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Peculiarities of NMR spectra of heterospin complexes

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Experimental investigation and theoretical simulation of the unusual phenomenon of multiple broadening and narrowing of NMR signals due to the temperature variation of a solution of the stereochemically non-rigid heterospin Ni^{2+} complex with stable nitroxide were performed. The investigation of the temperature dependence of the NMR signals of stereochemically non-rigid heterospin systems can be used for choosing conditions for growing heterospin single crystals containing molecules in a definite conformation.

Key words: NMR spectroscopy, nickel, chelate complexes, nitroxides, conformation equilibrium.

Development of principles for designing heterospin systems based on coordination compounds of paramagnetic ions of transition metals with stable nitroxyl radicals attracts intent attention of researchers working in the area of molecular magnets.[1—4] The use of methods of the standard chemistry of solutions has a great advantage for the synthesis of such magnetically active compounds. The variation of crystallization conditions (solvent or temperature) allows one to obtain the same heterospin compound as different polymorphs, whose magnetic properties, as a rule, differ substantially. This feature is especially valuable for the subsequent development of magnetostructural correlations. For the controlled action upon the solid phase structure, it is fruitful to have an information about the structure of molecular heterospin precursors and/or the ratio of their forms in a solution at different temperatures. In addition, using NMR spectroscopy, one can obtained a detailed information about the magnetic properties of molecular precursors of heterospin solid phases formed during crystallization from a solution.[5] This results in an increasing interest in studying peculiarities of NMR spectra of heterospin systems with the purpose for using NMR spectroscopy for design of molecular magnets. However, the study of paramagnetic complexes is accompanied by a much difficult NMR monitoring of paramagnetic species in a solution. The problem of studying such complexes is that they have rather broad lines in NMR spectra and, in addition, that complexes, especially non-rigid, can exist in a solution as several conformations. Studying the heterospin Ni^{2+} complex with 3-imidazoline nitroxyl as a model system, we found that the ratio of conformations with the temperature variation can change in a complicated manner, and it was unexpected that the population over conformations can sharply change at a small temperature increment. In addition, the transition from one conformation of the heterospin complex to another can be accompanied by a change in the sign of the paramagnetic shift in the NMR spectra, which changes the region of its detection. The effect of multiple broadening and narrowing of resonance NMR lines with the variation of the temperature of solutions of the complexes was also unexpected for us. This work is devoted to analysis of these effects.

Results and Discussion

Simulation. The specificity of the NMR phenomenon in paramagnetic systems is determined by the character of the electron-nuclear or hyperfine coupling (HFC) between unpaired electrons and resonating nuclei, which leads to the paramagnetic broadening and the shift of resonance lines. Quantitative analysis of signal broadenings due to HFC is reduced to the solution to the Bloch equations modified by McConnell who introduced the chemical exchange into them. Analysis

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of these equations gives the expression for the observed paramagnetic broadening (Δ) of signals[7]:

$$\Delta = \frac{P_M}{\tau_M}\left[\frac{\left(\dfrac{1}{T_{2M}}\right)^2 + \dfrac{1}{T_{2M}\tau_M} + \omega^2}{\left(\dfrac{1}{T_{2M}} + \dfrac{1}{\tau_M}\right)^2 + \omega^2}\right], \quad (1)$$

where τ_M is the time of stay of the resonating nucleus in a certain paramagnetic environment, P_M is the molar fraction of the paramagnetic complex in the sample, ω is the paramagnetic shift of the resonance line, and T_{2M} is the time of transversal relaxation of the nucleus in the complex. It is seen from Eq. (1) that the Δ value is a complex function of τ_M, T_{2M}, and ω. In some cases, analyzing the observed Δ values, one can use simplified formulas. The character of simplification in each particular case is determined by the ratio of the $(\tau_M)^{-1}$, $(T_{2M})^{-1}$, and ω values. For example, in the case of fast exchange, we have

$$\Delta = P_M/T_{2M}. \quad (2)$$

However, in the general case, it is necessary to use the complete equation (1) rather than its approximation. It is especially significant to operate with Eq. (1) in analysis of NMR spectra of heterospin complexes of paramagnetic ions of transition metals with organic radicals because for these objects the situation is additionally impeded by the presence of the spin-spin interaction between unpaired electrons of paramagnetic centers of the molecule. In this case, the use of approximate analytical expressions can result in a substantial violation of functional relations between the parameters. For understanding of the experimental ^{1}H NMR data for the Ni^{2+} complexes with the nitroxyl radical discussed below, we have to preliminarily consider the results of simulation of the character of changing paramagnetic broadening.

Some difficulty in using Eq. (1) is due to the fact that Δ is a nonlinear function of four variables and also that these variables can depend to a great extent on the nature of the complexes under study (paramagnetic metal ion, coordination polyhedron, its structure and composition) and experimental conditions (temperature, concentration). Therefore, it is reasonable to examine Eq. (1) in stages, remaining unchanged certain values of some parameters or limits of their variations.

The functional dependence

$$\Delta = \Delta(T,\omega), \quad (3)$$

where T is the temperature of the sample under study, is shown in Fig. 1. The three-dimensional plot was obtained under the condition that $P_M = 1$ and τ_M is specified by the formula

$$\tau_M = [h/(kT)]\exp[(\Delta H - T\Delta S)/RT]. \quad (4)$$

It was also accepted in the simulation that $\Delta H = 15 \cdot 10^3$ cal mol^{-1}, $\Delta S = 20$ cal mol^{-1} K^{-1}, and $T_{2M} = 10^{-2}$ s. These specific values of the parameters were chosen from the region of values that are rather characteristic of a wide scope of complex compounds.[7,8] The functional temperature dependence of the paramagnetic shift was given by the expression

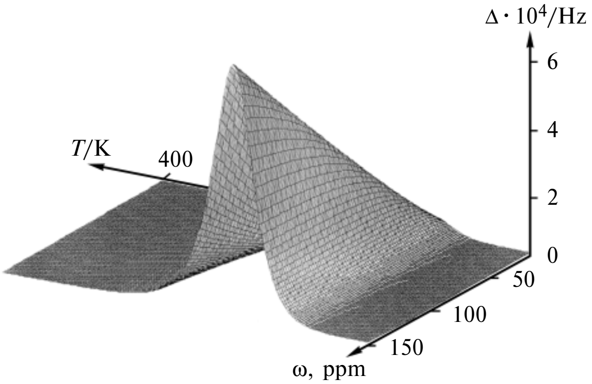

Fig. 1. Simulation of the dependence of the paramagnetic broadening $\Delta(T,\omega)$ at unchanged ΔH and ΔS.

$$\omega = [aS(S + 1) \cdot 10^6]/(33.89T), \quad (5)$$

where the HFC constant $a = 0.1$ Oe, and S is the spin of the complex.[9]

The graphical representation of the $\Delta(T,\omega)$ dependence (see Fig. 1) revealed two important tendencies of the common character inherent in the discussed functional dependence. First, the broadening maximum of the resonance line shifts with the temperature change. Second, the variation of the temperature increases both the maximum values and the interval of paramagnetic broadening of the resonance signal due to a quadratic dependence of the Δ value on the paramagnetic shift with approaching the maximum of paramagnetic broadening.

We note also the following circumstance. Since $d\tau_M/dT < 0$, beginning from a certain temperature (T_0) corresponding to the maximum of paramagnetic broadening τ_M and Δ begin to decrease with the temperature increase (see Fig. 1). Now if at some temperature $T_1 > T_0$ we increase τ_M, then the $\Delta(T,\omega)$ function should gain one more maximum at $T_2 > T_1$. It follows from Eq. (4) that τ_M can be increased, *e.g.*, by the variation of the thermodynamic parameters. The $\Delta(T,\omega)$ dependence, under the assumption that at $T_1 = 300$ K ΔS decreased to 10 cal mol^{-1} K^{-1}, is presented in Fig. 2. For a definite paramagnetic system, the reason for this decrease must be informative physically, and some of these reasons are discussed henceforth. Here it is important to note that the second maximum appears indeed in the plot of the functional dependence with changing τ_M (see Fig. 2).

Evidently, if at the temperature $T_3 > T_2$ the τ_M value changes again, the third maximum, *etc.*, appears in the $\Delta(T,\omega)$ plot. Thus, the resonance signal, whose position in the NMR spectrum is determined by the paramagnetic shift ω, can undergo, in principle, multiple narrowings and broadenings. In other words, the $\Delta(T,\omega)$ function is modulated due to the variation in the τ_M

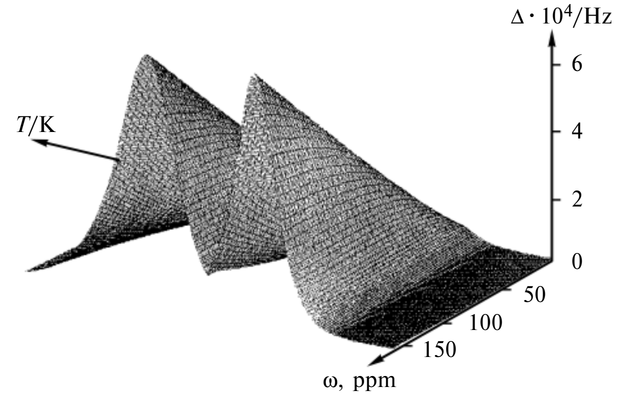

Fig. 2. Dependence $\Delta(T,\omega)$ at a single jumpwise change in ΔS.

parameter. The experimental manifestation of this effect depends on both the HFC parameters and a possibility of varying the temperature in substantially wide limits. The artificial change in the τ_M value simulated by us due to a decrease in ΔS can represent, in the physical sense, some temporal ordering in the system of nuclear spins.

It is noteworthy that the primary expression (1) used in simulation was obtained for the description of the chemical exchange when the resonating nucleus within the τ_M time exists in the first coordination sphere of the paramagnetic ion. In the general case, the exchange should be considered as a process due to which the resonating nucleus changes its position between the states with different magnetic environments. For example, the following variants are possible.

1. Exchange occurs when the ligand molecule periodically enters into the first coordination sphere of the paramagnetic metal ion being, as a result, in different magnetic environments in different time moments. In this case, the observed paramagnetic shifts should be

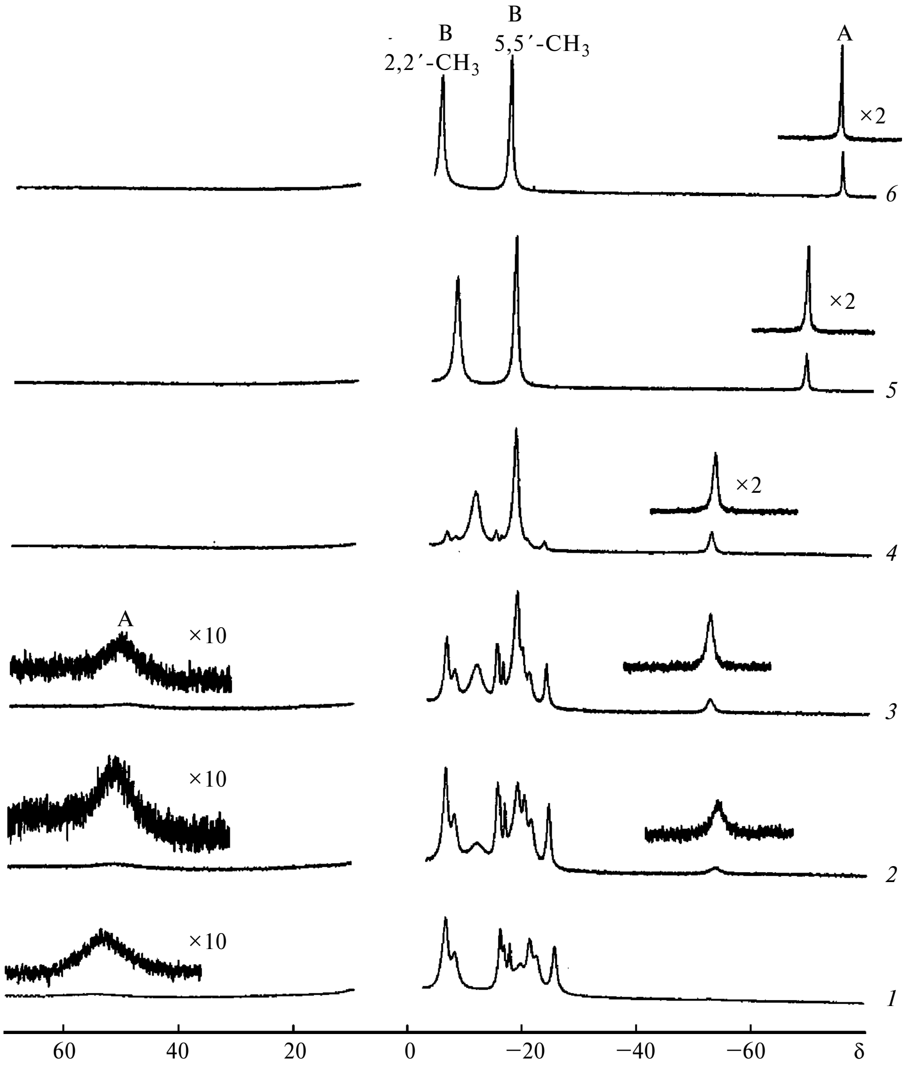

Fig. 3. Transformation of the ^{1}H NMR spectrum of a solution of **1** in CH_2Cl_2 with temperature changing: 213 (*1*), 226 (*2*), 232 (*3*), 238 (*4*), 260 (*5*), and 293 K (*6*). A is the signal from the proton of the =CH— fragment (50—60 ppm and −50—60 ppm); B are the signals from the CH_3 groups (0—30 ppm).

linear functions of the molar concentration of the complex, and the ω(T) function should obey the Curie law.

2. Different conformations of the complex, which differ only in geometry of the coordination unit (*e.g.*, square ↔ tetrahedron), which are inherent in different magnetic moments, are at equilibrium. The run of the experimental ω(T) plot for this process should be described by a function containing an exponent.

3. The temperature variation affects the spatial structure of the coordinated ligand molecule in the paramagnetic complex in a solution and, hence, the character of HFC. In this case, it is difficult to predict *a priori* the character of the temperature ω(T) plot.

Experiment. Below we present the experimental results of the temperature dependence of the paramagnetic shift and broadening of the signal from the proton of the =CH— fragment of the enaminoketone group in the ^{1}H NMR spectrum of heterospin bischelate **1**.

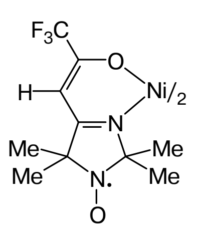

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Figure 3 illustrates the typical transformation of the spectrum of a solution of **1** with the temperature variation.

The experimental ω(1/T) dependence of the signal from the proton of the =CH— fragment has a complicated character and does not obey the Curie law in the region of high fields (Fig. 4, *a*). Below 240 K this signal decreases in intensity and a new signal appears simultaneously in the low field. Its paramagnetic shift increases with a decrease in the temperature of the sample, following the Curie law (Fig. 4, *b*). The experimental Δ(1/T) plot for the signal from a proton of the =CH— fragment of the enaminoketone group is also complicated (Fig. 5). It contains two pronounced maxima, which confirm the principal validity of the model consideration performed above. In fact, Fig. 5 experimentally confirms that in similar systems the NMR signals can undergo multiple narrowing and broadening with changing temperature. Note that the intensity of the maximum at 264 K is approximately triple as low as the maximum at 252 K (see Fig. 5). At the same time, both maxima in a similar theoretical plot are the same in intensity (see Fig. 2). The indicated distinction is due to the fact that the plot in Fig. 2 was obtained under the assumption on a simultaneous for all molecules (jumpwise) change in the entropy value. Under real conditions, a definite time (Δ*t*) is required for the transition from one magnetic environment to another during the gradual temperature change. In the general case, each state can be characterized by the corresponding set of parameters P_1, τ_1, ω_1, Δ_1 and P_2, τ_2, ω_2, Δ_2. Until the value $\omega' = \omega_1 - \omega_2$ at a given temperature remains comparable with the $(1/\pi\Delta t)$ value, the observed spectrum is partially averaged or even contains signals from two states. Precisely this explains the shape of the signal from a proton of the =CH— fragment observed by us during the temperature change (Fig. 6) and presented in the ω(1/T) and Δ(1/T) plots (Figs. 4 and 5, respectively). The reasons for the transformation of the ^{1}H NMR signal of complex **1** can be explained by the known data on stereochemical non-rigidity of this compound.[10] These data assume the existence of the complex in a solution in different conformations

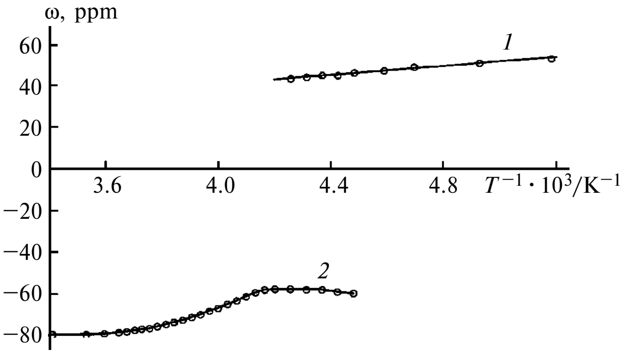


Fig. 4. Experimental ω(1/*T*) dependence of the signal from the proton of the =C—H— fragment of complex **1** in low (*1*) and high fields (*2*).

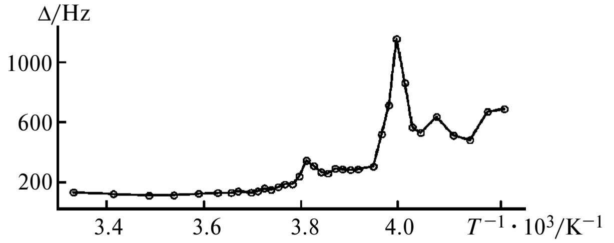
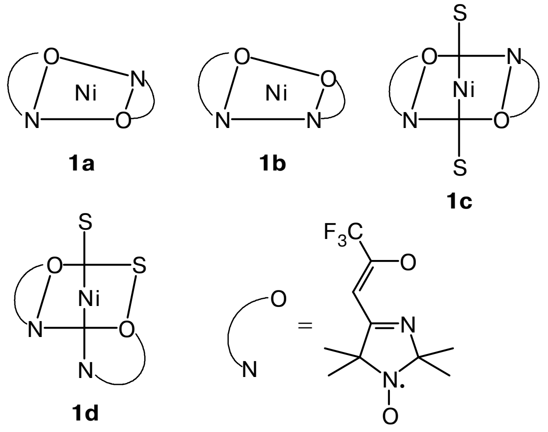


Fig. 5. Experimental Δ(1/*T*) dependence of the signal from the proton of the =CH— fragment of complex **1**.



1a **1b** **1c** **1d**

S is solvent molecule.

Two signals from the proton of the =CH— fragment can be detected in the 283—248 K temperature region in the spectrum of a solution of **1** in CD_2Cl_2 (see Fig. 6). The temperature interval of their appearance ranges only within 1—2 K. A possibility of NMR detection of so fine effects for heterospin systems is significant to demonstrate the sensibility of the method and, especially, to monitor the state of molecules in a solution in

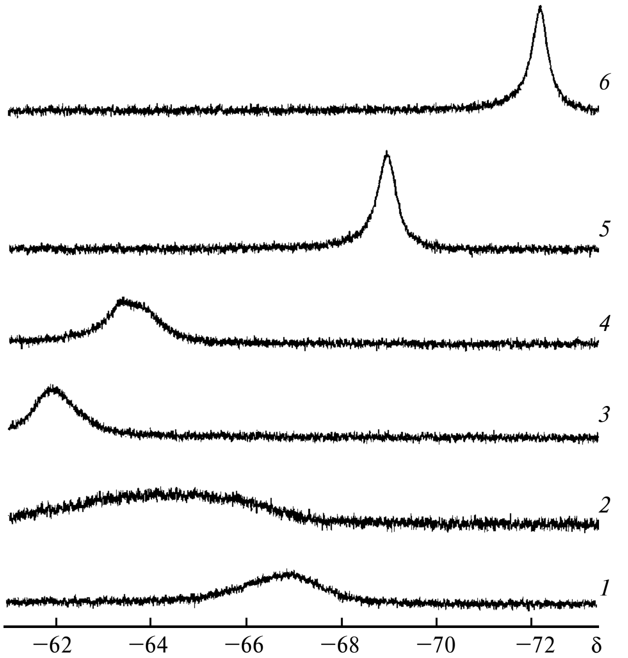
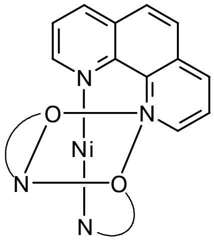


Fig. 6. Change in the signal from the proton of the =CH— fragment of complex **1** in the region of high fields with temperature changing: 248 (*1*), 251 (*2*), 260 (*3*), 263 (*4*), 273 (*5*), and 283 K (*6*).

designing molecular magnets. The presence of two signals can be related to the existence of molecules **1** in a solution as two conformations with the tetrahedral environment of the metal (**1a** and **1b**).

Stereochemical non-rigidity of molecules **1** can completely be suppressed by the additionally introduced bidentate ligand. The introduction of this ligand into molecule **1** transforms, in fact, all possible conformations into a single one (of the **1d** type). The model complex **2** with this configuration was synthesized by the reaction of bischelate **1** with phehanthroline.[11]

The ^{1}H NMR spectra of complex **2** at two temperatures are presented in Fig. 7. It is noteworthy that for **2** the signal from the proton of the =CH— fragment in the whole temperature interval of the measurements is detected in low fields (note that the same situation is observed for the mixed ligand complex **1** with 2,2′-dipyridyl, the structure of whose coordination site is completely similar to that in molecule **2**). The $\omega(1/T)$ and $\Delta(1/T)$ plots for the signal from the proton of the =CH— fragment in the ^{1}H NMR spectrum of complex **2** are presented in Fig. 8. The linear plot distinctly indicates that the Curie law is fulfilled and the structure of the mixed ligand complex **2** remains unchanged, unlike bischelate **1**, during temperature change. The data presented favor the fact that at a temperature below 240 K complex **1** in a solution (see Fig. 3) tends to take the *cis*-octahedral conformation of the **1d** type. Three conformations coexist at a higher temperature: two distorted tetrahedral and one *trans*-octahedral. For the tetrahedral conformations the signal from the proton of the =CH— fragment is detected in substantially higher fields (−50 to −80 ppm) than those for the *trans*-octahedral conformation (of the **1c** type). For the *trans*-octahedral complex,[12] *e.g.*, a solution of **1** in CD_3OD where only $NiL_2(CD_3OD)_2$ molecules exist, the signal from the proton of the =CH— fragment is detected in high fields at approximately −7 ppm. Also note that only solids of molecular magnets with the $NiL_2(ROH)_2$ composition and the *trans*-octahedral structure of the coordination unit are always crystallized from alcohol solutions of **1**.[12]



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Note some more specific feature of the NMR spectra of the Ni^{II} complexes with nitroxyl radicals. When the temperature of the sample under study increases, the paramagnetic shift of the signal from the proton of the =CH— fragment (in high fields) in the spectra of complex **1** increases (see Figs. 3 and 4, *a*) rather than decreases (in the absolute value), as it is demanded by the Curie law. This effect is related to the specifics of heterospin systems and can be explained rather simply. Since different in nature paramagnetic centers are present in complexes with radicals, we may assume that they can induce paramagnetic shifts with different signs. This assumption was confirmed in studying the temperature plot of the ^{1}H NMR spectrum of the specially synthesized complex **3** containing the diamagnetic analog of spin-labeled enaminoketone in complexes **1** and **2**.

Complex **3** was obtained by the reaction of an aqueous solution of $Ni(OAc)_2$ with an ethanolic solution of

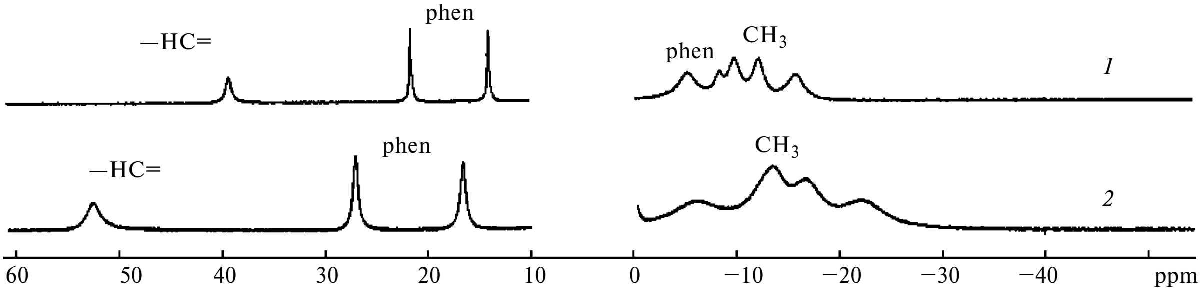


Fig. 7. ^{1}H NMR spectra of complex **2** at 313 (*1*) and 243 K (*2*).

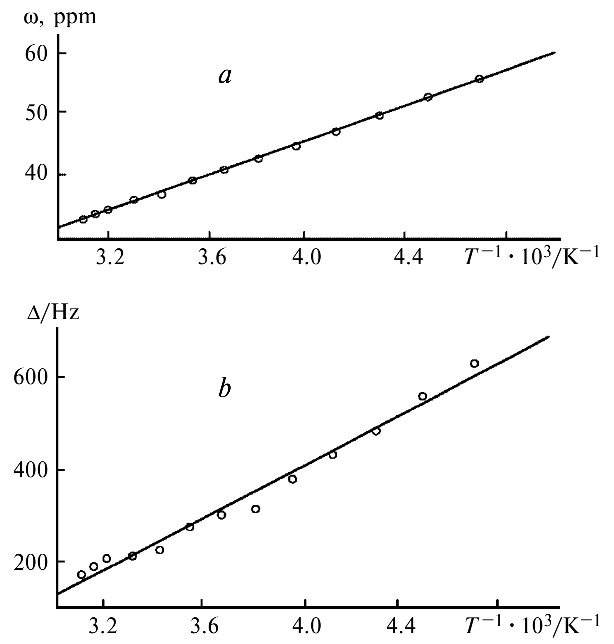
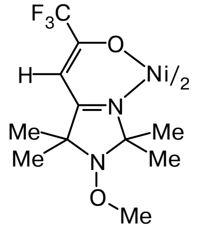


Fig. 8. The ω(1/*T*) (*a*) and Δ(1/*T*) (*b*) plots for the signal from the proton of the =CH— fragment in the spectrum of complex **2**.

the corresponding enaminoketone. Crystallization from a hexane—methanol mixture gives this complex as well formed crystals suitable for X-ray diffraction study. The structure of molecule **3** is presented in Fig. 9, *a*; the main bond lengths and bond angles are given in Table 1. As in the complexes with the paramagnetic ligand, in molecule **3** the coordination of the metal atom with the ligand is bidentate using the O and N atoms of the enaminoketone groups. Six-membered chelate cycles that formed are virtually planar (deviations of the atoms from the root-mean-square plane do not exceed 0.04 Å). The angle between the chelate planes in the solid is 76.8°. The nickel atom is localized on the second-order axis, which determines symmetry of the whole molecule as C_2. Unlike similar paramagnetic enaminoketone ligands containing the nitroxyl group, the imidazoline heterocycles in molecule **3** have the shape of an envelope with the inflection over the C(4)...C(5) line and an angle between the planes of the envelope of 15.5°. As a whole, the structure of **3** is molecular (Fig. 10), and only weak van der Waals contacts exist between the molecules in the solid phase. The compound has some specific features of the chemical behavior, in particular, unlike the heterospin complex **1**, complex **3** is not able to the formation of octahedral conformations. Therefore, unlike **1**, when crystallized from alcohol solutions, **3** forms the solid with the molecular structure with the distorted tetrahedral environment of the Ni^{2+} ion.



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As in the case of the tetrahedral conformations of complex **1**, at high temperatures the signal from the proton of the =CH— fragment in complex **3** is observed in the high field (Fig. 11). When the temperature decreases, this singlet behaves rather complicatedly due to the stereochemical nonridgidity of the molecule. Below 294 K it begins to be divided into two signals: below 233 K the higher-field signal is first broadened and then (below 203 K) is split into still two signals (here one should take into account a possibility of the appearance of different signals from different conformations and also from diastereomers because, as it has been mentioned above, in molecules **1** the imidazoline heterocycle is planar and in molecules **3** it has the shape of an envelope). However, for us the only thing is significant: the temperature plot of the paramagnetic shifts of all three signals from the =CH— fragments in the spectrum of **3** follows the Curie law, *i.e.*, with the temperature decrease

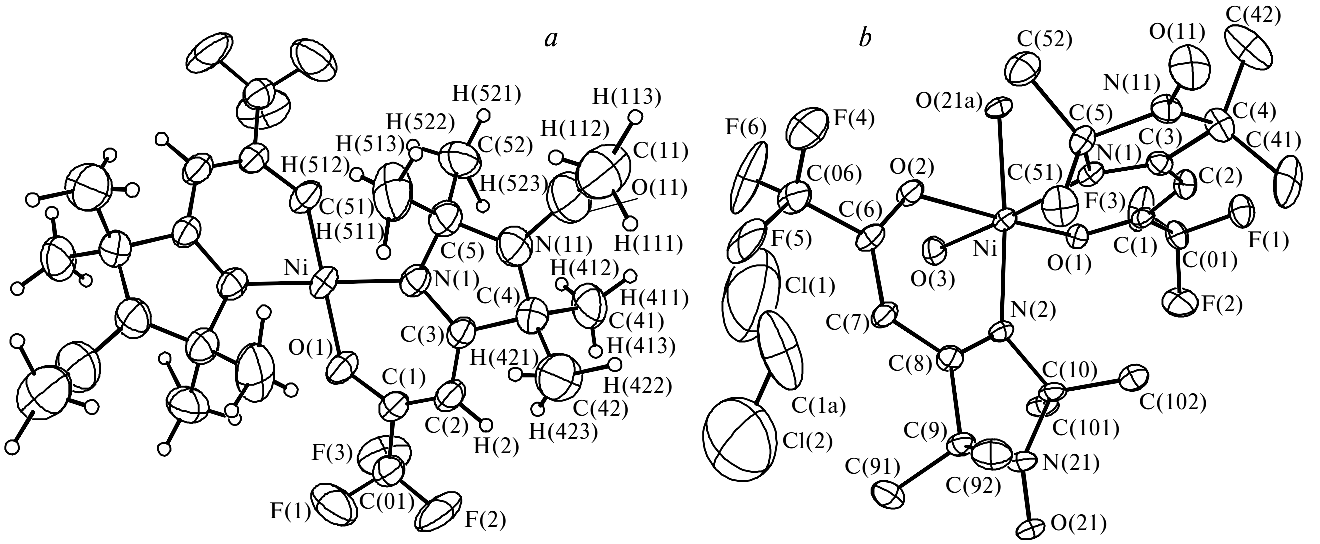

Fig. 9. Structures of molecule **3** (*a*) and molecular fragment **4** (*b*).

Table 1. Main bond lengths (*d*) and angles (ω) in molecules **3** and **4**

Bond	*d*/Å		Angle	ω/deg	
	3	**4**		**3**	**4**
Ni—O(1)	1.907(1)	1.995(5)	O(1)—Ni—N(1)	92.67(5)	90.5(2)
Ni—N(1)	1.952(1)	2.100(7)	C(1)—O(1)—Ni	125.7(1)	127.0(5)
Ni—O(3)		2.125(7)	O(1)—C(1)—C(2)	128.1(2)	127.9(8)
O(1)—C(1)	1.286(2)	1.273(9)	C(1)—C(2)—C(3)	123.4(1)	124.5(8)
C(1)—C(2)	1.339(2)	1.365(11)	N(1)—C(3)—C(2)	124.6(1)	126.8(8)
C(2)—C(3)	1.418(2)	1.440(11)	N(1)—C(3)—C(4)	112.7(1)	115.5(7)
C(3)—N(1)	1.309(2)	1.291(10)	N(11)—C(4)—C(3)	100.8(1)	98.3(6)
C(3)—C(4)	1.503(2)	1.523(11)	C(4)—N(11)—C(5)	110.3(1)	113.0(6)
C(4)—N(11)	1.457(2)	1.460(11)	N(1)—C(5)—N(11)	103.6(1)	102.6(6)
N(11)—O(11)	1.314(2)	1.263(8)	C(3)—N(1)—C(5)	110.4(1)	110.5(7)
N(11)—C(5)	1.463(2)	1.489(10)	C(3)—N(1)—Ni	125.1(1)	122.9(6)
C(5)—N(1)	1.461(2)	1.466(10)	C(5)—N(1)—Ni	124.5(1)	126.3(5)
O(11)—C(11)	1.337(4)		N(11)—O(11)—C(11)	123.9(2)	
Ni—O(2)		2.013(6)	O(2)—Ni—N(2)		89.6(2)
Ni—N(2)		2.112(7)	C(6)—O(2)—Ni		126.6(5)
Ni—O(21a)		2.131(6)	O(2)—C(6)—C(7)		130.1(8)
O(2)—C(6)		1.273(10)	C(6)—C(7)—C(8)		123.1(9)
C(6)—C(7)		1.368(12)	N(2)—C(8)—C(7)		126.4(8)
C(7)—C(8)		1.436(12)	N(2)—C(8)—C(9)		114.9(7)
C(8)—N(2)		1.313(10)	N(21)—C(9)—C(8)		98.8(6)
C(8)—C(9)		1.517(12)	C(9)—N(21)—C(10)		113.9(7)
C(9)—N(21)		1.444(10)	N(2)—C(10)—N(21)		100.8(6)
N(21)—O(21)		1.295(8)	C(8)—N(2)—C(10)		110.8(7)
N(21)—C(10)		1.515(10)	C(8)—N(2)—Ni		124.2(6)
C(10)—N(2)		1.484(10)	C(10)—N(2)—Ni		125.1(5)

the absolute value of the paramagnetic shift increases (Figs. 11 and 12, *a*). The paramagnetic broadening of the lines undergoes multiple broadenings and narrowing (Fig. 12, *b*), as for the complex with the radical **1**. Therefore, the deviation of the ω(*T*) plot from the Curie law for **1** (see Fig. 4), is due, in fact, to the induction of the paramagnetic shifts with different signs of the Ni^{II} ion and nitroxyl fragments, which determines the rather complicated character of a change in the paramagnetic shift of the proton of the =CH— fragment in the spectrum of **1** with the temperature change (see Fig. 3).

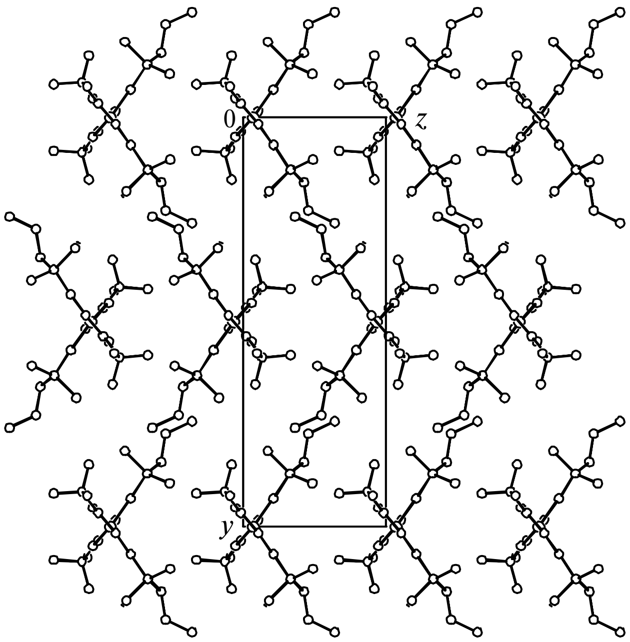

Fig. 10. Projection of structure **3** on the (100) plane.

Also note that, when the temperature changes, the signal is not detected in the spectrum of **3** in the region of low fields, as it takes place in the spectrum of **1** (see Fig. 3). This indicates one more effect of the influence of the presence of the paramagnetic ligand in the structure of the complex on the NMR spectra. In a heterospin molecule, with the temperature change the dynamics of the structure of the stereochemically non-rigid molecule of the complex changes the character of the interaction of spins, which can influence on the value of spin density and also its sign (in certain conformations), and this is detected, in fact, in the spectrum of **1** at temperatures below 240 K. Therefore, NMR allows the detection of the temperature regions where the exchange interaction between paramagnetic centers can be substantially different in character. If the structure of molecules is retained in main features during crystallization from a solution, then in the solid the exchange interactions can also differ substantially.[10] Thus, the study of the exchange-modulated hyperfine interaction provides a valuable information about the molecular dynamics in solutions of coordination compounds of paramagnetic ions of transition metals with stable nitroxyl radicals.

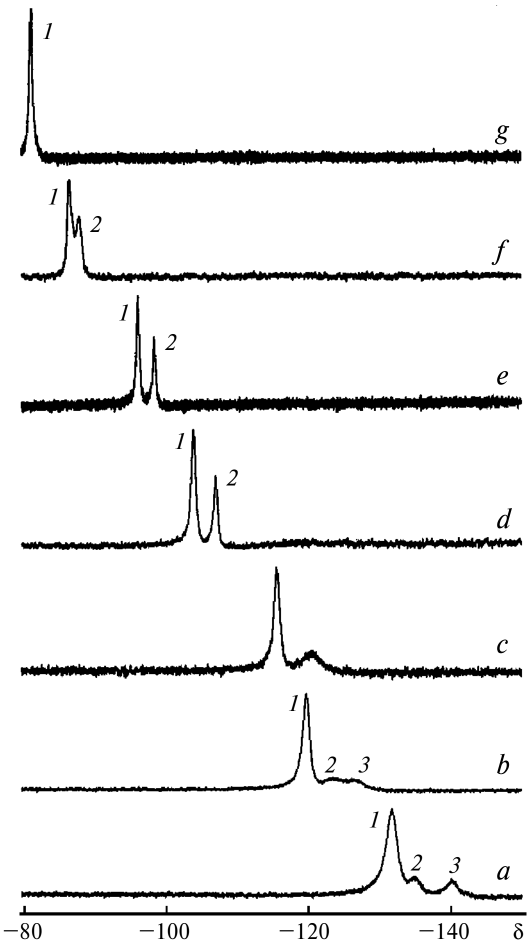

Fig. 11. Change in the signal from the proton of the =CH— fragment of molecule **3** with temperature changing: 193 (*a*), 203 (*b*), 213 (*c*), 243 (*d*), 263 (*e*), 283 (*f*), and 303 (*g*); numbering of signals corresponds to that in Fig. 12.

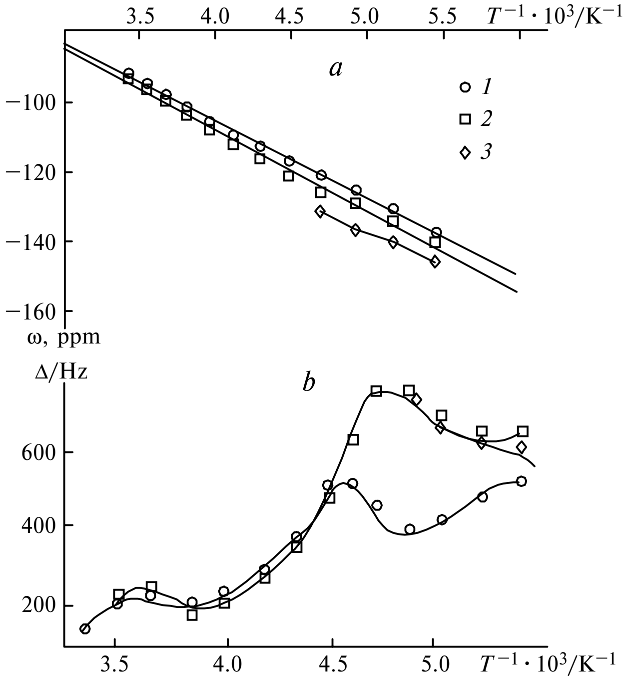

Fig. 12. Experimental ω(1/*T*) (*a*) and Δ(1/*T*) (*b*) plots of the signals from the protons of the =CH— fragments for different conformations of molecule **3**; numbering of signals corresponds to that in Fig. 11, *a*.

In continuation, we present a particular example as an illustration of the target synthesis of the heterospin solid containing the structural fragment in a certain conformation. We succeeded previously to obtain the solid of **1** as two polymorphs.[10] They both have the layered polymeric structure appeared due to the coordination by the Ni^{2+} ion of the O atoms of the nitroxyl groups of two adjacent bischelate molecules. However, in one modification (α) the oxygen atoms are coordinated to the *trans*-positions of the coordination octahedron, whereas in another modification (β) they are coordinated to the *cis*-positions. Under standard conditions, the α-modification is thermodynamically more stable, and the β-modification is gradually (on heating, rapidly) transformed into it.[10] For this reason, we easily obtained **1** in the form of the α-modification. We succeeded to isolate the β-modification from a solution in CH_2Cl_2 only on fast evaporating of the solvent, which is accompanied by cooling of the mixture. When single crystals of the β-modification are grown, the latter are always formed as doped crystals to the α-modification, and they were mechanically separated. The performed detection of the temperature plot of the ^1H NMR spectrum of a solution of **1** in CH_2Cl_2 (see Fig. 3) evidently showed that molecules **1** tend to take the *cis*-octahedral conformation (of the **1d** type) at the temperature below 238 K. Indeed, we easily obtained single crystals of **1** in the β-modification by the crystallization of **1** from a solution of anhydrous CH_2Cl_2 at a temperature below −40 °C. When we conducted such crystallizations without a special protection from moisture, we succeeded to isolate the previously unknown compound $[NiL_2(H_2O)] \cdot CH_2Cl_2$ (**4**), which in the solid phase is also layered polymeric. The structure of the fragment of $[NiL_2(H_2O)] \cdot CH_2Cl_2$ is presented in Fig. 9, *b*, and the scheme of the formation of the polymer layer in **4** is shown in Fig. 13. In structure **4** the paramagnetic ligands perform different functions: one of them is bidentate-cyclic (as in structure **3**), and the second ligand is tridentate bridging-cyclic (see Fig. 13). The environment of the metal atom is a distorted octahedron, whose equatorial plane is formed by the O atoms and one N atoms of the enaminoketone groups of the paramagnetic ligands and the O atom of the water molecule, and the axial positions are occupied by the bridging O atom of the nitroxyl group of the tridentate ligand of the adjacent molecule and the second N atom (the main bond lengths and angles are presented in Table 1). Thus, the direct coordination of the O atom of the nitroxyl group of the adjacent molecule results in the formation in structure **4** of polymeric chains extended

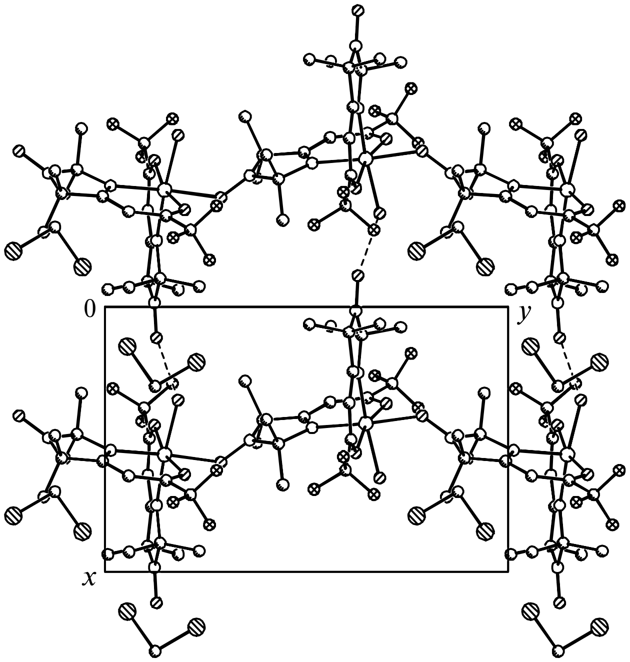

Fig. 13. Projection of structure **4** to plane (001).

along the [010] direction. The chains are linked between each other to form layers by H bonds formed between the O atom of the nitroxyl group of the bidentate paramagnetic ligand of the adjacent molecule and the coordinated water molecule (Fig. 13). The CH_2Cl_2 molecules are bound to the chains by weak hydrogen bonds of the Cl—Ow type (3.556 Å). It is important that, regardless of the conditions of the crystallization of **1** from a CH_2Cl_2 solution at a low temperature (both in the presence or absence of moisture), molecules of **1** in a solution tend to take the conformation of the **1d** type, whose structural motive is retained in both the solid of the β-modification[10] and the solid of **4**.

Thus, despite many effects capable of appearing in NMR spectra of heterospin compounds (which somewhat complicates the analysis procedure), the study of the temperature dependence of the spectra of such systems can be highly efficient for choosing the solvent and temperature regime during the growth of heterospin crystals in which multispin molecules exists in a certain conformation.

Experimental

Solutions of complexes in $CDCl_3$ and CD_2Cl_2 with concentrations from $3 \cdot 10^{-2}$ to 10^{-1} mol L^{-1} were studied on a Bruker DPX-250 spectrometer (250 MHz) in the 323—183 K temperature interval. The accuracy of temperature measurement was ±1 K. Signals were assigned on the basis of previously published data.[6] Before measurements, samples of compounds were thoroughly dried *in vacuo* at 333 K for 20 h. Solvents were purified according to standard procedures. Theoretical and experimental curves were plotted in the MathCAD 7.0 Pro program package. Correlation coefficients for complexes **2** and **3** were calculated using the least-squares method.

A set of experimental reflections for complex **3** was obtained on an Enraf Nonius CAD4 automated four-circle diffractometer and for **4** on a Bruker P4 instrument (Mo-Kα radiation, a graphite monochromator, θ/2θ scan with a variable velocity) using a standard procedure. The absorption for **3** was applied by curves of azimuth scan, and that for **4** was ignored. Structures were solved by the program of direct methods and refined by the full-matrix least-squares method in the anisotropic approximation for all nonhydrogen atoms. Positions of hydrogen atoms were localized in difference electron density syntheses and refined in the isotropic approximation along with nonhydrogen atoms. The resulting values of the R factors are the following: $R_1 = 0.0474$, $wR_2 = 0.1264$ for **3** and $R_1 = 0.0772$, $wR_2 = 0.1776$ for **4**. All calculations in the solution and refinement of structures were performed using the SHELX97 program complex. The main bond lengths in molecules **3** and **4** are presented in Table 1. The coordinates and equivalent thermal factors of nonhydrogen atoms were deposited in the Cambridge Crystallographic Data Centre.

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References

1. A. Caneschi, D. Gatteschi, and P. Rey, *Progr. Inorg. Chem.*, 1991, **39**, 331.
2. O. Kahn, *Molecular magnetism*, VCH, New York, 1993.
3. H. Iwamura, K. Inoue, and T. Hayamizu, *Pure Appl. Chem.*, 1996, **68**, 243.
4. V. I. Ovcharenko and R. Z. Sagdeev, *Usp. Khim.*, 1999, **68**, 381 [*Russ. Chem. Rev.*, 1999, **68**, 243 (Engl. Transl.)].
5. T. Yoshida and S. Kaizaki, *Inorg. Chem.*, 1999, **38**, 1054.
6. A. M. Atskanov, A. V. Podoplelov, K. E. Vostrikova, V. I. Ovcharenko, S. V. Larionov, L. B. Volodarskii, A. K. Mikitaev, and R. Z. Sagdeev, *Sibirskii Khim. Zh.* [*Siberian Chem. J.*], 1991, No. 2, 57 (in Russian).
7. V. K. Voronov, *Metod paramagnitnykh dobavok v spektroskopii YaMR* [*Method of Maramagnetic Additives in NMR Spectroscopy*], Nauka, Sib. Otd-nie, Novosibirsk, 1989, 168 pp. (in Russian).
8. R. S. Drago, *Physical Methods in Chemistry*, W. B. Saunders Co., Philadelphia—London—Toronto, 1977.
9. V. K. Voronov, T. E. Moskovskaya, and V. I. Glukhikh. *Koord. Khim.*, 1979, **5**, 218 [*Sov. J. Coord. Chem.*, 1979, **5** (Engl. Transl.)].
10. V. I. Ovcharenko, G. V. Romanenko, V. N. Ikorskii, R. N. Musin, and R. Z. Sagdeev, *Inorg. Chem.*, 1994, **33**, 3370.
11. V. I. Ovcharenko, G. V. Romanenko, I. V. Korobkov, V. N. Ikorskii, I. V. Ovcharenko, R. N. Musin, K. E. Vostrikova, A. V. Podoplelov, O. V. Shishkin, and Yu. T. Struchkov, *Zh. Strukt. Khim.*, 1998, **39**, 901 [*J. Struct. Chem.*, 1998, **39** (Engl. Transl.)].
12. V. N. Ikorskii, V. I. Ovcharenko, Y. G. Shvedenkov, G. V. Romanenko, S. V. Fokin, and R. Z. Sagdeev, *Inorg. Chem.*, 1998, **37**, 4360.

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