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Influence of the Solvent Nature on the Spin Equilibrium in Solutions of the Cobalt(II) Phenylborate Hexa-*n*-Butylsulfide Clathrochelate by the Paramagnetic NMR Spectroscopy Data

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Abstract—The spin state of the cobalt(II) phenylborate hexa-*n*-butylsulfide clathrochelate in solutions is studied by paramagnetic NMR spectroscopy. This cage complex is shown to undergo the temperature-induced spin transition in solvents of different nature (acetonitrile, chloroform, dichloromethane, and benzene). The previously developed method for an analysis of paramagnetic shifts in NMR spectra allows the determination of the thermodynamic parameters (enthalpy and entropy) of the spin equilibrium in the solutions. In spite of the conformational rigidity of the macrobicyclic tris(dioximate) molecules, substantial changes in the electronic structures and spin equilibrium parameters are observed depending on the polarity of the solvent used. This provides opportunities for fine tuning of spin switch characteristics by changing this parameter of the medium.

Keywords: spin transition, paramagnetic NMR, clathrochelates, cobalt(II) complexes

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INTRODUCTION

The preparation of new functional materials, whose properties are determined at the molecular level, is the most important problem of modern materials science. Spin switches exhibiting bistability depending on the environmental conditions are among these molecular materials [1]. Owing to this unique property, they can successfully be applied in modern molecular electronics [2], spintronics [3, 4], magnetic resonance imaging [5], sensorics [6–8], and food chemistry [9]. In the most cases, spin switches are based on transition metal complexes capable of both manifesting the properties of single-molecule magnets and undergoing spin transitions. The first of them exhibit quantum bistability when the external magnetic field changes and, therefore, they are promising for the use in quantum calculations [10]. The complexes of the second type undergoing the spin transition manifest bistability for the total electron spin moment (S) depending on the environmental conditions, in particular, on changing temperature [11] and/or pressure [12], under electromagnetic field application [13], or changing acidity of the medium [14]. The complexes of iron(II) [15, 16] and cobalt(II) [17, 18] ions experiencing the spin transition were studied most widely. The latter complex can exist in two spin states: the low-spin state with the total electron spin quantum number $S = 1/2$ and the high-spin state with $S = 3/2$.

The most important characteristic of a spin switch is the half-transition temperature ($T_{1/2}$) at which the corresponding spin states are equally populated. From the practical point of view, the half-transition temperature is most convenient to accomplish a specified spin switch. This parameter reflects the electronic structure of the molecule and naturally depends on its chemical nature (i.e., on the order of covalent and donor—acceptor bonds in the molecule). Therefore, the targeted molecular design of transition metal complexes with a specified $T_{1/2}$ is undoubtedly an urgent problem in the development of new “smart” magnetoactive materials and devices.

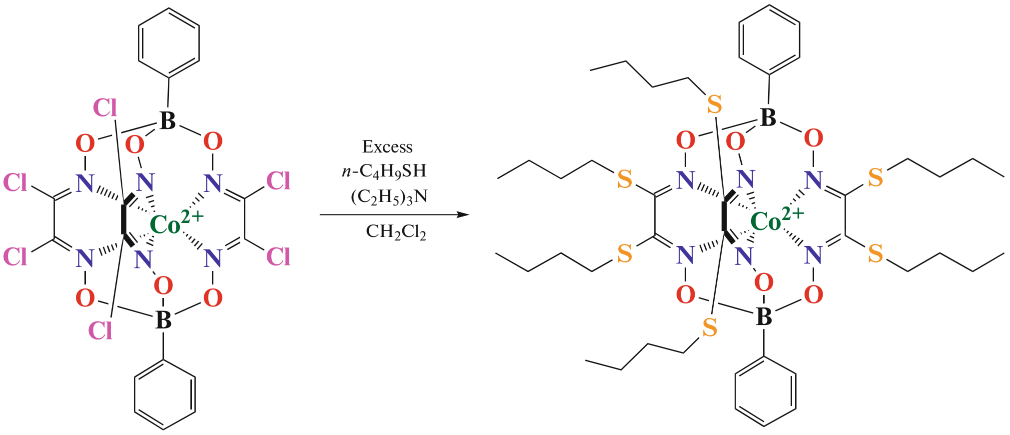
Macrobicyclic tris-α-diiminates of transition metals (clathrochelates [19, 20]) possess unique physical and physicochemical properties due to the 3D geometry of their macropolycyclic encapsulating ligands providing their conformational rigidity and the entire isolation of the central metal ion from external factors [19, 20]. Owing to these specific features, the cobalt(II) clathrochelates have high magnetic anisotropy and chemical stability in various media, which allowed them to be proposed as promising paramagnetic labels for structural biology [21], paramagnetic probes for MRI [22], monoionic monomolecular magnets [23], and spin switches [24]. However, in spite of a high conformational rigidity of their 3D molecules, the nature of the external medium can exert a significant effect on the magnetic characteristics of these metal-centered systems. In particular, the influence of polymorphism of the crystals of one of the cobalt(II) clathrochelates on the electronic structure parameters and remagnetization barrier for its polymorphic crystalline forms has previously been found [25, 26]. This was a prerequisite for the further study of the influence of the nature of the medium on these parameters in both the solid phase and solutions. For these purposes, we chose the typical representative of cobalt(II) clathrochelates formed by the macrobicyclic phenylborate hexa-*n*-butylsulfide ligand. This complex was found [27] to exhibit the temperature-induced spin transition in crystals. In this work, we used our earlier developed [28, 29] approaches of paramagnetic NMR spectroscopy to study the characteristics of the spin transition of this cobalt(II) clathrochelate in solvents of different nature.

EXPERIMENTAL

The cobalt(II) phenylborate hexa-*n*-butylsulfide clathrochelate (**I**) (Scheme 1) synthesized according to a known procedure [27] was used. Its hexachloroclathrochelate precursor was synthesized by the template condensation on the cobalt(II) ion matrix [19]. The composition and structure were confirmed by the elemental analysis and ^{1}H NMR spectroscopy data. Elemental analyses to carbon, nitrogen, and hydrogen were carried out on a Carlo Erba microanalyzer (model 1106).

For $C_{42}H_{64}B_2N_6O_6S_6Co$			
Anal. calcd., %	C, 49.31	H, 6.26	N, 8.22
Found, %	C, 49.33	H, 6.17	N, 8.25

^{1}H NMR ($CDCl_3$; 300 K; δ, ppm): 0.60 (br.s, 30H, CH_2-CH_3), 0.93 (br.s, 12H, CH_2), 6.53 (br.s, 12H, $S-CH_2$), 10.05 (br.s, 2H, *para*-Ph), 10.58 (br.s, 4H, *meta*-Ph), 16.45 (br.s, 4H, *ortho*-Ph).



I

Scheme 1.

^{1}H NMR spectra were recorded for solutions of complex **I** in CD_3CN, CD_2Cl_2, $CDCl_3$, and C_6D_6 at different temperatures on a Bruker Avance 300 spectrometer (300.22 MHz). Chemical shifts (δ, ppm) in the spectra were determined relative to the residual signal of the solvent (δ_{H}^{1} for CD_3CN, CD_2Cl_2, C_6D_6, and $CDCl_3$ is 1.94, 5.32, 7.26, and 7.16 ppm, respectively). The ^{1}H NMR spectra were detected using the following parameters: spectral range 250 ppm, detection time 0.1 s, relaxation delay time 0.1 s, pulse duration 9.0 μs, and acquisition number 512. If it was necessary to increase the signal/noise ratio, the determined free induction decays were processed using exponential weighing with the coefficient to 3 Hz.

All quantum-chemical calculations for a molecule of complex **I** were performed using the ORCA 5.0.3 software [30] in the framework of the density functional theory (DFT). The geometry was optimized for both the low-spin (S = 1/2) and high-spin (S = 3/2) states using the B3LYP hybrid functional [31], def2-TZVP basis set [32], and approximation of the RIJCOSX integrals [33] to shorten the calculation time. The molecular structure of this clathrochelate previously determined by single-crystal XRD was used as the initial approximation [27]. The g tensor and hyperfine coupling tensors for protons of the molecule of complex **I** were determined from the calculated geometries of the high- and low-spin states using the B3LYP hybrid functional [34] and def2-TZVP basis set.

The contact shift was calculated by the following equation:

$$\delta_i^{\mathrm{c}} = \frac{4\pi\mu_{\mathrm{B}}^2}{9kT} g^{iso}\rho_i, \qquad (1)$$

where g^{iso} is the isotropic g tensor, and ρ_i is the spin density on the ith nucleus.

RESULTS AND DISCUSSION

We have previously developed the method for studying the spin state of the transition metal complexes in solutions using paramagnetic NMR spectroscopy [28]. Unlike the more popular Evans method, the efficiency of this approach is independent of the purity of the studied sample. The essence of the approach is the detection of NMR signals for this paramagnetic complex in the solution followed by an analysis of the NMR signals. In this case, the experimentally observed chemical shift is determined by three components: diamagnetic, contact, and dipole contributions (Eq. (2)).

$$\delta = \delta_{\mathrm{dia}} + \delta_{\mathrm{c}} + \delta_{\mathrm{d}}. \qquad (2)$$

The last two contributions are determined by the interaction of the magnetic moments of the nucleus and electron. Their isotropic part results in the contact Fermi shift, and the anisotropic part gives the dipole shift. From the physical point of view, the first shift is caused by the spin density redistribution on the nucleus through the system of molecular orbitals (Eq. (1)), whereas the second shift is due to the dipole–dipole interaction of magnetic moments. As a consequence, the dipole shift directly depends on the mutual arrangement of interacting particles in the space (Eq. (3)), which forms a basis for the concept of paramagnetic labels for studying spatial structures of biological macromolecules [35]

$$\delta_{\mathrm{d}} = \frac{1}{12\pi r^3} \times \left[\Delta\chi_{\mathrm{ax}}\left(3\cos^2\theta - 1\right) + \frac{3}{2}\Delta\chi_{\mathrm{rh}}\sin^2\theta\cos 2\varphi\right], \qquad (3)$$

where r, θ, and φ are the spherical coordinates of the nucleus in the system of coordinates of the magnetic susceptibility tensor (χ), and $\Delta\chi_{\mathrm{ax,\,rh}}$ are the axial and rhombic anisotropies of tensor χ.

The molecule of the studied cobalt(II) complex has the axial C_3 pseudosymmetry. In this case, Eq. (3) is simplified

$$\delta_{\mathrm{d}} = \frac{1}{12\pi r^3}\left[\Delta\chi_{\mathrm{ax}}\left(3\cos^2\theta - 1\right)\right]. \qquad (4)$$

Different spin states of complex **I** are characterized by different numbers of lone electrons and their distributions in the molecule, which evidently affects the contact and dipole shifts in the NMR spectra. Thus, the study of the paramagnetic NMR shifts allows one to establish the spin state of clathrochelate **I**, which is the purpose of the aforementioned approach of paramagnetic NMR spectroscopy. When the both spin states are populated and the equilibrium between them is rapidly (in the NMR time scale) established, the observed chemical shift will be weighted average

$$\delta = \delta^{\mathrm{LS}}\eta^{\mathrm{LS}} + \delta^{\mathrm{HS}}\eta^{\mathrm{HS}}, \qquad (5)$$

where δ^{LS} and δ^{HS} are the chemical shifts of a given nucleus in the low- and high-spin states of the molecule, respectively; η^{LS} and η^{HS} are the populations of these states, and $\eta^{\mathrm{LS}} + \eta^{\mathrm{HS}} = 1$.

For the temperature-induced spin transition, the populations of the spin states are temperature-dependent according to the thermodynamic parameters

$$K = \frac{\eta_{\mathrm{T}}^{\mathrm{HS}}}{\eta_{\mathrm{T}}^{\mathrm{LS}}} = e^{\frac{-\Delta H + T\Delta S}{RT}}, \qquad (6)$$

where K is the equilibrium constant of this transition; ΔH and ΔS are the corresponding enthalpy and entropy for this process, respectively; and R is the universal gas constant.

The Curie law is usually used in an analysis of the spin equilibrium by the method of paramagnetic NMR spectroscopy, whence it follows that the temperature dependence of the paramagnetic shift obeys the equation

$$\delta^{\mathrm{par}} = \frac{C}{T}. \qquad (7)$$

Nevertheless, we have previously shown [36, 37] that Eq. (7) is valid only for the contact shift in the NMR spectra of the cobalt(II) complexes in the high-spin state. The temperature dependence of the dipole shift is described by quadratic Eq. (8), which is a consequence of zero-field splitting.

$$\delta^{\mathrm{d,\,HS}} = \frac{A}{T} + \frac{B}{T^2}. \qquad (8)$$

In the case of the low-spin state of the cobalt(II) ion, Eq. (7) is valid for both contributions to the paramagnetic shift, since an idea of zero-field splitting is inappropriate for the state with $S = 1/2$.

Thus, in the framework of the present work, we propose to describe the experimentally observed chemical shift for the cobalt(II) complexes as follows:

$$\delta_T = \delta^{\mathrm{dia}} + \frac{a}{T} + \left(\frac{b}{T} + \frac{c}{T^2}\right)\frac{e^{\frac{-\Delta H + T\Delta S}{RT}}}{1 + e^{\frac{-\Delta H + T\Delta S}{RT}}}, \qquad (9)$$

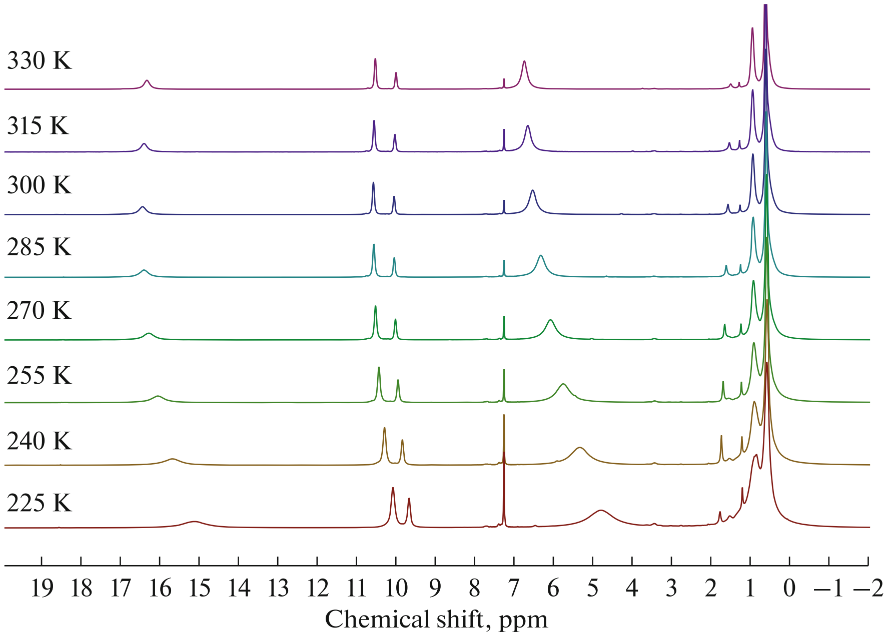


Fig. 1. ^{1}H NMR spectra of a solution of complex **I** in $CDCl_3$ recorded in a temperature range of 225–330 K.

where a, b, and c are the parameters of the model. The model becomes solvable for spectra recording at three different temperatures, which is quite appropriate for routine NMR experiments.

Equation (9) was used to determine the spin equilibrium parameters of two aforementioned forms of complex **I** in solvents of different nature (acetonitrile, benzene, chloroform, and dichloromethane). The ^{1}H NMR spectra of solutions of complex **I** detected in a wide temperature range indicate the occurrence of the temperature-induced spin transition, whereas Eqs. (7) and (8) assume a monotonic decrease in the chemical shifts with increasing temperature (Fig. 1).

An analogous pattern is observed for other solvents studied (Fig. 2) indicating, on the one hand, that the aforementioned spin transition 1/2 → 3/2 occurs in all cases. On the other hand, the chemical shifts of signals of its protons differ significantly for these solutions of complex **I**. The relative difference between them will be more substantial if the corresponding diamagnetic contribution, which depends weakly on the solvent nature, is subtracted.

The approximation of the experimentally observed chemical shifts using Eq. (9) made it possible to determine the thermodynamic parameters of the studied spin transition in all solvents (Table 1) and to visualize the temperature dependence of the spin state population (Fig. 3).

A correlation is observed between the solvent polarity and thermodynamic parameters of the aforementioned spin equilibrium: the enthalpy of transition ΔH and the temperature of half-transition $T_{1/2}$ increase with an increase in the dielectric permeability of the solvent, which can be related to an increase in the charges on the donor nitrogen atoms of the macrobicyclic ligand upon its interaction with the polar solvent molecules (Fig. 4).

To conclude, the spin state of the cobalt(II) phenylborate hexa-*n*-butylsulfide clathrochelate in solutions was studied using the proposed method of paramagnetic NMR spectroscopy. This cage complex was

Table 1. Thermodynamic parameters of the spin transition 1/2 → 3/2 for complex **I** in different solvents

Solvent	ΔH, kJ/mol	ΔS, J K^{-1} mol^{-1}
$CDCl_3$	8.2 (0.1)	33.3 (0.1)
CD_3CN	10.8 (0.4)	37.5 (0.2)
C_6D_6	7.1 (0.1)	30.2 (0.1)
CD_2Cl_2	9.6 (0.3)	36.5 (0.2)

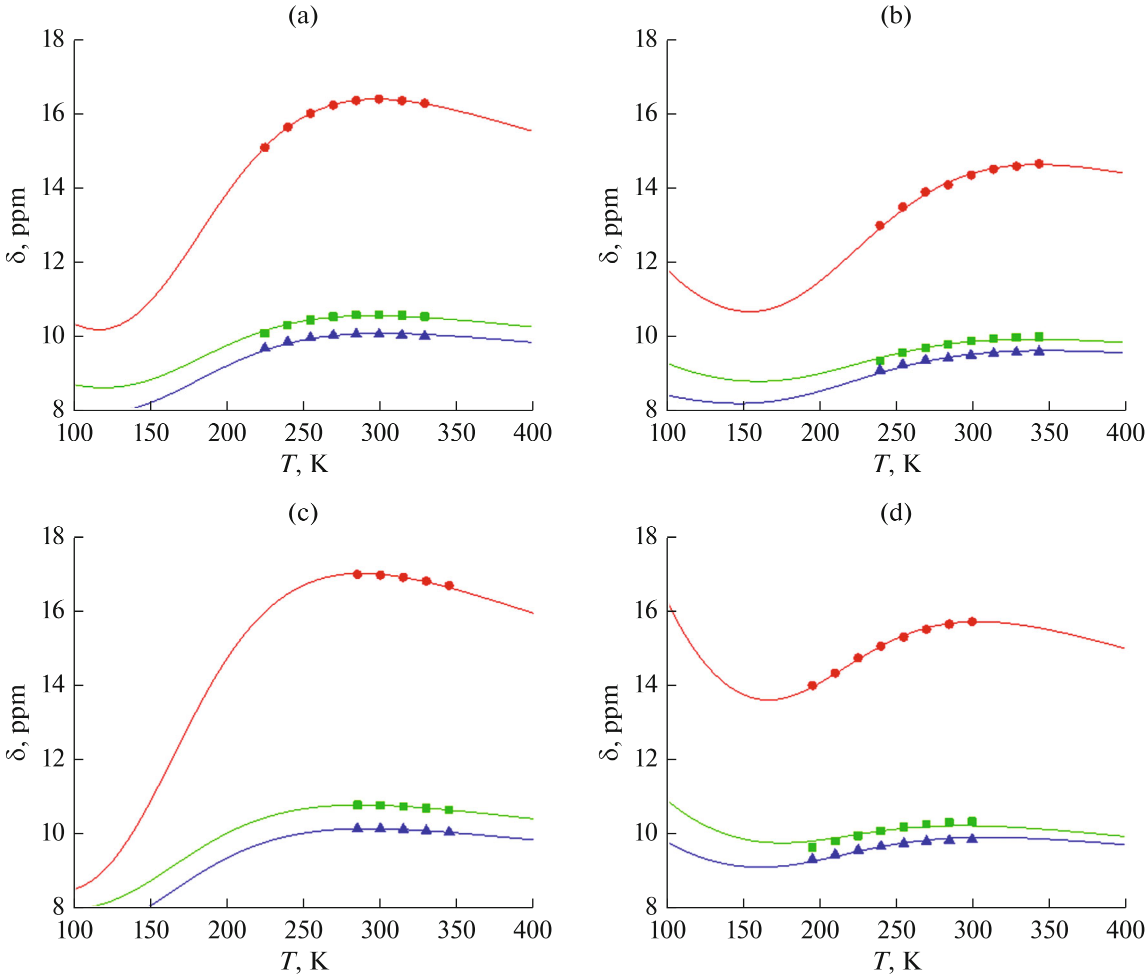


Fig. 2. Temperature dependences of the chemical shifts in the ^{1}H NMR spectra of complex **I** in different solvents: (a) $CDCl_3$, (b) CD_3CN, (c) C_6D_6, and (d) CD_2Cl_2. Data for the following protons of the macrobicyclic molecule of complex **I**: (●) *ortho*-Ph, (■) *meta*-Ph, and (▲) *para*-Ph. Solid lines correspond to the approximation using Eq. (9).

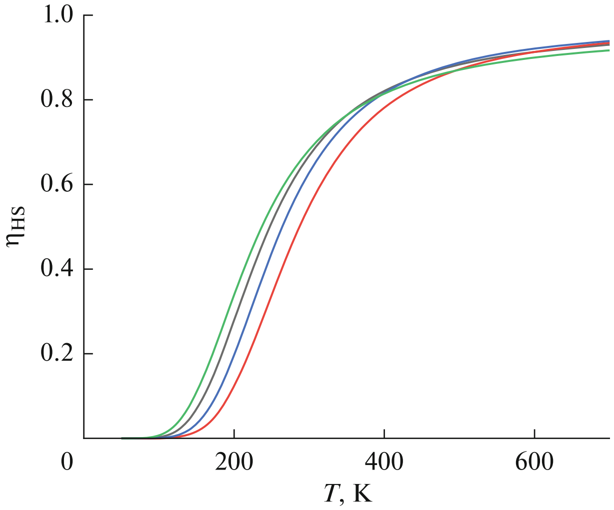


Fig. 3. Dependences of the population of the high-spin state of complex **I** in $CDCl_3$ (black color), CD_3CN (red color), C_6D_6 (green color), and CD_2Cl_2 (blue color).

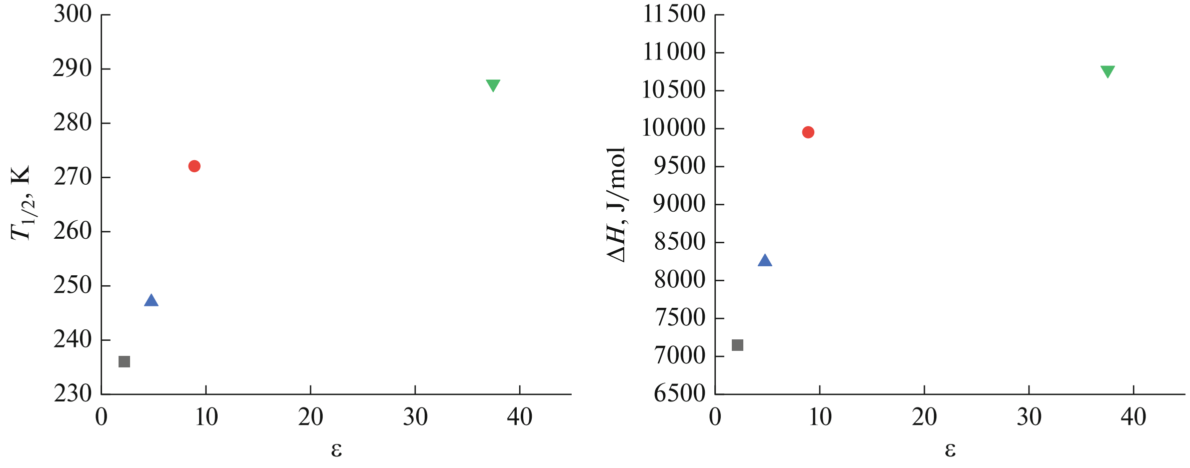


Fig. 4. Influence of the dielectric permeability of the solvent in the enthalpy Δ*H* and half-transition temperature $T_{1/2}$ of the spin equilibrium in solutions of complex **I** in (▲) $CDCl_3$, (▼) CD_3CN, (■) C_6D_6, and (●) CD_2Cl_2.

found to undergo the temperature-dependent spin transition in a medium of solvents of different nature, and the thermodynamic characteristics of the corresponding spin equilibrium were determined. In spite of the conformational rigidity of the polyazomethine quasi-aromatic 3D molecule, substantial changes in its electronic structure and spin equilibrium parameters are observed depending on the solvent polarity, which provides possibilities for fine tuning of characteristics of a spin switch using a change in the polarity of the medium.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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