to the 1:1 complex, lines for excess components are observed in the NQR spectrum of a mixture of SnCl<sub>4</sub> with 3-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>COC1. Hence, in the reaction of SnCl<sub>4</sub> with 3- and 4-ROC<sub>6</sub>H<sub>4</sub>COC1, complexes with a trigonal-bipyramidal structure are formed with the participation of the carbonyl oxygen atom only, as an electron-donor center.

Several electron-donor centers are also present in the molecule of  $4-CH_3SC_6H_4COC1$  and can participate in the complexation with  $SnCl_4$ . The  ${}^{35}Cl$  NQR spectrum of their 2:1 mixture is doublet in character. Its high-frequency line belongs to the chlorine atom in the COC1 grouping. It is only inappreciably higher than of the individual  $4-CH_3SC_6H_4COC1$ . The other line of the doublet is much lower than the lines of the individual  $SnCl_4$ . The spectrum obtained indicates the formation of a complex with the participation of its sulfur atom and not the carbonyl oxygen atom. In the NQR spectrum of a 1:1 mixture of  $SnCl_4$  with  $4-CH_3SC_6H_4$ -COC1, not only lines of the  $2(4-CH_3SC_6H_4COC1)\cdot SnCl_4$ , but also of the individual  $SnCl_4$  are observed (see Table 2). These data indicate the formation of trans-octahedral complex, in which all four Sn-C1 bonds are equivalent. In the NQR spectrum of the complex, their chlorine atoms have one signal.

The above data, and those already obtained in [1], show that the formation and structure of the complexes of SnCl<sub>4</sub> with  $XC_6H_4COCl$  depend on the nature of the substituent X. If a carbonyl oxygen atom of the ligand participates as an electron-donor center, complexes are formed with a trigonal-bipyramidal structure, and in the case of the participation of the sulfur atom of X =  $CH_3S$  substituent, the complexes formed have a trans-octahedral structure. The shifts of the  ${}^{35}$ Cl NQR frequencies of the chlorine atoms of the ligand ( $\Delta$ vC-Cl) and of the axial Sn-Cl bond ( $\Delta$ vSn-Cl) in the  $4-XC_6H_4$ COCl·SnCl<sub>4</sub> complexes, with respect to the mean values of the NQR frequencies of the corresponding initial components, satisfactorily correlate with one another [1]. If the data in the present work are taken into account, the correlational equation has the form  $\Delta$ v<sub>C-Cl</sub> = -0.888 - 0.965 $\Delta$ vSn-Cl (r = 0.977, s = 0.147). Only the point corresponding to the 4-CH<sub>3</sub>CH<sub>2</sub>OC<sub>6</sub>H<sub>4</sub>COCl·SnCl<sub>4</sub> complex deviates noticeably from this correlation. The correlation does not hold for the shifts of the NQR frequencies for 2- and  $3-XC_6H_4$ COCl·SnCl<sub>4</sub> complexes. It is possible that these shifts form an inherently similar linear correlation.

## LITERATURE CITED

- 1. G. V. Dolgushin, I. M. Lazarev, V. P. Feshin, and M. G. Voronkov, Dokl. Akad. Nauk SSSR, <u>265</u>, No. 6, 1416 (1982).
- 2. G. V. Dolgushin, I. M. Lazarev, V. P. Feshin, and M. G. Voronkov, Zh. Obshch. Khim., 54, No. 6, 1430 (1984).
- 3. S. E. Basmussen and N. C. Broch, Acta Chem. Scand., 20, No. 2, 1351 (1966).
- 4. B. Chervier, J. M. Carpentier, and R. Weiss, Acta Crystallogr., 28, No. 9, 2659 (1972).
- 5. B. Chervier, J. M. Carpentier, and R. Weiss, J. Am. Chem. Soc., <u>94</u>, No. 16, 5718 (1972).
- 6. G. Wulfsberg and A. Weiss, Ber. Bunsenges. Phys. Chem., <u>84</u>, 474 (1980).
- 7. D. Biedenkapp and A. Weiss, Z. Naturforsch., 19, 1518 (1964).
- 8. E. V. Bryukhova, V. V. Korshak, V. A. Vasnev, and S. V. Vinogradova, Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 599 (1972).
- 9. T. Deeg and A. Weiss, Ber. Bunsenges. Phys. Chem., <u>80</u>, 2-11 (1976).

STUDY OF STRUCTURES OF COMPLEXES OF PROFLAVINE WITH DINUCLEOTIDES IN AQUEOUS SOLUTION BY THE <sup>1</sup>H NMR METHOD

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UDC 541.59+539.1.12.43

We present the results of an investigation of the interaction of proflavine with isomeric diribonucleoside monophosphates CpG and GpC using the proton magnetic resonance method (270 MHz). On the basis of the proposed technique, starting from the concentration dependences of the proton chemical shifts of the dye in a mixture with the dinucleotides, we calculated the association constants of the molecules, the values of the chemical shifts for the proflavine protons in the complexes, and the most probable structures of the 1:1 and 1:2 complexes of the dye with the dinucleotides.

The <sup>1</sup>H NMR spectroscopy method is highly effective for determining the structure of complexes of aromatic molecules of acridine dyes in aqueous solution [1-3]. There is significant interest in the study of the interaction between the dye and the nucleotides which are the component parts of the double helix of the nucleic acid molecules. It is known that acridine dyes forming complexes with nucleic acids disrupt the matrix synthesis and consequently lead to a change in cell growth and division. Experimental studies [4] are evidence that complementary dinucleotides associate in solution with formation of sections of the double helix which are the very shortest fragments of native nucleic acids. It is reasonable to assume that complexes of dyes and antibiotics with the sections of the double helix formed by complementary dinucleotides may serve as model systems for binding of dye with nucleic acids. In a number of papers [5-7] it has been shown that antibiotics preferentially bind with a quite definite sequence of bases in the dinucleotide chain. This assumes that the anitbiotics interact with different sections of the nucleic acids with considerably different binding constants. For possible resolution of these questions, we need to have quanti-

Sevastopol Instrumentation Institute. Translated from Zhurnal Strukturnoi Khimii, Vol. 27, No. 6, pp. 73-78, November-December, 1986. Original article submitted August 27, 1985; revision submitted January 13, 1986.