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"SPIN PHYSICS, SPIN CHEMISTRY, AND SPIN TECHNOLOGY"

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## Study of conformations of 1-phenyl-3-(quinolin-8-ylamino)prop-2-en-1-one by NMR, UV-spectroscopy and DFT calculations

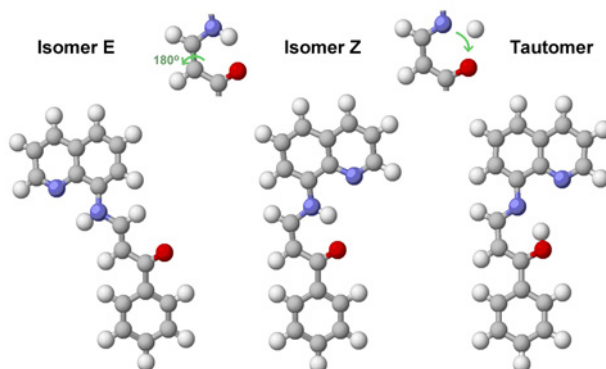
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Due to their high reactivity, enaminones are a large class of organic compounds that play an important role in organic synthesis. They are also widely used for the synthesis of biologically active molecular candidates – antibacterial, anti-inflammatory, anticonvulsant and anticancer agents. Enaminones can serve as promising ligands for the synthesis of metal complexes. The study of the tautomerism of the enaminone molecules and the determination of their conformations is important because the various conformations of the enaminones have different reactivity in the synthesis of metal complexes. Enaminon molecules also contain double bonds, which determine the possibility of their E-Z photoisomerization. In order to determine the presence or absence of photoisomerization of molecules of various chemical compounds, NMR and UV spectroscopy are usually used.

This work is aimed at the synthesis and study of the structure and tautomeric transformations of 1-phenyl-3-(quinolin-8-ylamino)prop-2-en-1-one molecules. The molecules of this enaminone can exist in three conformations – isomer E, isomer Z and enol-tautomer (Fig. 1). 1D and 2D NMR, as well as UV-spectroscopy allowed us to establish that almost all molecules of the studied substance, regardless of the polarity of the solvent (hexane, carbon tetrachloride, chloroform, acetone, acetonitrile, dimethyl sulfoxide), are the Z-isomer. It agrees with the results of the calculations performed by the DFT method with CAM-B3LYP functional and the def2-TZVP basis set. Exposure to UV radiation with  $\lambda = 365$  nm or heating a solution of the enaminone in dimethyl sulfoxide transforms some part of the enaminone molecules into the E-isomer (about 10%).



**Fig. 1.** The possible conformations of 1-phenyl-3-(quinolin-8-ylamino)prop-2-en-1-one.

## A lipid system in the ionic liquid – water mixtures studied by magnetic resonance measurements and molecular dynamics

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An ionic liquid (IL) is a salt in the liquid state. Ionic liquids have many potential applications. For instance, they can be used as electrolytes or powerful solvents. However, the toxic effects of ILs to biological objects are discussed if leaked into the environment. Investigations of the interaction of the ionic liquid with the biomembranes can be important to uncover the effects of ionic liquids on the biological bodies.

In this work, we discuss the features of the phase behavior and molecular mobility of a system consisting of lecithin at a concentration of 2% by weight in a mixture of solvents of ethylammonium nitrate (EAN) with deuterated water ( $D_2O$ ).

Analysis of spectra by the  $^{31}P$  NMR spectroscopy revealed two lipid phases in the systems: lamellar phase in the lecithin –  $D_2O$  system, and an isotropic phase in the lecithin – EAN system. In a  $D_2O$  – EAN mixture, the ratio of these two phases correlates with the proportions of  $D_2O$  and EAN solvents.

Diffusion NMR experiments were carried out using the pulsed-field gradient method. The self-diffusion coefficient (SDC) value related to lipids in EAN can be associated with the movement of diffusing micelles with a size  $\sim 20$  nm recorded in the  $^{31}P$  spectrum as an isotropic signal; the SDC related to lipids in  $D_2O$  may be associated with the movement of diffusing vesicles with a size of  $\sim 100$  nm.

As the proportion of  $D_2O$  in the  $D_2O$ -EAN solvent mixture increases, the self-diffusion coefficients related to the ionic liquid and lipids increase, i.e. the system becomes more mobile, which may be due to a decrease in viscosity.

According to NMR relaxometry data, the transverse magnetization decays for the lipid system in a mixture of  $D_2O$ -EAN solvents (in the ratios from 80/20 to 20/80), are due to the sum of contributions from three components, which indicates the presence in the system of components with different molecular mobility: “liquid-phase” and components associated with the movement of diffusing micelles and vesicles observed in  $^{31}P$  spectra.

Using molecular dynamics method, a uniform distribution of particles in the system (ratio of EAN/ $H_2O$  is 35/65) was observed with formation of a network of hydrogen bonds between ethylammonium and nitrate ions with  $H_2O$  molecules. For the EAN system with water, the SDC of the EAN components is increased significantly, as was observed in the diffusion NMR experiments. This can be explained by the fact that the hydration of EAN ions weakens the strong Coulomb and hydrogen interactions between cations and anions, which leads to a decrease in viscosity. An analysis of the radial distribution function showed that water hydrates the polar part of the  $[NH_3]^+$  cation more preferentially than the  $[NO_3]^-$  anion.

## Mixed-valence iron complexes as multifunctional magnetic materials

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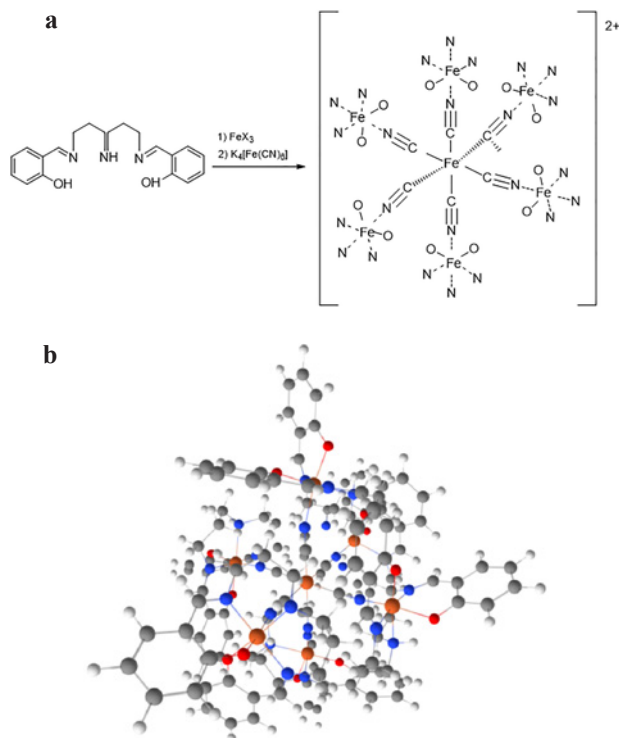
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Now, there is great interest in the search for materials that can be used to create fundamentally new devices for recording and storing information. This requires substances whose properties change reversibly under the influence of external factors. Molecular magnets are promising representatives of such compounds.

Multinuclear mixed-valence iron complexes have been synthesized, and their magnetic properties have been studied in this work. Three heptanuclear complexes with the general structural formula have been used as samples  $[\text{Fe}(\text{II})(\text{CN})_6\{\text{Fe}(\text{III})(\text{L})\}_6]\text{X}_2$ , where L = dianion of N,N'-bis[(2-hydroxyphenyl)methylene]-4-azaheptane-1,7-diamine (Salten), X = Cl (complex **1**), L = Salten, X = NCS (complex **2**), L = dianion of N,N'-



**Fig. 1.** **a** Synthetic route for preparation of the complex **2**; **b** 3D view of the complex **2**.

bis[(2-hydroxy-4-octadecyloxyphenyl)methylene]-4-azaheptane-1,7-diamine (18 Salten), X = Cl (complex **3**).

A liquid crystalline thermotropic phase for complex **3** has been identified by polarizing microscopy. The magnetic properties of these complexes have been studied by EPR and vibrational magnetometry in the temperature range from 5 to 300 K. The structure and properties of the synthesized compounds have been modeled by *ab initio* methods.

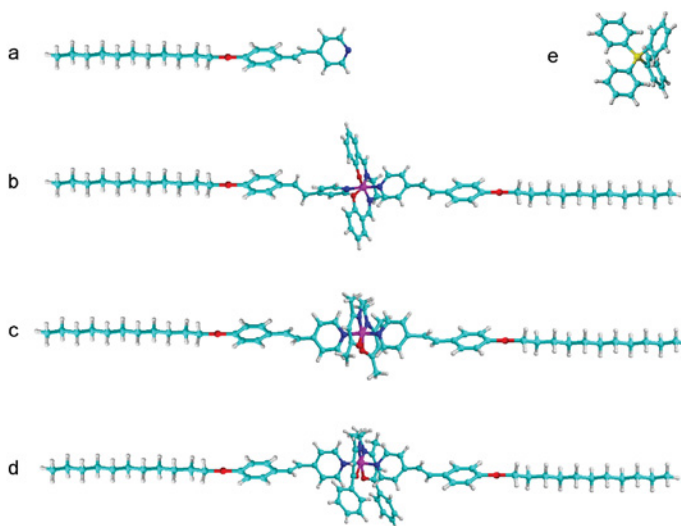
## Study of a series of the Fe(III) complexes with photoisomerizable axial ligands by NMR, EPR and UV-spectroscopy

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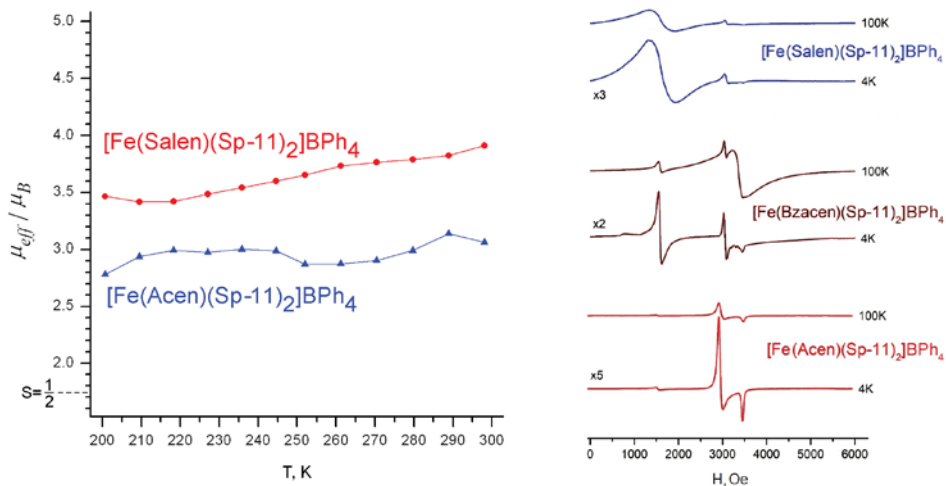
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The study of spin crossover (SCO) materials based on transition metal ions is promising for the development of technical devices: displays and memory in electronic devices. In order to obtain such materials, bistable molecular systems are required, which can exist in two different electronic states. Spin-variable Fe(III) complexes are such systems. The spin transition in them can be induced by external exposures (temperature, light, etc.). The spin state of complexes also depends on many factors: the composition and structure of ligands, the presence or absence of a counterion and solvate, the intensity of intra- and intermolecular interactions. The problem of the relationship between the structure and magnetic properties of the complexes is relevant, so it is important to establish the correlation between them. The introduction of a photosensitive fragment (for example, a C=C or N=N group) into the ligand makes the complexes potentially photoisomerizable with the prospect of their application in devices where the magnetic properties of a substance can be controlled by light.

A series of complexes with the general chemical formula  $[\text{Fe}(\text{SB})(\text{Sp})_2]\text{BPh}_4$  have recently been studied [1]. UV irradiation of such complexes leads not only to *cis-trans* isomerization of the 4-styrylpyridine axial ligands, but also to their cyclization with



**Fig. 1.** Photoisomerizable ligand 4-undecyloxystyrylpyridine which mentioned below as Sp-11 (a). Structure of the synthesized Fe(III) complexes  $[\text{Fe}(\text{Salen})(\text{Sp}-11)_2]\text{BPh}_4$  (b),  $[\text{Fe}(\text{Acen})(\text{Sp}-11)_2]\text{BPh}_4$  (c),  $[\text{Fe}(\text{Bzacen})(\text{Sp}-11)_2]\text{BPh}_4$  (d), in which the axial ligands are Sp-11 and the counterion is  $\text{BPh}_4$  (e).



**Fig. 2.** EPR spectra of the complexes in powders (left). Temperature dependences of  $\mu_{\text{eff}}$  for the solutions of the studied complexes in  $\text{CH}_2\text{Cl}_2$  at  $C_M = 5$  mmol/L obtained by NMR (right). The complex  $[\text{Fe}(\text{Bzacen})(\text{Sp-11})_2]\text{BPh}_4$  was not studied by NMR due to its low solubility.

detachment from the central ion, i.e., to the destruction of the complexes. Therefore it is more reasonable to use 4-styrylpyridine with long alkyl chains, which is not subject to cyclization under UV irradiation, as axial ligands.

In this work, several Fe(III) complexes with photoisomerizable axial ligands have been first synthesized, characterized and studied. The general chemical formula of the complexes is  $[\text{Fe}(\text{SB})(\text{Sp-11})_2]\text{BPh}_4$ , where Sp-11 is 4-undecyloxystyrylpyridine (Fig. 1a), SB are dianions of Schiff bases: Salen, Bzacen and Acen [1]. The complexes were studied in solutions by UV-visible and NMR spectroscopy, in the solid state and in vitrified solutions by EPR spectroscopy.

The UV-vis spectra of the complexes show intense absorption bands in the region of 350 nm, which belong to the  $n-\pi^*$  and  $\pi-\pi^*$  transitions of the  $\text{C}=\text{C}$  and  $\text{C}=\text{N}$  groups of ligands. A weakly intense absorption band at 680–720 nm, which belongs to low-spin complexes, appears only in  $\text{CH}_2\text{Cl}_2$  solutions. The effect of the chemical structure of the equatorial ligand on the spin state of the Fe(III) ion in complexes was studied in powders and in solutions of  $\text{CH}_2\text{Cl}_2$  (Fig. 2). The EPR method revealed an incomplete spin crossover in the complexes in powders and vitrified solutions in the temperature range 4–340 K. The NMR measurements indicate that an incomplete smooth spin crossover between the LS and HS states is observed in the solution of the  $[\text{Fe}(\text{Salen})(\text{Sp-11})_2]\text{BPh}_4$  complex. In a solution of the  $[\text{Fe}(\text{Acen})(\text{Sp-11})_2]\text{BPh}_4$  complex, the number of LS ions noticeably exceeds the number of HS ions.

These conclusions differ from the results obtained for analogous complexes with unsubstituted 4-styrylpyridine [1]. Thus, in this work it is shown that long alkoxy chains in ligands lead to additional intermolecular interactions, which in turn cause a change in the spin properties of the complexes.