PARAMAGNETIC SHIFTS IN COMPLEXES OF N-VINYLIMIDAZOLE WITH MANGANESE, IRON, COBALT, NICKEL, AND COPPER CHLORIDES

V. K. Voronov, Yu. N. Ivlev,
E. S. Domnina, and G. G. Skvortsova

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The observed paramagnetic shifts and broadenings of the resonance lines in the PMR spectrum of N-vinylimidazole upon the addition of its complexes with manganese, iron, cobalt, nickel, and copper chlorides are compared.

It is known that the effect of an uncompensated electron spin of a paramagnetic complex leads to a shift in the resonance lines in the PMR spectra [1]. Since these shifts are determined in particular by the probability of the residence of the unpaired electron at the site of the resonating nucleus, with the appropriate approach they can be the source of information regarding the character of the electron-nuclear interaction. On the basis of this, the hyperfine interaction parameters in radicals, paramagnetic complexes, and diamagnetic molecules have been compared [2].

Continuing our study of the electron-nuclear interaction in five-membered nitrogen-containing rings [3,4], we compared the observed paramagnetic shifts (δ) of the resonance lines in the PMR spectrum of N-vinylimidazole (Lig) upon the addition of paramagnetic complexes of the $MeCl_2 \cdot 4Lig$ type to the test sample. The chlorides of Mn(II), Fe(III), Co(II), Ni(II), and Cu(II) were taken as electron acceptors. The synthesis of the complexes was reported in [5]. The method used to analyze the PMR spectra in the presence of paramagnetic additives was described in [6, 7]. The δ values are presented in Table 1 together with the concentration of the complexing salt and the sample temperature at which the δ values were determined.

TABLE 1. Paramagnetic Shifts in the PMR Spectrum of N-Vinylimidazole

Complexing salt	Paramagnetic shifts, δ, Hz*					Sample temp., °C	Complexing salt conc. · 10^3
	H-2	H-4	H-5	H-α	H-β-(trans)		
$MnCl_2$	3	21	16	7	3	80	8
$FeCl_3$	11	18	14	2	1	69	10
$CoCl_2$	30	44	29	4	1	62	36
$NiCl_2$	22	26	21	~0	~0	63	11
$CuCl_2$	8	11	6	~0	~0	67	6

*The signal of the β (cis)-vinyl proton is covered by the signal of nitromethane.

It follows from Table 1 that the paramagnetic shifts of the signals of the ring protons of Lig depend on the nature of the coordinating ion. This also explains the different broadening (Δ) of the resonance lines (Fig. 1), which is determined by the following functional dependence: $\Delta = \Delta(T_{2m}; w; \tau_m)$, where T_{2m} is the nuclear relaxation time in the paramagnetic complex, w is the shift of the line in the complex ($\delta = pw$,

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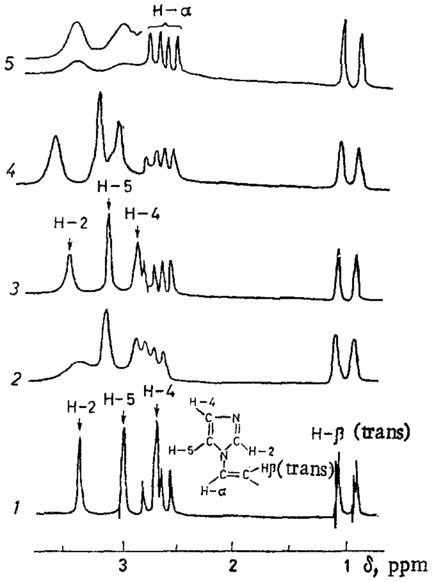

Fig. 1. PMR spectra of N-vinylimidazole without additives and with added paramagnetic complexes:* 1) without additives; 2) with $MnCl_2 \cdot 4Lig$; 3) with $FeCl_3 \cdot 4Lig$; 4) with $CoCl_2 \cdot 4Lig$; 5) with $CuCl_2 \cdot 4Lig$.

where p is the mole fraction of complex), and τ_m is the residence time of Lig in the coordination sphere of the complex [8]. Different Δ values will correspond to different T_{2m} and w values, which are determined by the nature of the complex for a given τ_m (which is temperature dependent).

The 4-H proton has the largest δ value in the investigated spectra. It is remarkable that it undergoes electrophilic substitution more readily than the other ring protons [9]. The δ value of the vinyl protons is substantially lower than δ of the ring protons. An exception to this is the spectrum of Lig with added $MnCl_2 \cdot 4Lig$, in which $\delta_{2\text{-}H}$ is equal to $\delta_{\beta\text{-}H(trans)}$ and is lower than $\delta_{\alpha\text{-}H}$ by a factor of 2.5. If one takes the conjugation of the double bond with the pyrrole nitrogen into account [10], on the basis of the relative $\delta_{ring\,H}$, $\delta_{\alpha\text{-}H}$, and $\delta_{\beta\text{-}H}$ values it can be concluded that delocalization of the unpaired spin density over the π system of the imidazole ring becomes appreciable when Lig interacts with $MnCl_2$.

EXPERIMENTAL

The PMR spectra were recorded with a JNM-4H-100 spectrometer. Nitromethane was used as the solvent and internal standard. The temperature of the samples containing paramagnetic additives was varied from 10 to 95°.

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*The PMR spectrum of Lig with added $NiCl_2 \cdot 4Lig$ is described in [7].