NMR spectra of paramagnetic complexes of 1-vinylimidazole with iron group metals

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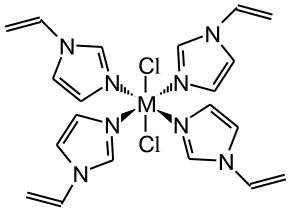
The high-resolution ^1H and ^{13}C NMR spectra of 1-vinylimidazole complexes with iron group metals were recorded. The contact coupling in these systems was established in the ^1H and ^{13}C NMR spectra. The applicability of the NMR spectra transformed by long-range hyperfine coupling for elucidating the molecular structure of the ligand was shown.

Key words: NMR spectroscopy, paramagnetic complexes, hyperfine coupling, 1-vinylimidazole.

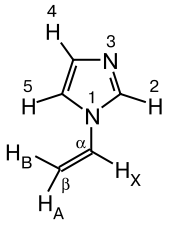
Nuclear magnetic resonance studies of paramagnetic complexes provide valuable information on the molecular structure. The electron—nuclear or hyperfine coupling (HFC) between lone electrons and resonating nuclei results in characteristic shifts and signal broadening, which serve as sources of information on the electronic and spatial structures of ligands in paramagnetic complexes.[1,2] By now, the mechanisms of the HFC have been studied for a rather narrow range of molecules.

In this study we recorded for the first time the high-resolution ^1H and ^{13}C NMR spectra of paramagnetic metal complexes of 1-vinylimidazole with Ni, Co, Cu and a diamagnetic complex with Zn.



1a—d

M = Zn (**a**), Co (**b**), Ni (**c**), Cu (**d**)



Results and Discussion

For the whole series of compounds, the ^1H NMR signals from the 1-vinyl substituent and the imidazole ring are separated into two groups, which is clearly illustrated by the spectrum of complex **1b**. At room temperature, the spectrum exhibits rather narrow signals for the vinyl-group protons (up to 50 Hz) with the paramagnetic shifts δ 7.8, 9.6, and 11.2 and three broadened signals of the imidazole ring (Δ = 250—400 Hz) at δ 33.6, 35.8, and 41.3 (Fig. 1, *a*). As the temperature decreases to 213 K, the signals of the vinyl-group protons shift downfield and are broadened to Δ ~130 Hz. The signals shift in different ways, so that at some temperature, two signals overlap. The resonance line for the H(5) proton is broadened to ~700 Hz, which is accompanied by a slight downfield shift (δ 38.7), whereas the signals of the other two protons, being broadened to ~500 Hz, substantially change their positions (Fig. 1, *b*).

The ^1H NMR spectrum of complex **1c** (Fig. 1, *c*, *d*) is similar to that of complex **1b** except that the paramagnetic shift of the signal for H_X decreases with lowering the temperature (Curie law does not hold). In the ^1H NMR spectrum of **1d**, the signals of the vinyl protons are markedly broadened even at room temperature (Δ value for the H_A signal is ~250 Hz and that for H_B and H_X is ~150 Hz). The signals of the imidazole protons merge to form a single, very broad band centered at δ 30 (Fig. 1, *e*). On cooling the sample, the width of the H_A proton signal increases to 1500 Hz, while the signal shifts downfield; the H_B and H_X signals are broadened to ~500 Hz, but the their paramagnetic shifts change in the opposite directions. The signals for the ring protons are broadened even at ~243 K to such an extent that become undetectable.

As expected, the ^{13}C NMR spectrum of complex **1b** contains five signals at room temperature. The C_α atom of the vinyl group is represented by a doublet at δ 171.2 due to the spin—spin coupling with the H_X proton

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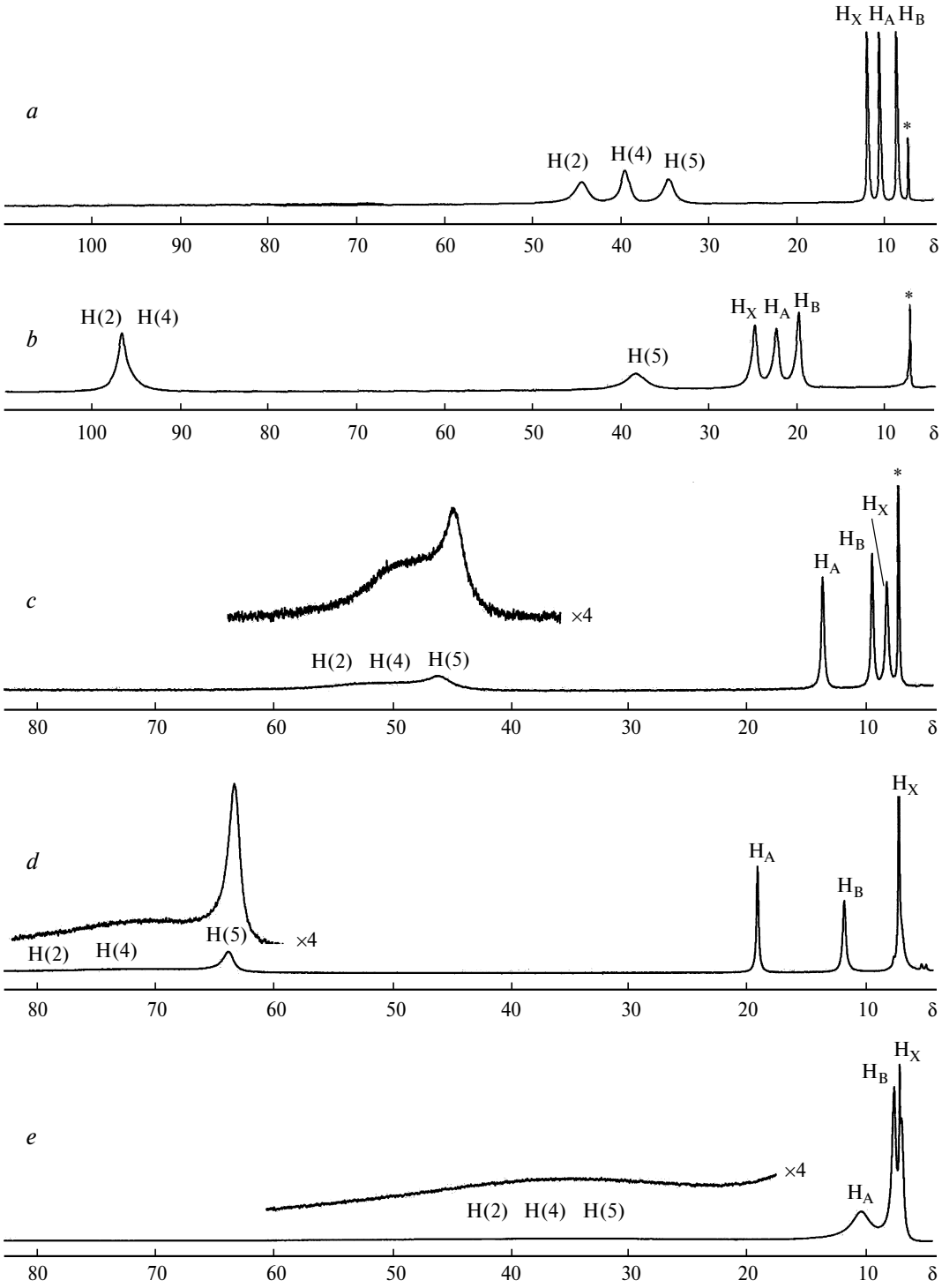


Fig. 1. ^{1}H NMR spectra of complexes **1b** (*a*, *b*), **1c** (*c*, *d*), and **1d** (*e*) in $CDCl_3$ at 300 (*a*, *c*, *e*) and 223 K (*b*, *d*) (signals of the residual protons of solvent are asterisked).

(^1J = 179 Hz), and the C_β atom is responsible for a triplet due to the spin—spin coupling with the H_A and H_B protons (δ 125.0, ^1J = 161 Hz). The C atoms of the imidazole ring are responsible for three highly broadened signals at δ 308, 388, and 497 (Fig. 2). The low-field signal of C(2) with Δ ~1200 Hz proved to be the broadest one. The ^{13}C NMR spectrum of complex **1c** shows only the signals for the C_α and C_β atoms of the vinyl group at δ 196.0 and 120.3, respectively. No signals from the C(2), C(4), and C(5) atoms were found in the ^{13}C NMR spectrum of

Table 1. ^{1}H and ^{13}C NMR spectra of complexes **1a—d** ($CDCl_3$, $T = 298$ K)

Compound	δ_H						δ_C				
	H_A	H_B	H_X	H(2)	H(4)	H(5)	C_α	C_β	C(2)	C(4)	C(5)
1a	5.13	5.48	6.99	8.25	7.26	7.29	128.8	105.8	137.2	128.2	117.1
1b	9.34	7.56	11.0	40.2	33.7	34.6	171.2	125.0	497	388	308
1c	12.8	9.1	8.31	45.0	45.0	42.3	196.0	120.3	—	—	—
1d	10.0	7.0	7.60	30.0	30.0	30.0	—	—	—	—	—

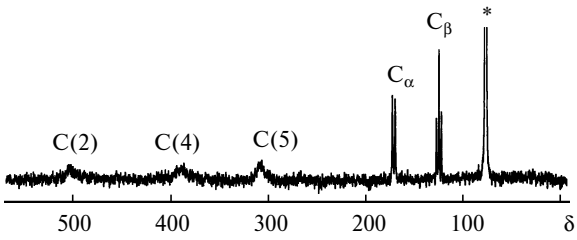


Fig. 2. ^{13}C NMR spectrum of complex **1b** in $CDCl_3$ at 298 K (signal from solvent is asterisked).

compound **1c**, apparently, due to substantial paramagnetic broadening. For the same reason, no signals from the C atoms were detected in the ^{13}C NMR spectrum of complex **1d**. This can be explained in the following way. According to the theory, the HFC pattern in the NMR spectra depends, in particular, on both the relaxation time of the electron spin and the HFC constant A (or the contact shift). According to published data, the paramagnetic cobalt ion has a much shorter electron relaxation time (compared to nickel ions and, the more so, copper ions), *i.e.*, the NMR spectra of this ion should, in principle, be most accessible for recording.

The ^{1}H and ^{13}C NMR spectra of complexes **1a—d** in $CDCl_3$ at 298 K are presented in Table 1.

The paramagnetic shifts found experimentally were used to calculate the HFC constants A for the nuclei (Table 2). The A values were found from the equation[3]

$$A = \{33.89\delta_p T/[S(S+1)]\} \cdot 10^{-6},$$

where δ_p is the paramagnetic shift; T is the sample temperature/K; S is the total spin of the paramagnetic complex.

According to known data,[4,5] the ion in complexes **1a—d** has an octahedral environment. In terms of the spectroscopic series, 1-vinylimidazole should be classified as a weak-field ligand.[6] Therefore, the calculations were carried out for $S = 3/2$.

Analysis of the calculated HFC constants A and the behavior of the dependences $\delta_p = f(T)$ (Fig. 3) led to the following conclusions. The contact HFC in the paramagnetic complexes in question is mainly transmitted along

Table 2. HFC constants A ($T = 298$ K)

Compound	$A \cdot 10^2$/Oe					
	H(2)	H(4)	H(5)	H_X	H_A	H_B
1b	8.7	7.2	7.4	1.1	1.1	0.56
1c	10.0	10.0	9.5	0.36	2.1	0.98
1d	6.0	6.0	6.0	0.16	1.3	0.41

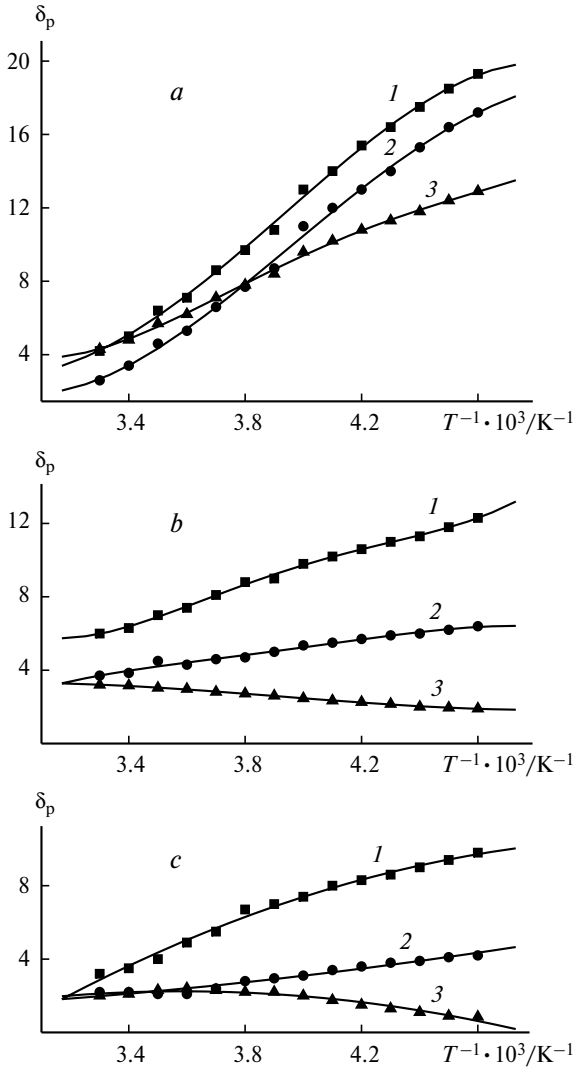
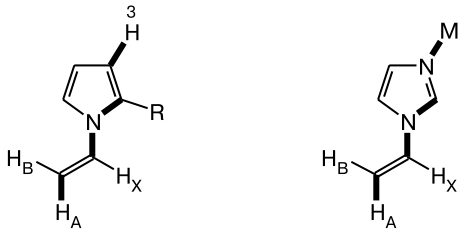


Fig. 3. Dependence $\delta_p(T)$ for the H_A (*1*), H_B (*2*), and H_X (*3*) protons of the vinyl group in complexes **1b** (*a*), **1c** (*b*), and **1d** (*c*).



a *b*

Fig. 4. Experimental long-range spin-spin coupling constants in substituted pyrroles $^6J_{H(3),H_A} = 0.4$ Hz (*a*) and W-shaped fragment ensuring efficient delocalization of the unpaired spin (*b*).

the σ-bonds of the 1-vinylimidazole molecule. The rather high HFC constants for the vinyl group are due to the involvement of the unpaired electron spin density into the π-system of the vinyl group. This is also indicated by relatively great shifts observed for the C_α and C_β atoms. Of most interest is the fact that the paramagnetic shifts of H_A are greater than the shifts of the H_B and H_X protons. The higher sensitivity of the position of the H_A signal is due to the transfer of spin density along a zigzag- or W-shaped fragment. This accounts for the long-range spin—spin coupling through six bonds between the H(3) and H_A protons in substituted 1-vinylpyrroles[7] (Fig. 4). Thus, the HFC through more than three chemical bonds obeys the same rule as the long-range spin—spin coupling in diamagnetic molecules. This feature can be used to elucidate the structures of ligands in paramagnetic complexes.

Experimental

Complexes **1a—d** were prepared by previously described procedures.[8] NMR spectra were recorded on a Bruker DPX-250 spectrometer in $CDCl_3$ using a capillary with HMDS placed in the NMR tube as an external standard. The temperature measurements were carried out using a standard BVT3300 block with the temperature being maintained to an accuracy of ±0.5 °C. The signals from the imidazole ring atoms were assigned by using paramagnetic agents and recording the spectrum with excess ligands in the sample.[9] The ^{13}C NMR spectra were recorded by a standard procedure, the relaxation delay between the pulses was ~10 ms, and the number of scans was up to 400000. For vinyl group protons, the assignment was done using 2D heteronuclear $^1H—^{13}C$ HSQC correlation experiments[10] optimized to the direct $^1J_{C,H} = 160$ Hz constant. The recording of the 2D HSQC spectra provided a reliable assignment of the H_X proton signals based on the cross-peak at the C_α resonance frequency and the H_A and H_B proton signals having cross-peaks with the C_β resonance signal. No $^1H—^{13}C$ heteronuclear correlations were detected for the imidazole ring due to rather broad signals. The paramagnetic shifts were measured relative to the ^1H and ^{13}C chemical shifts of diamagnetic complex **1a**.

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References

1. V. K. Voronov, *The Method of Paramagnetic Agents in NMR Spectroscopy*, Nauka, Novosibirsk, 1989, 168 pp. (in Russian).
2. J. Bertini and C. Luchinat, *Coord. Chem. Rev.*, 1996, **150**, 1.
3. V. K. Voronov, T. E. Moskovskaya, V. I. Glukhikh, A. I. Rezvukhin, E. S. Domnina, and G. G. Skvortsova, *Koord. Khim.*, 1979, **5**, 218 [*Sov. J. Coord. Chem.*, 1979, **5** (Engl. Transl.)].
4. V. K. Voronov, V. A. Shagun, V. V. Keiko, E. S. Domnina, and G. G. Skvortsova, *Zhurn. Struktur. Khim.*, 1980, **21**, 71 [*J. Struct. Chem. (USSR)*, 1980, **21** (Engl. Transl.)].
5. A. A. Kashaev, E. A. Zel´bst, M. P. Demidov, Yu. L. Frolov, N. N. Chipanina, E. S. Domnina, and G. G. Skvortsova, *Koord. Khim.*, 1978, **4**, 785 [*Sov. J. Coord. Chem.*, 1978, **4** (Engl. Transl.)].
6. A. D. Garnovskii, A. P. Sadimenko, O. A. Osipov, and G. V. Tsintsadze, *Zhestko-myagkie vzaimodeistviya v koordinatsionnoi khimii* [*Soft—Hard Interactions in the Coordination Chemistry*], Izd. Rostov. Univ, Rostov, 1986, 272 pp. (in Russian).
7. I. A. Ushakov, A. V. Afonin, V. K. Voronov, Z. V. Stepanova, L. N. Sobenina, A. I. Mikhaleva, and B. A. Trofimov, *Zhurn. Organ. Khim.*, 2002, **38**, 1836 [*Russ. J. Org. Chem.*, 2002, **38** (Engl. Transl.)].
8. G. G. Skvortsova, E. S. Domnina, Yu. I. Ivlev, N. I. Chipanina, V. I. Skorobogatova, and Yu. A. Myachin, *Zhurn. Obshch. Khim.*, 1972, **42**, 596 [*J. Gen. Chem. USSR*, 1972, **42** (Engl. Transl.)].
9. E. E. Zaev, V. K. Voronov, M. S. Shvartsberg, S. F. Vasilevsky, Yu. N. Molin, and I. L. Kotjrevsky, *Tetrahedron Lett.*, 1968, **5**, 617.
10. G. Bodenhausen and D. J. Ruben, *Chem. Phys. Lett.*, 1980, **69**, 185.

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