# IR AND UV SPECTRA OF COMPLEXES OF N-VINYLAZOLES WITH ORGANOHALOSTANNANES

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Analysis of the absorption bands in the IR and UV spectra of complexes of N-vinylazoles with organohalostannanes shows that coordination occurs only through the "pyridine" nitrogen atom of the ligand. The greatest shifts in the absorption bands in the IR and UV spectra and changes in their intensities are displayed in complexes of N-vinylazoles with alkyltrichloro- and phenylhalostannanes; this corresponds to the increased electron-acceptor capacity of these organotin compounds.

A study of the IR and UV spectra of complexes of N-vinylazoles with halogens, hydrogen halides, and chlorides of transition metals enabled us to establish the donor-acceptor character of the interaction of these heterocyclic ligands with inorganic partners (for example, see [1, 2]).

In the present study we have analyzed the absorption bands in the IR and UV regions of the spectra of complexes of N-vinylimidazole (I), N-vinylbenzimidazole (II), N-vinylbenzotriazole (III), and N-ethylimidazole (IV) with organohalostannanes (Table 1). The method used for their preparation and the chemical properties of the complexes were previously described in [3].

The formation of complexes with heterocyclic molecules, the electron-donor properties of which are determined by the presence of a nitrogen atom which has an unshared pair of electrons, is manifested spec-

TABLE 1. N-Vinylazoles and Their Complexes with Organohalostannanes

| No. | Compound | mp, °C | No. | Compound | mp, °C |
|---|---|---|---|---|---|
| I | N-Vinylimidazole | 80 (10)$^{a}$ | XV | $2I \cdot (C_6H_5)_2SnCl_2$ | 170 |
| II | N-Vinylbenzimidazole | 130 (3)$^{a}$ | XVI | $2I \cdot C_6H_5SnCl_3$ | 208 |
| | | | XVII | $I \cdot (CH_2{=}CH)_3SnCl$ | 100 (6)$^{a}$ |
| III | N-Vinylbenzotriazole | 102—103 (2)$^{a}$ | XVIII | $2I \cdot SnCl_4$ | 261—262$^{c}$ |
| | | | XIX | $2II \cdot (C_2H_5)_2SnCl_2$ | 99 |
| IV | N-Ethylimidazole | 73—75 (3)$^{a}$ | XX | $2II \cdot (C_2H_5)_2SnBr_2$ | 113 |
| V | $I \cdot (C_2H_5)_3SnCl$ | 100 (12)$^{a}$ | XXI | $2II \cdot C_2H_5SnCl_3$ | 196 |
| VI | $I \cdot (C_2H_5)_3SnBr$ | 90 (6)$^{a}$ | XXII | $2II \cdot (C_6H_5)_2SnCl_2$ | 143 |
| VII | $2I \cdot (C_2H_5)_2SnCl_2$ | 168 | XXIII | $2II \cdot C_6H_5SnCl_3$ | 275 |
| VIII | $2I \cdot (C_2H_5)_2SnBr_2$ | 183 | XXIV | $2II \cdot SnCl_4$ | 280—281$^{c}$ |
| IX | $2I \cdot C_2H_5SnCl_3$ | 166 | XXV | $2III \cdot C_2H_5SnCl_3$ | 115 |
| X | $I \cdot (C_3H_7)_3SnCl$ | 67,5—68 | XXVI | $2III \cdot C_6H_5SnCl_3$ | 169 |
| XI | $I \cdot (C_4H_9)_3SnCl$ | —$^{b}$ | XXVII | $2III \cdot SnCl_4$ | 245—248 |
| XII | $2I \cdot (C_4H_9)_2SnCl_2$ | 125—126 | XXVIII | $IV \cdot (C_2H_5)_3SnCl$ | 90 (4)$^{a}$ |
| XIII | $I \cdot (C_6H_5)_3SnCl$ | 96—96,5 | XXIX | $IV \cdot (C_2H_5)_3SnBr$ | 99 (4)$^{a}$ |
| XIV | $I \cdot (C_6H_5)_3SnBr$ | 99—100 | XXX | $2IV \cdot SnCl_4$ | 230 |

[a] This is the boiling point in degrees centigrade (mm). [b] This compound decomposed during vacuum distillation at 1 mm. [c] With decomposition.

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TABLE 2. Characteristic Frequencies ($cm^{-1}$) in the IR Spectra of N-Vinylazoles and Their Complexes with Organohalostannanes[a,b]

| I | V | VI | VII | VIII | IX | X | XI | XII | XIII | XIV | XV | XVI | XVII | XVIII | Assignment of the frequencies |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 3130sh | | | 3130 s | | | 3150 m | 3150 m | 3149 s | | | | |
| 3115 m | 3112s | 3110 m | 3110 m | 3130 s | 3130 m | 3110m | 3120 s | 3120 s | 3121 s | 3121 s | 3132 s | 3140 m | 3120 s | 3140 s | $\nu_{C-H}$ |
| 1510 s | 1513s | 1514 s | 1510s | 1513 s | 1520 s | 1515 s | 1512s | 1507 s | 1532 m,sh | 1532 m,sh | 1515 s | 1520 s | 1515 s | 1513 s | $\nu$ Ring |
| 1493m | | | | | | 1505s | | | 1510 s | 1510 s | | | | | |
| 1323m | 1332 m | 1340 m | 1340m | 1338 m | 1340m | 1330m | 1340m | 1338m | 1330 m | 1330 m | 1340 m | 1340 m | 1335 m | 1340m | $\delta$ Ring |
| 1105 m | 1100 m,sh | 1105 m,sh | | 1100 s | 1103 s | 1090 s | 1095 s | 1095 s | 1118 m | 1118 m | 1102 s | 1090 s | 1090 s | 1091 s | |
| 1078 m | 1090 s | 1090 s | 1088 s | 1085 s | | | | | 1095 vs | 1095 vs | 1087 s | 1070 s | | | |
| 902 m | 926 m | 930 m | 930 m | 935 s | 900m | 927 m | 932s | 935 s | 935 s | 935 s | 935 s | 948 s | 948 s | 945 s | $\gamma_{CH}$ Ring |
| 883 m | 892 m | 900 m | 900 m | 900 m | | 895 m | 900s | 900 m | 890 m | 890 s | | 903 s | | 912 m | |
| 815 m | 837m | 840 m | 857 m | 842 m | 850 m | 840 m | 845 m | 845 m | 830 m | 830 m | 840 m | 847 m | 835 m | 850 m | $\gamma_{CH}$ Ring |
| | 817m | | | | | | | | 450s → 457 s | 445 s→457 s | 444 m→460 m | 440 m→460 | | | $\nu_{Sn-C}$ |

TABLE 2. Continued

| II | XIX | XX | XXI | XXII | XXIII | XXIV | III | XXV | XXVI | XXVII | IV | XXVIII | XXIX | XXX | Assignment of the frequencies |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1503 s | 1505s | 1505 s | 1516 s | 1510 s | 1515 s | 1510 s | 1168 s | 1213 s | 1212 s | 1212 s | 1511 s | 1520 s | 1520 s | 1522 s | $\nu$ Ring |
| | 1485 s | 1485 s | 1485 s | 1485 s | 1485 s | 1475 s | 887 s | 915 s | 915 s | 923 s | 1108 s,sh | 1107 s,sh | 1107s, sh | | $\delta$ Ring |
| 1460 s | 1465s | 1465 s | 1465 s | 1465s | 1455 s | 1450 s | | | | | 1077 s | 1093 s | 1093 s | | |
| | 1420 w | 1420 w | 1420 w | 1432 w | 1435w | 1440 m | | | | | | | | | |
| 1234 s | 1242 s | 1242 s | 1243 s | 1240 s | 1250 s | 1240 s | | | | | 906 s | 935 s | 935 s | 930 s | $\gamma_{CH}$ Ring |
| 1160s | 1180 s | 1180 s | 1200 s | 1195s | 1200 s | 1192 s | | | | | 816 s | 825 s | 825 m | 855 s | $\gamma_{CH}$ Ring |
| 885s | 907 s | 907 s | 920 s | 915s | 918 s | 920 s | | | | | | | | | |
| | | | | 890s | 890 s | 900 m | | | | | | | | | |
| | | | | 440 m→457 s | 440m →455m | | | | | | | | | | $\nu_{Sn-C}$ |

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[a] With a UR-20 spectrometer. The solids were pressed into KBr pellets, while the liquids were recorded in a thin layer. [b] Abbreviations: s is strong, m is medium, w is weak, and sh is shoulder.

troscopically by a shift in the frequencies of the stretching vibrations of the ring (1580-1625 $cm^{-1}$) to the long-wave region of the spectrum [4]. In the spectra of N-ethyl and N-vinyl derivatives of azoles these bands become very weak and in most cases are overlapped by the intense band of the stretching vibrations of the $CH_2=CH$ group at 1640 $cm^{-1}$. In addition to this, the spectra contain intense bands of the stretching vibrations of the heteroring at 1480-1510 $cm^{-1}$, from the shift of which one can judge the character of the complexing. The shift of the absorption bands in the spectra of the investigated complexes as compared with the spectra of the free ligands is presented in Table 2. The characteristic shifts of the frequencies of the ring vibrations caused by the donor–acceptor interaction appear most distinctly in the spectra of complexes of ethylimidazole (IV) with $(C_2H_5)_3SnX$ (X = Cl, Br, I). In this case, one observed an increase in the frequency of the stretching vibrations of the heteroring from 1510 (in the ligand) to 1520 $cm^{-1}$ (in the complex), in the frequency of the skeletal vibrations of the ring from 1077 to 1093 $cm^{-1}$, and in the deformation vibrations of the ring CH groups from 816 to 826 $cm^{-1}$ and from 906 to 935 $cm^{-1}$. The shift in the 816 $cm^{-1}$ band is more significant for the complex of ethylimidazole (IV) with $SnCl_4$ ($\Delta\nu = 39$ $cm^{-1}$) than for complexes XXVIII and XXIX ($\Delta\nu = 9$ $cm^{-1}$). In the spectra of complexes of vinylimidazole I, a single band at 1510-1530 $cm^{-1}$ appears in most cases in place of the intense doublet at 1510 and 1493 $cm^{-1}$; there is also a doublet only in the spectra of X, XIII, and XIV, but this doublet has maxima that have higher values than in the spectrum of I. The bands of the ring skeletal vibrations are also shifted from 1323 to 1340 $cm^{-1}$ and from 1105, 1078 to 1100, 1090 $cm^{-1}$, and the frequency of the deformation vibrations of the ring CH groups is shifted from 902, 883 to 925-940, 890-900 $cm^{-1}$. As in the case of complexes of I with transition-metal halides, the observed changes in the spectrum of I make it possible to conclude that the coordination interaction is realized with the participation of the "pyridine" nitrogen atom of the ligand. The interaction of the electron-donor and electron-acceptor molecules in complexes of vinylazoles II and III is apparently similarly realized. The bands of the stretching and deformation vibrations of the ring (1503, 1460, 1234, 1160, and 885 $cm^{-1}$) are also shifted in the spectra of the complexes of vinylbenzimidazole II. In the second case, a shift in the bands from 1168 to 1212 and from 887 to 915-923 $cm^{-1}$ is observed. In addition to this, the presence of a band of stretching vibrations of the $CH_2=CH$ group and the same position of its frequency (1648 $cm^{-1}$) as in the spectrum of the ligand are common to the spectra of all of the complexes of N-vinylazoles. This is evidence for the absence of polymerization during the reaction of N-vinylazoles even with $SnCl_4$ and also evidence that the adducts formed in the reaction are not $\pi$ complexes with the participation of the electrons of the vinyl group.

The bands of the ligands at 800-900 $cm^{-1}$ are the most sensitive to complexing. The maximum value of their shifts ($\Delta\nu = 32$-$42$ $cm^{-1}$) is observed in the spectra of complexes VII, IX, XVI, XVIII, XXI-XXIV, and XXVII. This indicates that the tin atom has great acceptor capacity in $SnCl_4$ and organotrichlorostannanes. This capacity decreases as the number of organic substituents attached to the tin atom increases; this is manifested in the smaller shifts in the IR spectra of the complexes. On passing from organohalostannanes to their complexes, the bands of the stretching and deformation vibrations of the alkyl and phenyl groups bonded to the tin atom at 600-3000 $cm^{-1}$ do not change with respect to either frequency or intensity. The stretching vibrations of the Sn–C bond in the alkylhalostannanes are characterized by bands at 650-680 $cm^{-1}$ (rocking), 500-530 $cm^{-1}$ (asymmetrical), and 480-490 $cm^{-1}$ (symmetrical vibrations) [5]. Complexing with vinylazoles I-III does not lead to an appreciable shift in these bands. This is apparently evidence for the insensitivity of the vibrations of the Sn–C bond to the interaction under consideration. The band of the Sn–C stretching vibrations at 440-450 $cm^{-1}$ in the spectra of phenylhalostannanes is shifted to higher frequencies by 12-20 $cm^{-1}$ as a result of complexing. Investigation of the UV spectra of the organotin molecules provides evidence that the $Sn-C_{ar}$ bond has partial double bond character [6]. The donor–acceptor $N \rightarrow Sn$ interaction in the presence of the ionizing effect of the halogen atom apparently promotes an increase in the degree of double bond character of the $Sn-C_6H_5$ fragment in phenylhalostannanes during the formation of complexes by them. This also leads to the increase in the frequency of the vibrations in the IR spectra. The shift in the $\nu_{Sn-C}$ band to the long-wave region of the spectrum that is usually observed in the spectra of complexes of alkylhalostannanes is explained by the decrease in the force constant of the Sn–C bond due to the strong interaction in the $N \rightarrow Sn-Cl$ system [7].

Although the $CH_2=CH$ group forms a conjugated system [8] with the heteroring of N-vinylazoles, its frequency in the spectra of their complexes nevertheless remains unchanged as compared with the spectra of the ligands themselves. To ascertain the possibility of transfer of the effect of the $N \rightarrow Sn$ coordination interaction to the vinyl group, we measured the integral intensities of the absorption band at 1648 $cm^{-1}$ by the method of logarithmic transparency [9] (Table 3). The A values were calculated with allowance for the composition of the complex per single vinyl group. Dioxane, dimethyl sulfoxide (DMSO), and – in parallel manner for the liquid complexes of mono- and dichloroorganostannanes – carbon tetrachloride were used

TABLE 3. Integral Intensities of the $\nu_{C=C}$ Band of the $CH_2 = CH$ Group (1648 $cm^{-1}$) in the IR Spectra of N-Vinylazoles and Their Complexes with Organohalostannanes (dioxane solutions)

| Compound | $A \cdot 10^{-4} mole^{-1} \cdot l \cdot cm^{-2}$ | Compound | $A \cdot 10^{-4} mole^{-1} \cdot l \cdot cm^{-2}$ |
|---|---|---|---|
| I | 1,20 | II | 1,11 |
| V | 1,08 | XIX | 0,86 |
| VII | 1,21 | XXII | 0,89 |
| IX | 0,93 | III | 0,67 |
| XIII | 2,13 | XXV | 0,68 |
| XVI | 0,96 | XXVI | 1,36 |

TABLE 4. Absorption Bands in the UV Spectra of N-Vinylazoles and Their Complexes with Organohalostannanes[a]

| Compound | $\lambda_{max}$, nm (ε) | Compound | $\lambda_{max}$, nm (ε) |
|---|---|---|---|
| I | 230 (12350) | II | 226 (9500), 232 (9750), 250 (6200)<br>280 (3050), 288 (2550) |
| V | 230 (14850) | XIX | 226 (30700), 236 (40500),<br>282 (11500), 290 (10000) |
| VI | 230 (14550) | XXI | 228 (32200), 235 (32300),<br>281 (9000), 291 (7650) |
| VII | 226 (24800) | XXII | 223 (59000), 282 (13300),<br>291 (11800) |
| IX | 218 (26500) | XXIII | 220 (42300), 281 (10500),<br>291 (8000) |
| X | 230 (17700) | | |
| XIII | 216 (37200) | III | 220 (15000), 262 (6600),<br>270 (6350) |
| XV | 218 (38600) | XXVI | 215 (41900), 262 (12300),<br>270 (11400) |
| XVI | 216 (39800) | | |

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[a] With an SFD-2 spectrophotometer; the spectra were recorded from ethanol solutions.

as solvents for vinylazoles I-III and their complexes. A change in the solvent does not cause substantial changes in the intensities of the bands in either the spectra of the ligands or in the spectra of the complexes. Comparison of the intensity of the absorption band of the vinyl group of vinylazoles I-III and their complexes shows that in most cases the change in this value is within the limits of experimental error (~20%). An increase in the integral intensity of the bands occurs only in complexes of vinylazoles I and III with phenylhalostannanes (XIII, XXVI).

The λ band at 230 nm (ε 12,350) in the electronic absorption spectrum of vinylimidazole I is associated with $\pi \rightarrow \pi^*$ electron transitions (Table 4). The value of its maximum is retained in complexes of imidazole I with trialkylhalostannanes (V, VI, X) with a small increase in the extinction coefficient. An increase in the number of chlorine atoms in the organohalostannane molecules (VII, IX) leads to a hypsochromic shift in $\lambda_{max}$ and a further increase in ε. The maximum shifts (by 12-14 nm) are observed in the spectra of complexes of vinylimidazole I with phenylhalostannanes (XIII, XV, XVI) and ethyltrichlorostannane (IX).

The greatest effect in the UV spectra of complexes of vinylazoles II and III is also detected in the case of phenylhalostannanes (XXII, XXIII, and XXVI) – a hypsochromic shift of $\lambda_{max}$ and an increase in the ε values of the bands. Only an increase in the ε values at constant $\lambda_{max}$ occurs in the spectra of complexes of alkylhalostannanes. The maxima of the long-wave absorption bands are not shifted as a result of complexing, but an increase in their extinction coefficients is observed.

Thus complexing of N-vinylazoles with organohalostannanes is manifested in a change in the vibrational frequencies in the IR spectra that, in analogy with the preceding investigations, makes it possible to conclude that coordination occurs through the "pyridine" nitrogen atom of the ligand and that there is a free vinyl group in the complex. The increase in the integral intensity of the absorption band of the stretching vibrations of the $CH_2 = CH$ group in the spectra of the complexes as compared with the ligands is evidence for the effect of the coordinated nitrogen atom on the vinyl group through the electron system of the heteroring. However, the changes in the integral intensity do not make it possible to arrive at a definite conclusion regarding the mechanism of this transfer. A hypsochromic shift of the short-wave band of the ligands and an increase in the absorption coefficient of the bands of the $\pi \rightarrow \pi^*$ electron transitions are observed in the electronic absorption spectra of the complexes. The greatest effects are manifested in the complexes of

N-vinylazoles with alkyltrichloro- and phenylhalostannanes; that is in conformity with their increased electron-acceptor capacity. The formation of two types of complexes of 1 : 1 and 2 : 1 composition by N-vinylimidazole I is associated with the realization of tin coordination numbers of five and six. Complexes of I with triorganohalostannanes, which have the electron-acceptor capacity that is typical in the $R_{4-n}SnX_n$ series ($n = 1-4$), have the 1 : 1 composition. Complexes of vinylazoles I-III with a tin coordination number of six most likely have an octahedral structure. The change in the composition of the complexes in the investigated spectral range (400-3600 $cm^{-1}$) does not cause shifts in the vibrational frequencies. The analyses of the frequencies of the stretching vibrations of the Sn–Cl and Sn–N bonds that make it possible to identify the geometrical structures of the complexes will be the task of our subsequent studies.

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