Russian Chemical Reviews **79** (10) 835 – 847 (2010) © 2010 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2010v079n10ABEH004157

High-resolution nuclear magnetic resonance in paramagnetic complexes

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Abstract. The features of the phenomenon of nuclear magnetic resonance in paramagnetic systems are considered. Specific character of detection of high-resoluton NMR spectra modified by hyperfine coupling is analyzed. Examples of the use of specific features of nuclear magnetic resonance in paramagnetic complexes in studies of the structure and dynamics of multielectron systems are given. The need for further experimental investigations of the nature of paramagnetic shifts (especially, contact ones) of NMR signals not only of ^{1}H and ^{13}C, but also of other nuclei is emphasized. The bibliography includes 65 references.

I. Introduction

Shortly after discovery of the nuclear magnetic resonance (NMR) in condensed phases, it has been realized that this phenomenon would form the basis of a powerful method of exploration of structures and properties of substances. Numerous publications describing the use of NMR in various fields confirmed this prospect. High efficiency of the application of NMR for the solution of diverse problems concerned with the structure and behaviour of multielectron (molecular) systems is determined by both the progress in the elaboration of technical devices used in NMR spectroscopy and advances in the theoretical study of the phenomenon itself. The latter is confirmed, for example, by development of studies based on the analysis of the NMR spectra transformed by electron – nuclear or hyperfine interaction between the non-compensated electron spin (unpaired electrons) and resonating nuclei. Typically, these studies are carried out with the compounds the specifics of which is determined by electrons on the d or f orbitals. In particular, it was shown that the study of NMR in paramagnetic complexes offers valuable insight into the structure of molecules.

Despite considerable progress in studies on the features of NMR in paramagnetic compounds, there are several unsolved issues. To a large extent, this is due to the fact that investigations into the hyperfine coupling (HFC) by NMR are still scarce because of a limited number of paramagnetic systems where we can study the electron – nuclear interactions on the basis of the high-resolution NMR spectra using the existing methods. Therefore, it can be argued that the entire classes of paramagnetic complexes containing various heteroatomic compounds as ligands, are 'waiting for their turn' for the study of the nature of the intrinsic HFC.

In the present review, specific examples show the possibility of using specific phenomenon of NMR in paramagnetic systems for studying the structure and dynamics of molecular systems. Preference is given to the paramagnetic complexes of elements of the first transition group. It should be emphasized that the success of using specific features of NMR in the paramagnetic systems for solving problems related to the structure and dynamics of molecules is largely determined by the knowledge of the mechanisms of HFC and relaxation processes in the analyzed molecular system. No review articles that summarize the material in this area have been published over the past 20 years at least.

II. Nuclear magnetic resonance in paramagnetic systems

The features of NMR phenomenon in paramagnetic systems could be clarified as follows (see Refs 1 – 7 and references cited therein). If a resonating nucleus (*e.g.* a proton) is part of a paramagnetic molecule, *i.e.*, a molecule possessing a non-compensated electron spin moment, it is subjected to additional magnetic influence of the electron spin. This results in broadening and paramagnetic shifts (contact and pseudocontact shifts) of its resonance lines in comparison with the widths and positions of the lines in the NMR spectra of non-coordinated molecules.

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Received 23 April 2010
Uspekhi Khimii **79** (10) 915 – 928 (2010); translated by S E Boganov

The contact shift is observed if the probability of the residence of the unpaired electron in the site of the resonating nucleus differs from zero. This shift (ω_c) is proportional to the proton–electron interaction constant (A) and in the case of slight spin–orbit interactions, it is defined by the expression [1, 3]

$$\omega_c = -A \frac{\gamma_e}{\gamma_n} \frac{g\beta S(S+1)}{3kT}, \quad (1)$$

where γ_e and γ_n are the gyromagnetic ratios for the electron and the resonating nucleus, g is the so called g-factor of the paramagnetic compound, β is the Bohr magneton, S is the spin of the complex, k is the Boltzmann constant and T is the absolute temperature.

The value A (which can be both positive and negative) is determined by the magnetic moment of the unpaired electron of the paramagnetic species and orientation of the unpaired electron on the given nucleus. According to the Fermi formula,

$$A = \frac{4}{3}\pi g\beta g_n\beta_n\rho(N), \quad (2)$$

where g_n is the nuclear g-factor, β_n is the nuclear magneton, $\rho(N)$ is the density of the unpaired electron spin on the resonating nucleus. Transition of the unpaired electron from the coordinating ion to ligands and 'distribution' along the ligand molecule (*i.e.*, the delocalization mechanism) are determined by the specifics of the electronic structure of the paramagnetic complex.

The pseudocontact shift is due to dipole–dipole hyperfine coupling between the magnetic moments of the unpaired electron and the resonating nucleus. In an implicit form, this shift is given by the expression [1–3]

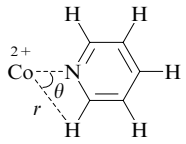
$$\omega_p = \frac{\text{const}}{T} f(g)f(\phi, r). \quad (3)$$

Here multipliers $f(g)$ and $f(\phi, r)$ (ϕ and r are polar coordinates) are determined by the magnetic anisotropy and geometry of the complex, respectively. The explicit form of these functional dependences and therefore the magnitude and sign of ω_p depend on the type of symmetry of the paramagnetic complex as well as on the nature of the coordinating ion.

For a paramagnetic ion moving at random in solution, the electric field around which has an axial symmetry, the pseudocontact shift is given by the McConnel–Robertson formula (here we consider the paramagnetic complexes of elements of the iron subgroup)[1, 3]

$$\omega_p = \frac{\beta^2(S+1)\left(3\cos^2\theta - 1\right)\left(g_\parallel - g_\perp\right)\left(g_\parallel + 2g_\perp\right)}{27kTr^3}, \quad (4)$$

where θ is the angle between the axis symmetry and the radius-vector pointing away from the centre of coordination of the ion to the proton; r is the distance between the paramagnetic ion and the resonating nucleus (radius-vector); $g_\parallel$ and $g_\perp$ are the electronic g-factors in directions parallel and perpendicular to the symmetry axis. A fragment of a paramagnetic cobalt complex is shown below where parameters r and θ from the expression (4) are marked.



It can be seen that the pseudocontact shifts characterize spatial structure of the paramagnetic molecule, therefore they are used in solving various structural problems.

Relaxation time (T_M) of the resonating nucleus in coordination sphere of the paramagnetic complex (and therefore the width of the resonance signal (Δ) in the NMR spectrum) can be set with the following expression:[1, 3, 4]

$$\frac{1}{T_M} = \Delta = Br^{-6} + C(\delta_c)^2, \quad (5)$$

where B and C are constants for the sample at the given temperature, δ_c is the observed contact shift of the resonance line.

For a complex in which the contact interaction is not manifested the relaxation time of the nucleus is determined by the distance from the coordinating ion to the resonating nucleus of the ligand molecule.

$$\frac{1}{T_M} = Br^{-6}. \quad (6)$$

Important information concerning structures of the multi-electron systems can be obtained when examining the phenomenon of NMR in paramagnetic compounds. This fact becomes evident if we consider that the expressions (1)–(6) defining parameters of the NMR spectra of paramagnetic systems are explicitly linked to electronic and spatial structures of molecules. The paramagnetic shifts are much larger than the chemical shifts in the spectra of diamagnetic compounds and besides have the characteristic temperature dependence. Different in nature relaxation effects may occur in paramagnetic substances, which significantly extends the potential of NMR as a research method. In particular, from temperature dependences of the paramagnetic shifts and the signal widths one can obtain the thermodynamic parameters of complex formation in solutions, address stereochemistry of complexes and mechanisms of ligand exchange. Some examples are given below † that illustrate the potential of the use of the NMR spectra modified by the electron–nuclear interaction for the investigation of structures of molecules.

First of all, it is necessary to illustrate the diversity of transformations of the NMR spectra under the influence of the electron–nuclear and hyperfine interactions. Figure 1 demonstrates the ^{1}H NMR spectra of 1-vinylimidazole (VIm) complexes with $CoCl_2$, $NiCl_2$ and $CuCl_2$ (Ref. 8). The spectra of a diamagnetic analogue of these complexes, *viz.*, $ZnCl_2 \cdot 4\,VIm$, and of 1-vinylimidazole are also shown for comparison. It is seen that the two upper spectra (the spectra of the diamagnetic samples) are very different from the others (the spectra of the paramagnetic compounds).

Yet another observation concerns the spectra of the cobalt, nickel and copper complexes, which also have their

† The exampls are taken from experiments carried out by the authors of this review. Other studies (rather few in number) in this research field are cited in the list of references to this review.

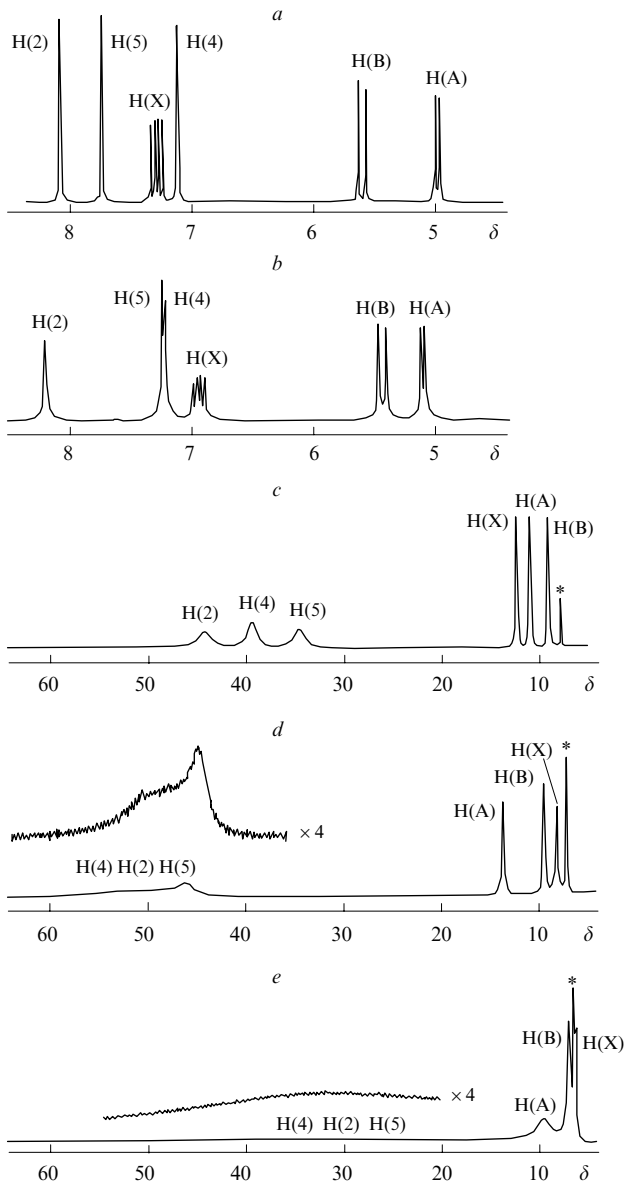
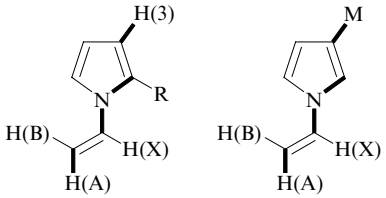


Figure 1. The ^{1}H NMR spectra ($CDCl_3$) of 1-vinylimidazole (*a*), the diamagnetic complex VIm with $ZnCl_2$ (*b*), the paramagnetic complexes of VIm with $CoCl_2$ (*c*), $NiCl_2$ (*d*), $CuCl_2$ (*e*).
Here and in other figures, signals of solvent are marked by an asterisk.

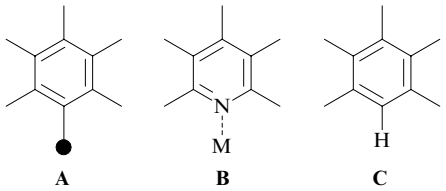
own characteristic features. In fact, in the spectrum of the cobalt complex there are signals for all six protons of VIm. As for the spectra of the nickel and especially copper complexes, the individual signals in them correspond to the protons of the vinyl group. The signals for the protons [H(2), H(4), H(5)] of the imidazole ring overlap in poorly resolved (for the nickel complex) or unresolved (for the copper complex) very wide signal. This is due to the fact that the electron spin relaxation times in these paramagnetic complexes significantly differ. The shortest relaxation time is in the cobalt complex (about 10^{-12} s), the longer one is in the copper complex (about 10^{-9} s). The smaller relaxation time the shorter the contact of the resonating nuclei with the non-compensated electron spin, and, of course, the changes in the NMR spectra are less pronounced, which is observed in the spectra under discussion. It should be added that, of the elements of the iron subgroup, it is the paramagnetic Co^{2+} ion that can be used as a shift reagent (the notion of 'shift reagents' will be explained below).

Yet another characteristic feature of the ^{1}H NMR spectra of the complexes under discussion is larger paramagnetic shift of a signal for the proton H(A) relative to the signals for two other protons H(B) and H(X) of the vinyl group. It is well seen in Figure 1 *e*. When searching for an explanation of this experimental fact, we paid attention to the long-range spin–spin coupling between protons H(3) and H(A) through six bonds in substituted 1-vinylpyrroles.[9]



It turned out that the increased sensitivity of the signal position for H(A) is explained by transfer of the electron spin density along the zigzag, *i.e.*, W-shaped, fragment. That is why a long-range spin–spin coupling takes place in 1-vinylazoles. Thus, the transmission of HFC through more than three chemical bonds obeys the same rule as the long-range spin–spin coupling in diamagnetic molecules. Naturally, this pattern can be used to determine the structures of ligands in paramagnetic complexes.

Apparently, the authors of the study [10] were among the first who had suggested a physically substantiated model of delocalization of the unpaired electron spin density in paramagnetic complexes. Their method was based on a comparison of hyperfine coupling constants in radical **A**, in the fragment of the paramagnetic complex **B** and the spin–spin coupling constant (J_{HH}) in the diamagnetic molecule **C**.



The mechanisms of the following perturbation effects were discussed: 1) effect of a given H nucleus on other nuclei through a carbon atom in a diamagnetic molecule; 2) influence of the unpaired electron at the same carbon atom; 3) effect of the unpaired electron spin density displaced from the coordinating ion M to a nitrogen atom. It was shown that the perturbation effect of the unpaired electron on ligands in the paramagnetic complex qualitatively conforms with the emerging effects of the unpaired electron spin in the radical and the nuclear spin in the diamagnetic molecule isostructural to the radical and the ligand. The method proposed in this study [10] was used to investigate the mechanism of HFC in complexes of azoles with elements of the first transition group.[11] The observed paramagnetic shifts in the spectra of paramagnetic complexes of 1-methylpyrazole and 1-ethylimidazole were compared with the spin–spin coupling constants in pyrrole, which is isostructural to pyrazole and imidazole.

It has been noted above that the shifts induced by HFC have characteristic temperature dependences. Figure 2 shows spectra of the cobalt and nickel complexes with 1-vinylimidazole recorded at temperatures between 300

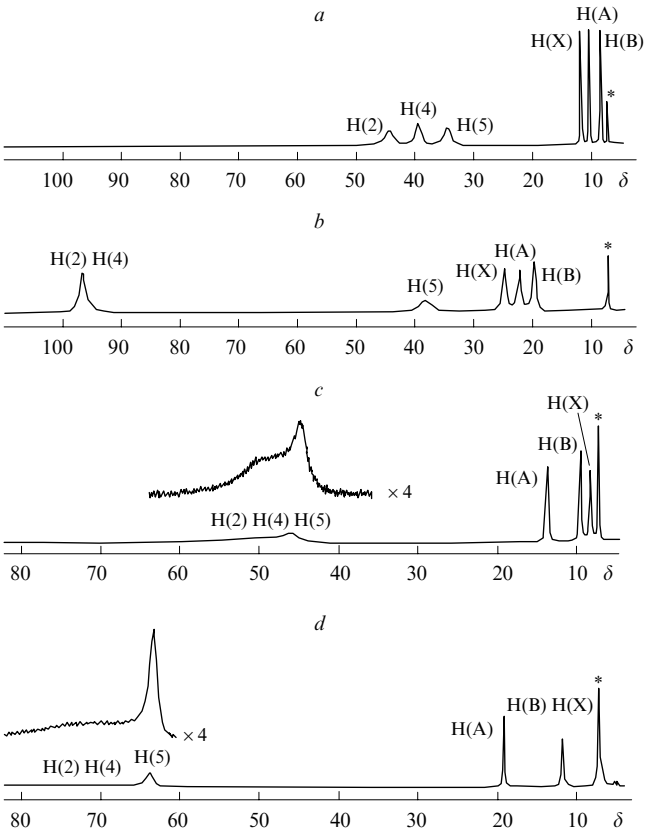


Figure 2. Temperature variations in the ^{1}H NMR spectra of the paramagnetic complexes of VIm with $CoCl_2$ (*a*, *b*) and $NiCl_2$ (*c*, *d*) at 300 (*a*, *c*) and 223 K (*b*, *d*).

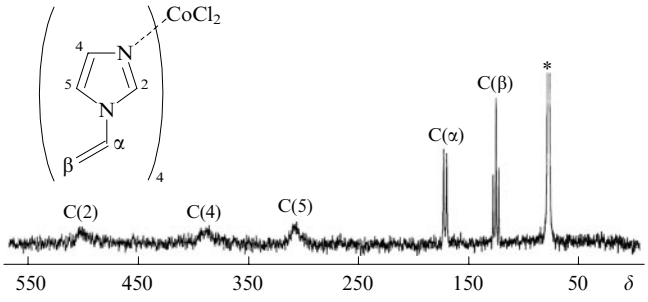


Figure 3. The ^{13}C NMR spectrum of the complex $(VIm)_4CoCl_2$ at 300 K (in $CDCl_3$).

and 223 K. As can be seen, the decrease in the temperature of the sample under study substantially affects the position and width of the resonance signals. In accordance with the theory of HFC, the paramagnetic shifts obey Curie's law. The establishment of this pattern or deviations from it (as Curie's law does not operate for some complexes) is another experimental source of information about the features of the molecular structure of the paramagnetic complex, whose NMR spectrum can be recorded.

Modern NMR spectrometers allow recording high-resolution spectra of paramagnetic systems within a broad spectral range (about 400 ppm for ^{1}H and 2000 ppm for ^{13}C). Fast workstations of such spectrometers can process large arrays of two-dimensional spectra enabling (at least, in principle) assignment of resonance signals. The use of temperature add-on device consoles allows complex dynamic studies of paramagnetic systems.

Why not all paramagnetic system (paramagnetic complexes, radicals) can be studied using high-resolution NMR? As it has already been mentioned above, HFC leads to the transformation of the NMR spectra by inducing paramagnetic shifts and broadening of the resonance signals; it is these that are the source of information on the structure of the molecular systems. But at the same time, these paramagnetic broadenings make the task of detecting NMR spectra of individual paramagnetic species problematic. This is especially true for the NMR signals of carbon, nitrogen and some other atoms making up the skeleton of the molecule. For example, broadening of the proton signals can reach hundreds and even thousands of Hertz. With respect to the signals of the carbon atoms, their broadening can be such that their detection becomes problematic. Figure 3 provides the ^{13}C NMR spectrum of the cobalt complex with 1-vinylimidazole recorded at room temperature without decoupling from protons.[8] As expected, the spectrum contains five signals. The signal for the atom C(α) of the vinyl group appears as a doublet due to the spin-spin coupling with the proton H(X), while the signal for the atom C(β) appears as a triplet owing to the spin–spin couplings with the protons H(A) and H(B). The carbon atoms of the imidazole ring give three highly broadened signals. The broadest is the low-field signal for the atom C(2). Only signals for the carbon atoms of the vinyl group [*i.e.*, C(α) and C(β)] are seen in the spectrum of the nickel complex with 1-vinylimidazole, whereas the signals for the carbon atoms of the imidazole ring cannot be detected because of their strong paramagnetic broadening. For the same reason, no signals for the carbon atoms are detected in the NMR spectrum of the copper complex.

III. A method of paramagnetic additives

The difficulties due to paramagnetic broadening can be overcome if the NMR spectra are recorded with an excess of ligands in the sample. The ligand concentration may exceed that of the paramagnetic ions several hundred times! Because of fast exchange of ligands located in the coordination sphere of the complex with the free ligand molecules, the observed spectrum becomes averaged, and it particularly retains information of HFC in the paramagnetic complex under study.[7] This methodology is based on the accounting for the influence of the exchange effects on the form of the NMR spectrum. From the theory of NMR it is known that upon fast exchange,

$$H(A) + B \rightleftharpoons H(B) + A,$$

the observed shift of the proton signal is determined by the following expression

$$\delta_H = P_A\delta_A + P_B\delta_B,$$

where P_A and P_B are mole fractions of H(A) and H(B), δ_A and δ_B represent chemical shifts of the signals for the protons surrounding A and B. In our case, this gives

$$\delta_H = P_f\delta_f + P_M\delta_M = \delta_f + (\delta_M - \delta_f)P_M = \delta_f + \omega P_M,$$

$$\delta_M - \delta_f = \omega,$$

$$P_f + P_M = 1,$$

where the subscript f relates to the free molecule and subscript M corresponds to the molecule coordinated with the paramagnetic ion.

The following explanation is appropriate here. The fundamental principles of the theory of NMR in the paramagnetic systems were developed by Bloembergen, McConnell, Solomon, Berkheim and other researchers in the 1950s–1960s.[7] But the wide-ranging application of the potential of HFC for solving various chemical problems started later, after development of a method of analysis of the NMR spectra, modified by additives of the paramagnetic complexes (the method of paramagnetic additives). Perhaps, the first investigation of this type[12] made use of the paramagnetic broadening for establishing features of intramolecular structures of heteroatomic compounds (taking 3- and 5-substituted pyrazoles as examples). Further development of the method of paramagnetic additives is documented in Refs 13–20. The pioneering studies by Hinckly,[21] Sanders and Williams[22] have also to be noted, as they stimulated numerous publications devoted to the use of the paramagnetic complexes of rare earth elements (lanthanides) with organic ligands in NMR spectroscopy. As a result, a new method was created that gives an access (at least, in principle) to structural information for molecules in the liquid phase, whose descriptiveness is often comparable with that accessible in X-ray analysis of solids.

The possibility of the use of the lanthanide complexes is related to the very short electron relaxation time for ions of rare-earth elements. Therefore, the complexation results in a minor broadening of the resonance signals, while the paramagnetic shifts are substantial. Due to this fact, such paramagnetic additives are called lanthanide shift reagents. The ^{1}H NMR spectra of a sample with and without paramagnetic additives are shown in Fig. 4.[23] Since the protons of the vinyl group bound to the nitrogen or sulfur atoms give the characteristic signals, their assignment using the technique of double resonance is straightforward. The signals for the benzene ring protons overlapping with each other, as well as the signal for H(X′) are responsible for unresolved multiplet at δ 6.87–7.65. Addition of tris(dipivaloylmethanato)europium in the sample results in a remarkable shift of signals relative their position in the spectrum recorded without the paramagnetic additive. The signals of the benzene ring protons do not overlap and therefore can be assigned, hence the whole spectrum becomes susceptible to the first-order analysis.

The most common paramagnetic additives have the following formulas: $MX_2 \cdot mR$, where M = Co, Ni; X is

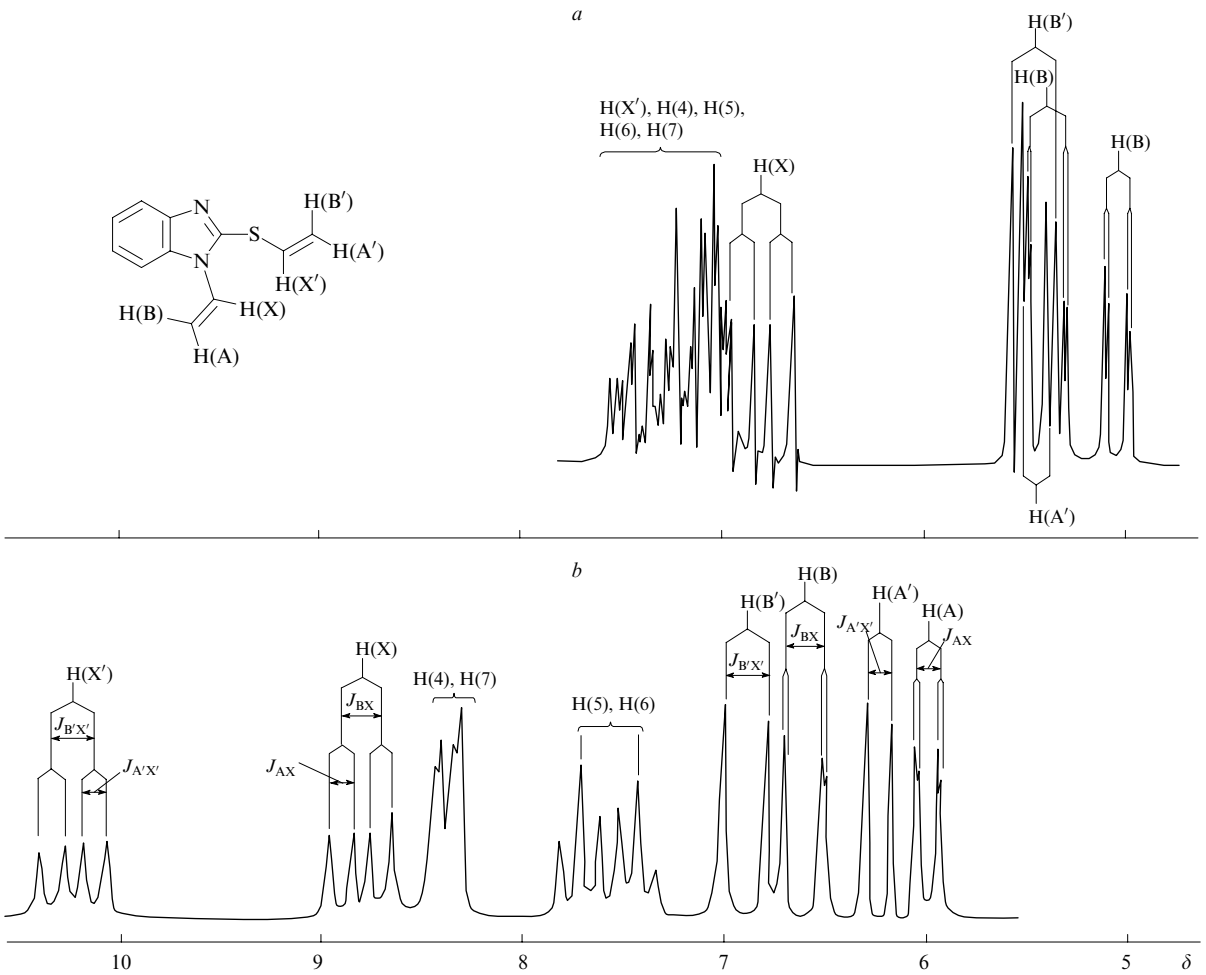
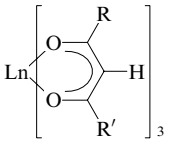
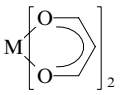


Figure 4. The ^{1}H NMR spectrum of *N*,*S*-divinyl-2-mercaptobenzimidazole without (*a*) and with addition (*b*) of tris(dipivaloylmethanato)europium $(DPM)_3Eu$.

halogen; R is the substrate molucule the spectrum of which has to be analyzed;



$R = R' = Bu^t \cdot Ln(DPM)_3$, $R = Bu^t$, $R' = C_3F_7 \cdot Ln(FOD)_3$, Ln = Eu, Yt, Pr, Cd); FOD is fluorinated β-diketone;



$M(acac)_2$

M = Co, Ni, Mn; acac is acetylacetonate.

About two thousand papers have been published to date where complexes of rare-earth elements have been employed for the analysis of the NMR spectra. These works can be divided into two groups. The first includes publications devoted to the use of lanthanide shift reagents just to simplify the NMR spectra, *i.e.*, the reagents play a 'passive' role. It has been found to be useful to utilize the lanthanide shift reagents together with partially deuterated samples, with the variation of the temperature of the sample, and also with alteration of the resonance frequency of the NMR spectrometer, with the use of the techniques of double resonance and intramolecular Overhauser effect. The spectra simplified in this way are usually analyzed according to the first-order rules. The chemical shifts and the spin–spin coupling constants are used to determine the molecular structure. This group also includes publications on establishment of enantiomeric composition. The use of the lanthanide shift reagents proved to be out fruitful for investigation of dynamic phenomena by NMR. This is because such reagents may increase the difference between the chemical shifts of the resonating nuclei being in different chemical environments, *i.e.*, they change the NMR time scale relative to the time scale of the process under study. Finally, there are several works where the lanthanide shift reagents were employed to study their complexation with some classes of compounds, particularly, to estimate steric effects, to determine the complexation constants, to elucidate coordinating sites, to check the additivity of the shifts for compounds with several coordinating sites, and so on.

The second group includes the works in which the lanthanide shift reagents play an active role, and the magnitudes of the paramagnetic shifts and the signal broadenings (*i.e.*, alteration of the relaxation times) are a source of information on the structure of the molecules coordinated to the paramagnetic ion. To the above discussion concerning the application of the paramagnetic complexes of rare-earth elements, it also should be added that they have proven to be effective in both their 'active' and 'passive' roles in studies of biological objects.

Comprehensive and simultaneous account of all factors affecting the induced paramagnetic shift in the NMR spectra is required to obtain adequate information on the structure of a molecule. According to the HFC theory, the shifts caused by the lanthanide shift reagents, in general, can be represented by the following expression:

$$\omega^{ijk} = D_j \frac{3\cos^2\theta_{ik} - 1}{r_{ik}^3} + D_j' \frac{\sin^2\theta_{ik}\cos(2\Omega_{ik})}{r_{ik}^3} + F_j A_{ik}, \quad (7)$$

where D_j and D_j' are constants depending on the nature of the lanthanide and defined by the tensor of its magnetic susceptibility; r, θ_{ik}, Ω_{ik} are spherical coordinates of the nucleus relative to the lanthanide ion; A_{ik} is the constant of the contact HFC; the quantity

$$F_j = g_j(g_j - 1)J(J+1)$$

is also defined by the nature of the lanthanide and by the state of its ion; J is its total angular momentum. Index j refers to the lanthanide used, i refers to the resonating nuclei (^1H, ^{13}C and so on), k indicates the number of the resonating nucleus of the given type.

In general, the unknown parameters are: 1) D_j and D_j' for each lanthanide; 2) variables x_{ik}, y_{ik}, z_{ik}, determining the position of the resonating nucleus relative to the lanthanide ion in the Cartesian coordinate system; 3) A_{ik} for each nucleus. Thus, six parameters are unknown, of which two (D_j and D_j') relate to the jth lanthanide and four (A_i, x_i, y_i, z_i) relate to the ith nucleus. If there are n nonequivalent nuclei and m lanthanides, the system of equations (7) will contain $(4n + 2m)$ unknown variables and the following condition must be met for its rigorous solution:

$$nm \geqslant 2m + 4n. \quad (8)$$

In practice, the systems of equations like (7) are solved using iterative procedures. To do this, some criteria are used that seek a minimum if the experimental and calculated shifts coincide. Details of this approach to the lanthanide shift reagents are considered by a number of researchers. The fruitfulness of this approach has been illustrated, *inter alia*, by Babailov[24,25] in his study of intramolecular chemical exchange in several complexes of 18-membered macrocyclic ethers with the lanthanide cations.

It was noted above that rigorous solution of the system of equations (7) requires fulfilment of the inequality (8). Consider an example. The molecule VIm has six nonequivalent nuclei (protons), therefore

$$6m \geqslant 2m + 24,$$

i.e., $m \geqslant 6$. To solve the system of equations (7) rigorously with the aim of ascertaining the spatial structure of VIm on the basis of paramagnetic shifts of these six protons, it is necessary to record the ^1H NMR spectra with addition of at least six different lanthanides. This same condition remains if the spectra of the paramagnetic complexes of VIm with lanthanides are recorded (of course, whenever possible in the experiment). If the paramagnetic shifts of the signals of the carbon nucleus (there are five of them) are also used, then

$$11m \geqslant 2m + 44,$$

i.e., $m \geqslant 5$. In this situation, the indispensable requirement is isostructural nature of the complexes of all lanthanides and independence of the constants A_i on the type of lanthanide.

In the case of complexes with axial symmetry, the parameter D_j' disappears and the system (7) can be solved provided the conditions are met[7]

$$nm \geqslant m + 4n. \quad (9)$$

Further simplification can be done, if the proton paramagnetic shifts are pseudocontact ($A_i = 0$) and the ligand molecule is flat, hence

$$nm \geqslant m + 2n. \quad (10)$$

Thus, using the approach based on the minimization procedures and accepting reasonable assumptions, one can get perfectly reliable structural information even with fewer

experimental data than it is necessary to meet the condition (8). The assumption that the substrate structure is invariabile upon complexations can be attributed to quite well-ground assumptions (here the method of paramagnetic additives is meant). This reduces the number of variables by $3(n-1)$ because in this case it is necessary to determine the position of the coordinating site only.

In particular, the unknown parameters for molecule VIm under the above restrictions are three Cartesian coordinates of the nitrogen atom by which the molecule is coordinated to the paramagnetic centre, two parameters determining anisotropy of the tensor of the magnetic susceptibility of the paramagnetic ion (D_j and D'_j) and five constants A_i for the carbon atoms. Consequently, inequality (8) in such a case can be rewritten as

$$(3+2+5)\,m \geqslant 2\,m+3+5,$$

i.e., $m \geqslant 1$. Thus, within the above restrictions it is sufficient to use only one lanthanide additive to get completely unambiguous information. Typically, one of the paramagnetic complexes of europium mentioned above, $Eu(DPM)_3$ or $Eu(FOD)_3$, is such lanthanide.

Processing of experimental data obtained with the paramagnetic broadenings used in the structural studies is analogous to that with the use of the paramagnetic shifts, namely the experimental broadenings (or the relaxation times) are compared to the theoretically calculated ones. The experimental broadenings can be obtained from a comparison of the spectra recorded with and without the paramagnetic additive, similarly to evaluation of the paramagnetic shifts. It is worth noting again that the paramagnetic broadenings depend only on the distances (r^6) from the coordinating ion. Therefore, under conditions of rapid exchange and in the absence of the contact contribution, structural information can often be obtained from the NMR spectra modified by complexation, even at the qualitative level of analysis. Fairly detailed analysis of various problems related to use of the features of HFC, especially in the lanthanide complexes, is documented (see Refs 4–7, 26–50 and references cited therein).

The above experimental and theoretical data refer to the ligand molecules that form the first coordination sphere of the paramagnetic ion. It is the NMR spectra of these molecules modified by HFC that are used to study the structures of the molecules. Application of the magnetic relaxation of nuclei can also be helpful to get information about the structures and properties of weak intermolecular associates between the transition metal complexes and organic molecules (taking the outer-sphere complexes as an example).[51] The possibility of using the paramagnetic shifts induced by hydrogen bonding between radicals and organic molecules in the structural studies has been demonstrated.[52]

Unlike complexes of rare-earth elements, the predominant pseudocontact character of the HFC is not obvious in the case of the complexes formed by elements of the iron subgroup. As a rule, establishment of this fact requires additional experiments. Therefore, using the shifts induced by paramagnetic ions of the elements of the first transition group in the structural studies, one should anticipate that there are pseudocontact (ω_p) and contact (ω_c) components. Typically, the method proposed by Molin and Zaev[53] is employed to separate them.

$$\omega^{Co} = \omega_c^{Co} + \omega_p^{Co} = K\omega^{Ni} + P\phi, \qquad (11)$$

where ω^{Co} and ω^{Ni} are shifts in the spectra of the cobalt and nickel complexes; K and P are constants, determined from the joint solution of Eqn (11) for several nuclei;

$$\phi = \frac{3\cos^2\theta - 1}{r^3}$$

is the geometrical factor in the McConnell–Robertson formula. By varying the values θ and r, one can find the 'best' values K and P (*i.e.*, one can achieve the smallest divergence between the calculated and experimental shifts). When the expression (11) is used, it is assumed that the quantity ω_p induced by the paramagnetic nickel ion is insignificant and that the mechanisms of delocalization of the uncompensated electron spins are similar in the nickel and cobalt complexes. It has been shown that, for example, the nickel chelate $Ni(acac)_2$, forming complexes with the composition 1 : 2, induces the contact shifts only, whereas $Co(acac)_2$ induces both the contact and pseudocontact shifts. The method of separation of the contact and pseudocontact contributions to the paramagnetic shifts is applicable to the axially located ligands (L) in complexes $M(acac)_2 \cdot L_2$ (M = Ni, Co), but is not applicable to the ligand acac.[6, 54]

The qualitative interpretation of the nature of the experimental contact and pseudocontact paramagnetic shifts is based on concepts developed back in the 1960s–1970s. It was found that transfer of the perturbation effect of the unpaired electrons to the resonating nuclei is carried out along both σ- and π-bonds (the σ- and π-mechanisms of delocalization). It is proved that with an increase in the distance from the coordinating ion fast damping of the unpaired spin density occurs in the case of delocalization along σ-bonds of unsaturated ligand molecules. Here the paramagnetic shifts have the same signs. If the unpaired spin density gets to the π-system, then significant paramagnetic shifts can be observed for signals of the nuclei separated from the central ion by several bonds (remote delocalization). Besides, the signs of the shifts alternate. The shift values can have the alternating signs in the spectra of saturated compounds as well, and electron–nuclear interaction can be revealed for nuclei remote from the coordinating ion. These experimental facts are explained by transfer of the perturbation effect of the electron spin not only through bonds (the spin delocalization), but also according to the mechanisms of the spin polarization and hyperconjugation. The predominant role of the pioneering studies of the nature of the hyperfine (first of all, contact) couplings should be noted here, which have been carried out by academicians Molin and Sagdeev in collaboration with other researchers of the Novosibirsk scientific school in our country.[10, 55–61]

The following remark should be added to the above considered utilization of the paramagnetic complexes, playing both 'active' and 'passive' roles, *i.e.*, without theoretical estimates of the paramagnetic shifts and broadenings. The manifestation of HFC in the NMR spectra is determined by the relaxation processes that are among the most complex areas of the magnetic resonance. In this regard, the comment by Eaton and Phillips,[1] which consists in that we poorly understand the relaxation processes in the paramagnetic systems and that any chelate and coordination compound of a transition metal can be 'a special case' requiring a particular consideration, is instructive. With this in mind, many specialists are seeking to carry out in-

depth studies of both the mechanism of HFC and the relaxation processes in the paramagnetic complexes using the paramagnetic additives to solve structural problems. Perhaps, this is the only approach that makes the researcher more confident in the reliability of information about the structure of molecules as obtained from analysis of the paramagnetic shifts and broadenings of signals in the NMR spectra.

Getting to the interpretation of the NMR spectra transformed by HFC, it is necessary to take into account the initial conditions of the experiment. The significance of this point is illustrated by the results of studies of stereochemically non-rigid heterospin nickel complexes with stable nitroxide radicals. These and similar heterospin systems attract the attention of researchers as the starting compounds to produce molecular magnets.[62] The ^{1}H NMR spectra of the heterospin nickel bischelate recorded at variable sample temperatures are discussed below.[63]

As noted at the outset of this review, the specificity of NMR in the paramagnetic systems is determined by the nature of the electron–nuclear and hyperfine coupling between the unpaired electrons and the resonating nucleus resulting in the paramagnetic broadening and shift of the resonance signals. Quantitative estimation of the signal broadenings related to the hyperfine coupling is reduced to solution of the Bloch equations modified by McConnell, who included there chemical exchange. Analysis of these equations leads to the following expression for the observed paramagnetic broadening of signals:[7]

$$\Delta = \frac{P_M}{\tau_M} \frac{(1/T_{2M})^2 + 1/T_{2M}\tau_M + \omega^2}{(1/T_{2M} + 1/\tau_M)^2 + \omega^2}, \quad (12)$$

Here P_M is the mole fraction of the paramagnetic complex in the sample, τ_M is the time of existence of the resonating nucleus in the given paramagnetic environment T_{2M} is the transverse relaxation time of the nucleus in the complex, ω the paramagnetic shift of the resonance line. Equation (12) shows that the quantity Δ is a complicated function of τ_M, T_{2M} and ω. Depending on the nature of the complexes under investigation and the variety of the experimental conditions, dispersion of the observed values of the given quantities may be quite broad, which remarkably hampers application of Eqn (12) for the analysis of the experimental spectra. Therefore, simplified formulas are usually employed to analyze the observed values Δ. The type of the simplification in each case is determined by the nature of the problem under solution, as well as by the type of object that specifies the relation between $(\tau_M)^{-1}$, $(T_{2M})^{-1}$ and ω. For example, if the main aim is to provide structural information, the most convenient is an approximate expression for Δ that meets the condition of fast exchange where the value of Δ is determined by expression (6).

IV. Nuclear magnetic resonance in heterospin complexes

A growing number of new paramagnetic systems (including heterospin systems) significantly expands the range of tasks to be solved. The analysis of the NMR spectra of heterospin complexes including paramagnetic ions of transition metals and organic radicals is additionally complicated due to the spin–spin coupling between unpaired electrons of the paramagnetic centres of the molecules. In this case, the use of the analytical approximations involved in expression (12) can lead to substantial deviation of functional relationship between the parameters. Therefore, the complete expression (12) must be applied instead. In order to justify this and to understand the experimental ^{1}H NMR spectra of the complexes of Ni(II) with nitroxide radicals, which are discussed later, it is necessary to examine the results of modelling changes in the paramagnetic broadening provided that all the variables on the right side of the expression (10) are significant.

As noted above, the complication of the use of equations (12) stems not only from the fact that Δ is a non-linear function of four variables, but also from that these variables can strongly depend on the nature of the complexes under study (on the structure and composition of the paramagnetic metal ion, on the coordination polyhedron), and on the experimental conditions (temperature, concentration). A step-by-step analysis of expression (12) with fixation of certain values of the parameters or their variation limits has been performed.[63]

Figure 5 shows the functional dependence

$$\Delta = \Delta(T,\omega), \quad (13)$$

where T is the temperature of the sample under study. The three-dimensional diagram has been obtained for $P_M = 1$, τ_M is defined by the common formula

$$\tau_M = \left(\frac{h}{kT}\right) \exp \frac{\Delta H - T\Delta S}{RT}. \quad (14)$$

This computer modelling was carried out taking the enthalpy change $\Delta H = 15\,103$ cal mol^{-1}, the entropy change $\Delta S = 20$ cal (mol K)$^{-1}$ and $T_{2M} = 10^{-2}$ s. The particular values used in this modelling are not fundamentally important. Nevertheless, the chosen values lie within typical limits.[64] Functional dependence of the paramagnetic shift on the temperature was set by the expression[6]

$$\omega = \frac{aS(S+1) \times 10^6}{33.89T}, \quad (15)$$

where $a = 0.1$ Œ, S is the spin of the complex.

Graphical representation of the dependence $\Delta = \Delta(T, \omega)$ (see Fig. 5) revealed two general trends. Firstly, upon variation of the temperature the maximum of broadening of the resonance line is displaced. Secondly, upon the

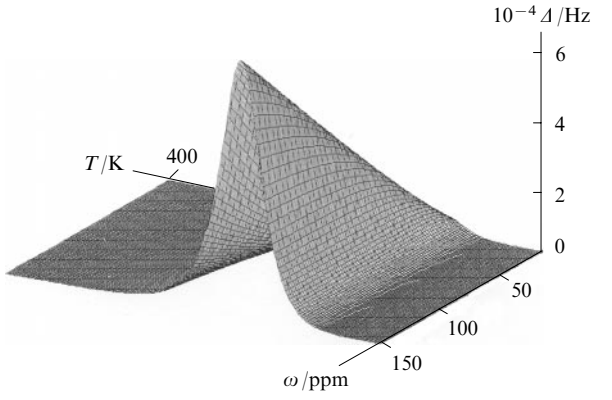


Figure 5. Fig.5. Modelling of the dependence $\Delta(T,\omega)$ at constant enthalpy and entropy.

temperature variation both the maximum values and the range of the paramagnetic broadening increase owing to squared relationship between Δ and the paramagnetic shift when approaching the maximum of the paramagnetic broadening.

Attention should be drawn to the following. Since $d\tau_M/dT < 0$, τ_M and Δ decrease with increasing temperature starting from the temperature (T_0) corresponding to the maximum of the paramagnetic broadening. Therefore, if τ_M increases at a certain temperature $T_1 > T_0$, the function $\Delta = \Delta(T,\omega)$ gets another maximum at $T_2 > T_1 > T_0$. As follows from expression (14), the increase in τ_M can be achieved, for example, by variation of the thermodynamic parameters. Figure 6 shows dependence $\Delta = \Delta(T,\omega)$ under the assumption that ΔS decreases to 10 cal (mol K)$^{-1}$ at $T_1 = 300$ K. Such a decrease should have its physical reasons for a particular paramagnetic system, and this, naturally, requires a special discussion. However, it is important here that the second maximum actually appears on the diagram when τ_M changes.

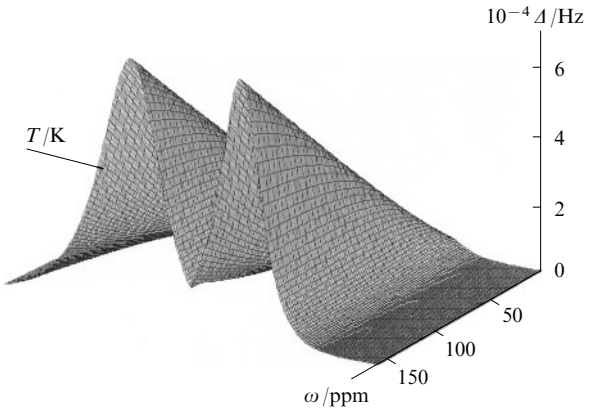


Figure 6. The dependence $\Delta(T,\omega)$ for a single jump-like change in entropy.

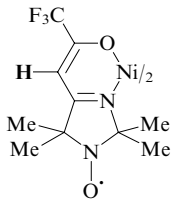
Obviously, if τ_M changes at the temperature $T_3 > T_2$ again, the third maximum appears on the diagram $\Delta = \Delta(T,\omega)$, an so on. Rather nontrivial result follows from this, consisting in that under suitable conditions the resonance signal, whose position in the NMR spectrum is determined by the paramagnetic shift ω, may undergo periodic narrowing and widening. In other words, the function $\Delta = \Delta(T,\omega)$ is turned to be modulated as result of variation of the parameter τ_M, characterizing the exchange processes in the system, in which HFC is under study. Experimental manifistation of this effect depends on both the HFC parameters and capability to vary the temperature in sufficiently wide interval. The change in τ_M as a result of diminution of ΔS physically represents temporal ordering in the nuclear spin system (temporal polarization). In fact, it is as if an additional channel were opened in the system for the energy exchange between the resonating system of nuclear spins and the lattice including a subsystem of electron spins. In principle, this determines new opportunities for emergence and detection of the magnetic resonance effects and for influence on the subsystems of the nuclear and electron spins if HFC occurs.

Note that expression (12) initially used for modelling was obtained to describe the so-called chemical exchange processes, implying that the resonating nucleus resides in the first coordination sphere of the paramagnetic ion for time τ_M. This exchange should be considered as an effect of a general nature, in which the resonating nucleus just alters the places with different magnetic environment. Hence the following situations are possible in the course of NMR detecting.

1. Indeed, an exchange takes place where the ligand molecule periodically enters the first coordination sphere of the paramagnetic metal ion and appears in different magnetic environment at different times. In this case, the observed paramagnetic shifts shall be a linear function of the molar concentration of the complexes and the dependence $\omega = \omega(T)$ has to obey Curie's law.

2. The dynamics described above for the ligand is not realized. However, there is an equilibrium between different conformations of the complex (for example, a classic equilibrium square > tetrahedron) that are characterized by different magnetic properties. The experimental dependences $\omega = \omega(T)$ for this (and similar) process have to be described by a function containing an exponent.

3. Variation of the temperature of the sample the NMR spectrum of which is recorded affects the spatial structure of the ligand in the paramagnetic complex, and ultimately it influences the character of HFC. It is easy to conclude that in this case the form of the temperature dependence $\omega = \omega(T)$ is not obvious *a priori*. Temperature dependence of the paramagnetic shift and broadening in the ^{1}H NMR spectrum of the signal for the proton of the fragment $=$CH$-$ in the enamine-ketone group of bischelate **1** is studied with the purpose of experimental verification of the performed modelling.



1

Figure 7 illustrates a typical transformation of the spectrum of such a complex upon change in the sample temperature directly in the NMR spectrometer probe.

Experimental dependence $\omega = \omega(T)$ of the signal for the proton of the fragment $=$CH$-$ has a complex character and in the region of high field does not obey Curie's law (curve 2 in Fig. 8). Below 240 K, the intensity of this signal decreases and simultaneously a new low-field signal arises whose paramagnetic shift increases with lowering of the sample temperature following Curie's law (Fig. 8, curve *1*). The experimental dependence $\Delta(1/T)$ of the signal for the proton of the fragment $=$CH$-$ also has a sophisticated form (Fig. 9). It has two distinct maxima supporting correctness of the performed modelling. Actually, Fig. 9 represents an experimental proof of the above suggestion that the NMR signal can undergo repeated narrowing and widening in such systems upon temperature change.

Note that intensity of the maximum of the signal at 264 K is approximately three times lower than that at 252 K (see Fig. 9). At the same time, both maxima in the corresponding theoretical dependence are of the same intensity (see Fig. 6). This disagreement is caused by that the graph in Fig. 6 has been modelled on assumption of simultaneous

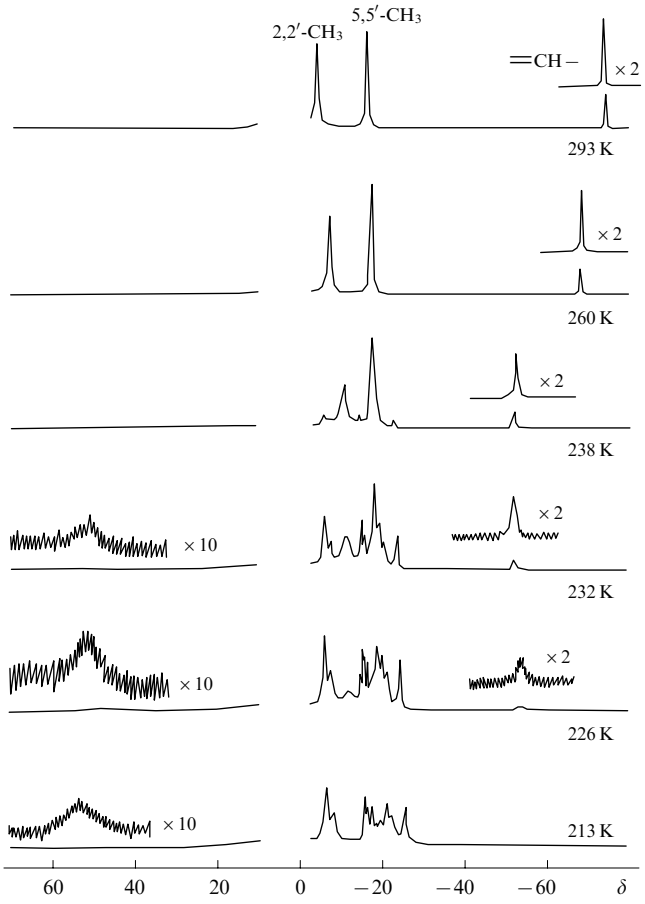


Figure 7. Transformation of the ^{1}H NMR spectrum of complex 1 in CH_2Cl_2 depending on the temperature of the sample.

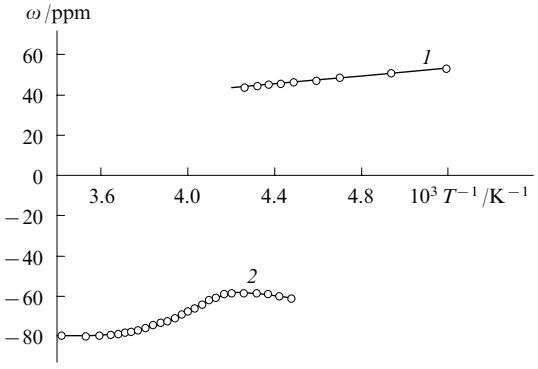


Figure 8. Experimental dependence $\omega(1/T)$ of the signal for the proton of the fragment =CH– in complex **1** in low (*1*) and high (*2*) fields.

(jump-like) change in entropy for all molecules. Under real conditions, the process of the state repopulation is stretched in the temperature scale and therefore the passage from one magnetic environment to another under gradual temperature changes requires some finite time (Δt). In general, each of those states may have its set of parameters P_1, τ_1, ω_1, Δ_1 and P_2, τ_2, ω_2, Δ_2. However, until the value of ω' ($\omega' = \omega_1 - \omega_2$), expressed in frequency units, remains comparable at the given temperature to the value ($1/\pi\Delta t$), the

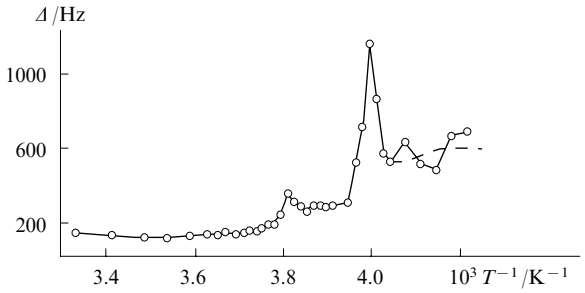
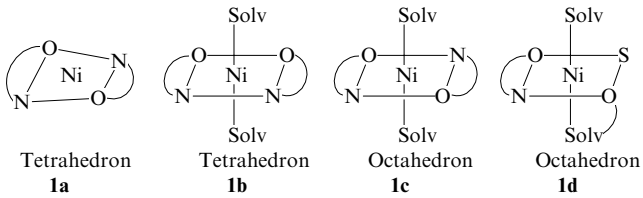


Figure 9. Experimental dependence $\Delta(1/T)$ of the signal for the proton of the fragment =CH– in complex **1**.

observed spectrum is partly averaged or even can contain signals from the two states. This explains the form of the signal for the proton of the fragment =CH– observed in the course of the temperature change (Fig. 10) and reflected on graphs of the dependencies $\omega(1/T)$ and $\Delta(1/T)$ (Fig. 8 and 9, respectively). The reasons for the transformation of the ^{1}H NMR signal of complex **1** have been explained [63] on the basis of the known data on stereochemical non-rigidity of this compound,[65] allowing simultaneous presence of its several conformers in solution.



Two signals for the proton of the fragment =CH– are detected in the temperature range 283–248 K (see Fig. 10). It is noteworthily that the temperature interval in which they appear is only of 1–2 K. The possibility of detection of these subtle effects in the heterospin systems with the use of

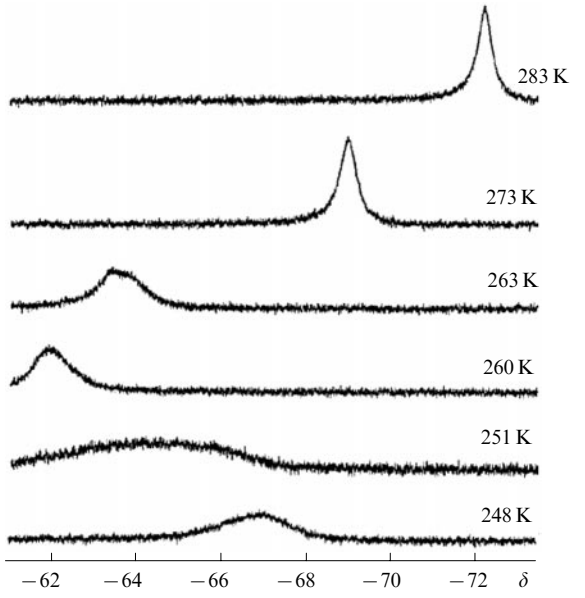
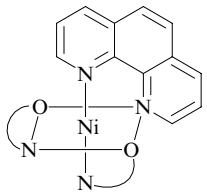


Figure 10. Variation of the signal for the proton of the fragment =CH– in complex **1** in the high field region depending on the temperature.

NMR is important not merely to demonstrate the exceptional sensitivity of this method but rather to monitor the state of molecules in solution in the course of molecular design of magnets.

Stereochemical non-rigidity of complex **1** can be completely suppressed by introducing an additional bidentate ligand. Such a ligand in complex **1** virtually converts all possible conformations to the only one (**1d**). Model complex **2** with this configuration was synthesized by reaction of bischelate **1** with phenanthroline (Phen).

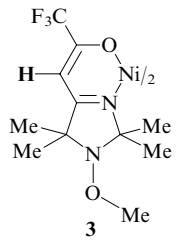


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Its ^{1}H NMR spectra at two temperatures are shown in Fig. 11. It is important to note that the signal for the proton of the fragment $=CH-$ in the whole temperature range lies in the low field. This clearly indicates that at the temperature <240 K complex **1** in solution has conformation **1d**. The plots of dependences $\omega(T)$ and $\Delta(T,\omega)$ of the signal for the proton of the fragment $=CH-$ in the NMR spectrum of complex **2** are shown in Figs 12 and 13. The fact that they are linear firmly indicates fulfilment of Curie's law and preservation of the structures of complex **2** (in contrast to bischelate 1) upon the temperature variation.

Attention is drawn to yet another feature of the NMR spectra of the Ni(II) complexes with nitroxide radicals. When the sample temperature increases, the paramagnetic shift of the high-field signal for the proton of the fragment $=CH-$ in the spectrum of complex **1** increases in absolute value (see Fig. 7) rather than decreases, as required by Curie's law. This effect can be explained quite easily. Since in the complexes with radicals there are paramagnetic centres of different nature, one can assume that they can induce paramagnetic shifts of different signs. This assumption was confirmed in studies of the temperature dependence of the ^{1}H NMR spectrum of complex **3** containing diamagnetic analogue of spin-labelled enamino ketone (complexes **1** and **2**), which was specially prepared for this study.

The behaviour of the signal for the proton of the fragment $=CH-$ depending on the temperature is shown in Fig. 14. As in the case of complex **1**, at high temperatures the signal for this proton is observed in high field. Due to the stereochemical non-rigidity of **3**, this singlet changes with a decrease in temperature in a rather complicated manner. Below 294 K, its splitting into two signals begins and below 233 K its high-field component broadens and then (below 203 K) splits into two signals. The temperature dependence of the paramagnetic shifts of all three signals



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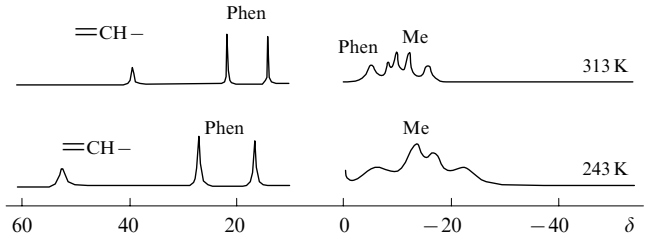


Figure 11. The ^{1}H NMR spectra of complex **2** in CH_2Cl_2.

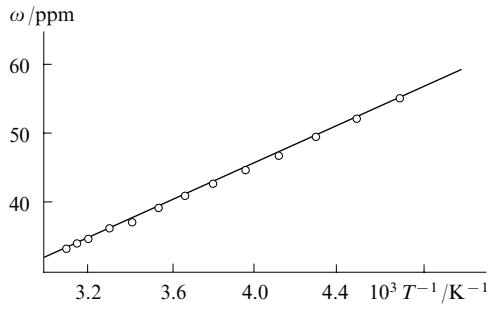


Figure 12. Dependence $\omega(1/T)$ of the signal for the proton of the fragment $=CH-$ in the spectrum of complex **2**.

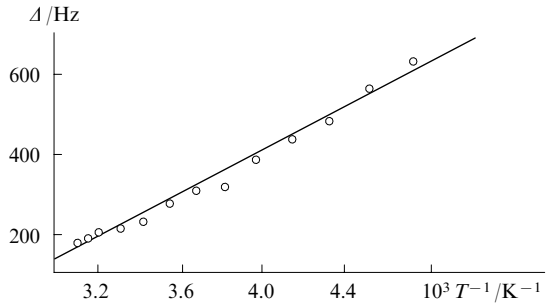


Figure 13. Dependence $\Delta(1/T)$ of the signal for the proton of the fragment $=CH-$ in the spectrum of complex **2**.

obey Cueri's law, *i.e.*, the absolute value of the shift increases as the temperature decreases (Figs. 14, 15). The paramagnetic broadening of these lines undergoes repeated narrowing and widening as in case of complex **1**. Consequently, deviation of the dependence $\omega(T)$ in the case of complex **1** from Curie's law is really caused by induction of paramagnetic shifts of different signs by the nickel ion and nitroxide fragment, which determines the complicated character of temperature-dependent changes in the paramagnetic shift of the signal for the proton of the fragment $=CH-$ in the spectrum of complex **1**.

Note also that, unlike complex **1** (see Fig. 7), in the spectrum of **3** there are no low-field signals at any temperature. This implies that the paramagnetic ligand in complex **3** is responsible for an additional factor influencing the NMR spectra. In a heterospin complex, temperature-dependent structural changes of a stereochemically non-rigid molecule affects the pattern of spin coupling, which can be reflected in both the value of spin density and its sign in the case of some conformations. Actually, it is this

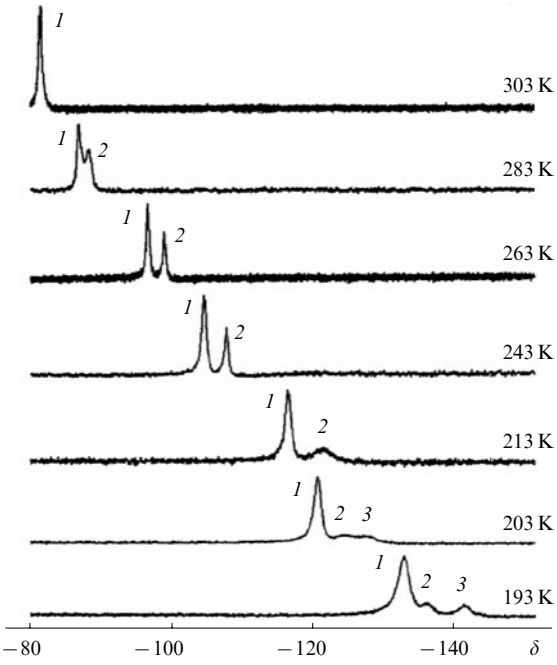


Figure 14. Alterations in the ^{1}H NMR spectrum in the region of the signal for the proton of the fragment $=$CH$-$ in complex **3** in CH_2Cl_2 depending on the temperature.
1–3 are the signal numbers.

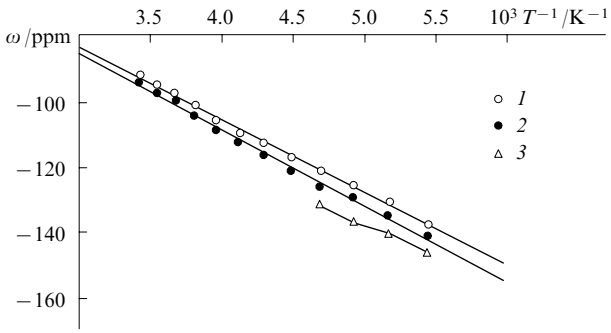


Figure 15. Experimental dependences $\omega(1/T)$ of the signals for protons of fragments $=$CH$-$ for different conformations of molecule **3**.

phenomenon that is observed in the spectrum of complex **1** at the temperature <240 K. Hence, using the NMR method it is possible to reveal the temperature regions with substantially different types of exchange interactions between the paramagnetic centres. If the structure of molecules mainly remains intact upon crystallization from solution, the exchange interactions in the solid phase formed will be substantially different as well.

Thus, the study of the hyperfine coupling modulated by the chemical exchange affords valuable insight into the dynamics of molecules in solutions of the paramagnetic ions of transition metals with stable nitroxide radicals. The following example illustrates synthesis of a solid-phase heterospin compound containing a stuctural fragment in a certain conformation. It was reported [65] that complex **1** was obtained in a solid form in two polymorphic modifications. They both had lamellar polymeric structures resulting from the coordination of Ni^{2+} ion to the oxygen atoms of the nitroxyl groups in two neighbouring bischelate molecules. However, in a modification (α) oxygen atoms are coordinated in *trans*-positions of the coordinating octahedron, whereas in the other modification (β) they are coordinated in *cis*-position. Under normal conditions, α-modification is more thermodynamically stable, and β-modification converts into it gradually (or fast upon heating). Therefore, it is easy to prepare complex **1** in α-modification. β-Modification can be isolated, for example, from CH_2Cl_2 solution only if fast solvent evaporation accompanied by the mixture cooling is carried out. Upon growth of single crystals of β-modification they are always formed as admixture to the crystals of α-modification; these modifications have to be separated by mechanical way. Analysis of the temperature dependence of the ^{1}H NMR spectrum of complex **1** in CH_2Cl_2 solution shows that molecules of **1** tend to take *cis*-octahedral conformation (of **1d** type) at temperatures <238 K. Indeed, crystallization of 1 from solution in dry CH_2Cl_2 at temperatures below -40 °C easily results in single crystals of β-modification.[65]

V. Conclusion

The state of the art of the theory of HFC gives prospects for future utilization of the method based on analysis of the NMR spectra modified by electron–nuclear and hyperfine coupling. Indeed, the combined use of HFC and other techniques of analysis of spectra can significantly increase the body of information. Even independent use of the fact of explicit dependence of the paramagnetic shifts and broadenings of signals on the spatial and electronic structure of paramagnetic complexes often makes it possible to obtain unique information on the structures and dynamics of compounds at the molecular level from the high-resolution NMR spectra.

As for problems related to HFC and requiring discussion, it is worth pointing at the necessity of researches aimed at extending our knowledge about the nature of electron–nuclear interactions in diverse paramagnetic complexes. It is important to continue studies of the nature of contact paramagnetic shifts and broadenings of signals on the basis of combined use of NMR on nuclei ^{1}H and ^{13}C. The ^{13}C NMR spectra provide valuable information about the features of the carbon skeleton of organic compounds and their complexes, whereas signals for the hydrogen nuclei within the periphery of molecules make the spectral information more complete. Very promising direction in such studies consists in modelling HFC using theoretical calculations, including *ab initio* quantum chemical calculations.

Yet another area in the study of HFC by the high-resolution NMR techniques involves detection of the NMR signals not only from nuclei ^{1}H and ^{13}C, but also from nuclei of other types. To date, only a limited number of experimental works has been published in this area and there are virtually no data on the nature of the paramagnetic shifts (especially, contact ones) of the NMR signals due to nuclei whose valence state is determined by electrons with the principal quantum number greater than two. Lastly, another important direction of studies should be mentioned, which relates to the investigation of temperature dependences of the paramagnetic shifts. There is also a limited number of experimental data in this area, the published results mainly concern the ^{1}H and ^{13}C NMR spectra of paramagnetic complexes fairly simple in their structure.

This review is prepared with the financial support of the Russian Foundation for Basic Research (Project No. 09-03-00386-a).

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