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IR Microscopy as a Method for Studying the Influence of An External Electric Field on the Spin Crossover Exemplified by the Fe(II) Complex with 2,6-Bis(pyrazol-1-yl)pyridine

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Abstract—The influence of the electric field on the spin state of the single crystal of $[Fe(1\text{-}Bpp)_2][BF_4]_2$ demonstrating the spin crossover phenomenon is studied. The spin state of the complex is determined by the indirect method: FT-IR microscopy. The experimental results show that the application of the external electrostatic field with an intensity of 13 kV/cm exerts no effect on the temperature of the magnetostructural transition of the compound within 0.2 K.

Keywords: coordination compounds, spin crossover, iron(II), FT-IR microscopy

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INTRODUCTION

Currently, there is a heightening of interest in finding alternatives to silicon compounds and silicon-based electronics in general. The compounds studied in the area of molecular magnetism can be such an alternative. These include, inter alia, the complexes demonstrating a phenomenon of the so-called spin crossover (SCO).

Spin-transition is a spin-state switching phenomenon on transition metal ions in coordination compounds under the stress of external perturbations. The SCO is accompanied by significant changes in the magnetic, optical, and mechanical properties of the coordination compound providing a scope for potential application as active elements in the hightech area, in particular, for manufacturing information storage devices, commutation instruments, sensors, and displays.

A change in the spin multiplicity of the metal ion can be induced by various external stimuli such as temperature, pressure and light irradiation (LIESST effect) [1–6]. Perhaps, the external electric field is the easiest and convenient way to implement the spin state control of SCO centers. This approach provides a considerably simplified technique for manufacturing new electronic devices based on the SCO compounds.

The possibility of the electric field influence on the spin transition temperature was theoretically substantiated [7]. The Ising model was used for the qualitative description and taking into account the interaction with the external electric field. The Hamiltonian of this system takes the form

$$H = -J\sum_{\langle ij\rangle}\sigma_i\sigma_j - \left[\frac{\Delta}{2} - k_BT\ln\frac{g_{HS}}{g_{LS}}\right]\sum_{i=1}^{N}\sigma_i + H_{el},$$

$$H_{el}(\{\sigma\}) = -\frac{p_{HS}^2 - p_{LS}^2}{6k_BT}E^2\sum_{i=1}^{N}\sigma_i,$$

where σ_i is the dummy spin operator with the eigenvalues ±1 for the high-spin (HS) and low-spin (LS) states of the *i*th molecule, J is the phenomenological parameter describing cooperativity, k_B is the Boltzmann constant, Δ is the strength of the ligand field, g_{HS}/g_{LS} is the ratio of degeneration multiplicities of two states, p_{HS} and p_{LS} are the macroscopic dipole moments of the crystal, and E is the intensity of the external electric field. If the crystal has a macroscopic dipole moment, then the external electric field interacts with the dipole moment of the crystal when the crystal is placed into the external field. If the macroscopic dipole moments of the crystal of the studied complex differ for its different spin states, the electric field application shifts the temperature of the magnetostructural transition estimated as follows:

$$T_{SCO}(E) \approx T_{SCO}(E = 0) - \frac{p_{HS}^2 - p_{LS}^2}{6k_B^2\Delta}E^2. \quad (1)$$

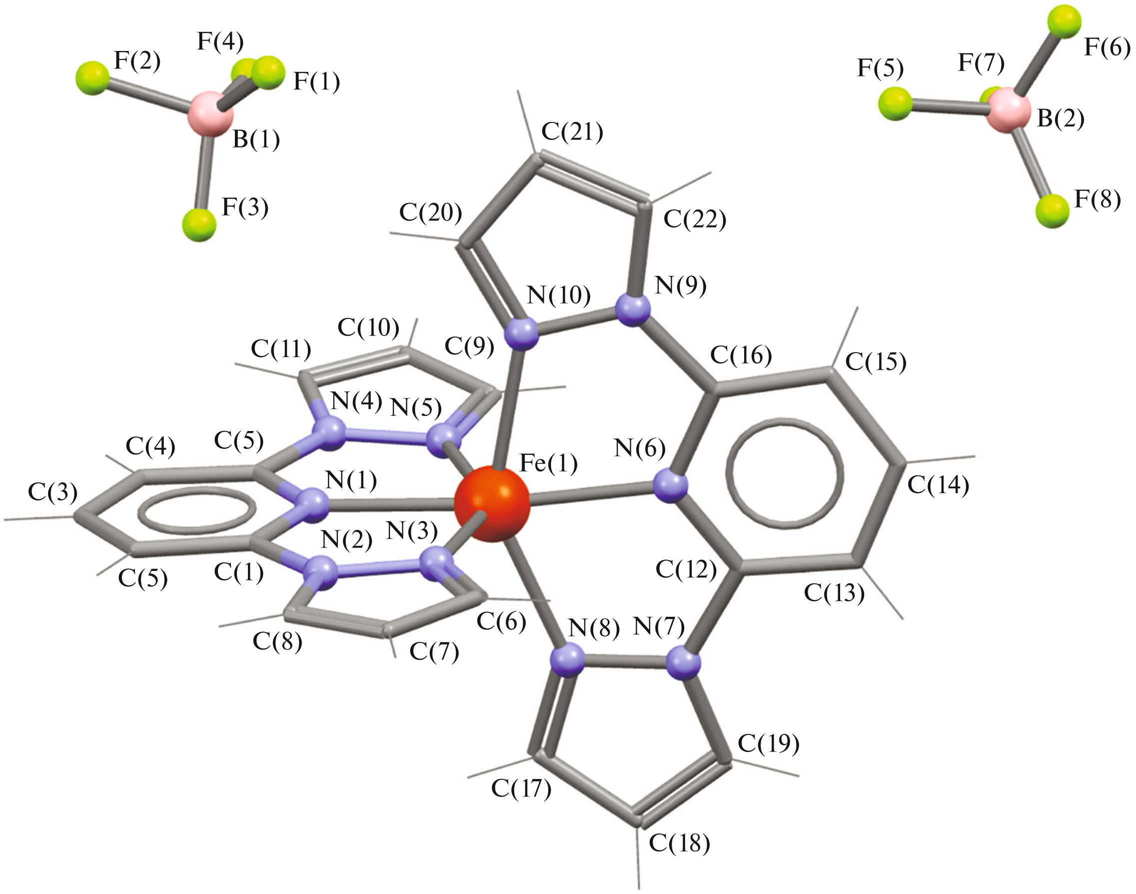

Fig. 1. Molecular structure of the $[Fe(1\text{-}Bpp)_2][BF_4]_2$ complex.

The considered model assumes the square dependence of the temperature of the spin transition shift on the electric field intensity.

This work is devoted to the influence of the external electrostatic field on the magnetostructural transition temperature in the $[Fe(1\text{-}Bpp)_2][BF_4]_2$ (1-Bpp is 2,6-bis(pyrazol-1-yl)pyridine) complex demonstrating the SCO effect studied by FT-IR microscopy.

EXPERIMENTAL

Studied compound. In the $[Fe(1\text{-}Bpp)_2][BF_4]_2$ complex [8], the Fe(II) ion is coordinated by the same two 1-Bpp ligands via the lone electron pair of the nitrogen atoms. The complex bears a positive charge, which is compensated by the BF_4^- anions (Fig. 1).

The thermally induced magnetostructural transition in this complex has a hysteresis at $T_\downarrow = 260.0$ K and $T_\uparrow = 262.5$ K ($T_\downarrow$ corresponds to the transition temperature on cooling of the sample, and $T_\uparrow$ corresponds to the transition temperature on heating). The photoinduced transition to the metastable HS state (LIESST effect) is possible at lower temperatures [8].

The magnetostructural transition in this compound is accompanied by a change in the color of the crystal. The crystal is red in the LS state and yellow in the HS state.

The influence of the external electrostatic field on the spin transition temperature was studied on a HYPERION 2000 IR microscope combined with a Bruker Vertex 80v FT-IR spectrometer (Bruker, Germany).

A HYPERION 2000 IR microscope is equipped with a Linkam FTIR600 temperature-controlled sample stage capable of changing the temperature of the studied sample from 80 to 600 K. To affect the sample by the external electric field, electrodes (planar plates fed with a voltage from a high-voltage source) were mounted on the BaF_2 object plate of the temperature stage. The distance between the plates was 1.5 ± 0.1 mm. The voltage of the air breakdown between the electrodes at this distance was 3.5 ± 0.2 kV. A Sh0105 high-voltage power unit (Nauel, Russia) served as a high voltage source providing the potential difference on the leads up to 30 kV.

A single crystal of $[Fe(1\text{-}Bpp)_2][BF_4]_2$ with the cross section in the plane of the probing IR beam

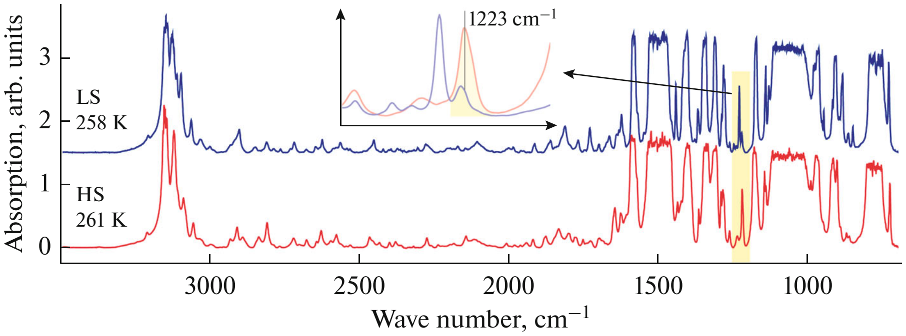

Fig. 2. Absorption spectra in the mid-IR range for the single crystal of $[Fe(1\text{-}Bpp)_2][BF_4]_2$ in the LS (258 K) and HS (261 K) states.

equal to ~0.2 × 0.2 mm was chosen for measurements. The crystal thickness was lower than 0.2 mm.

The cyclic training of the sample was conducted prior to IR spectra measuring: the temperature of the sample was varied in the range of the magnetostructural transition within 248–270 K more than 100 times to reveal possible structural defects of the crystal. The multiple thermal SCO transitions induced in the single crystal of $[Fe(1\text{-}Bpp)_2][BF_4]_2$ did not result in the visible structural degradation of the crystal, which demonstrated a high structural resistance of the complex to transitions of this type.

Spectra were measured in the medium-IR range from 550 to 4000 cm^{-1}. The absorption spectra of the single crystal at the temperatures lower (258 K) and higher (261 K) than the spin transition temperature with the distinguished area that clearly demonstrates the differences in the IR spectra of two magnetostructural states of the complex are presented in Fig. 2. The spectrum recorded at 258 K corresponds to the LS state, and the spectrum at 261 K corresponds to the HS state. The IR spectra of the single crystal contain the absorption band at 1223 cm^{-1}, which is shifted to 1232 cm^{-1} upon the transition from the HS to LS state. After the transition from the LS to HS state, the intensity and position of the absorption band return to the initial values. The change in the absorption band intensity is accompanied by a change in the sample color. This absorption band unambiguously characterizes the magnetostructural state of the studied single crystal and can act as a characteristic band for the determination of the spin state in temperature experiments and experiments with an external electric field.

The process of the nucleation of the new phase in the single crystal of the SCO compound on passing through the magnetostructural transition temperature (T_{SCO}) cannot be repeated and is unique every time. Therefore, the transition temperatures T_{SCO} obtained in independent experiments on the detection of the hysteresis loop can also differ (in spite of the previously performed cyclic training of the sample). It is very important to determine the degree of reproducibility of T_{SCO} in this work, because this value would introduce an error into the determination of the external electric field influence on T_{SCO}. In order to evaluate the accuracy of reproducibility of the magnetostructural transition temperature, we carried out comparative experiments on the detection of the hysteresis loop in the absence of an external electric field with a temperature increment of 0.2 K but with the shift of the temperature points by 0.1 K for various experiments. The obtained temperature dependences of the intensity of the characteristic absorption line at 1223 cm^{-1} detected for the same single crystal in the ranges 258.0–261.4 and 258.1–261.5 K with a temperature increment of 0.2 K are presented in Fig. 3. The presented plots show that the detected accuracy of T_{SCO} reproducibility for single crystals of $[Fe(1\text{-}Bpp)_2][BF_4]_2$ is 0.1–0.2 K. Thus, the amplitude of the external electric field influence on T_{SCO} should be not lower than 0.2 K for the reliable detection of this effect.

The temperature dependences of the intensities of the characteristic absorption line at 1223 cm^{-1} in the absence and in the presence of the external electric field are compared in Fig. 4. The temperature range 258.1–261.5 K with an increment of 0.2 K was chosen for both experiments. A voltage of 2 ± 0.2 kV corresponding to the intensity 13 ± 1 kV/cm limited by the breakdown voltage of the gap between the plates was fed to the plates for IR spectra recording in the presence of an external electric field.

RESULTS AND DISCUSSION

The data presented in Fig. 4 show that the external electric field with an intensity of 13 ± 1 kV/cm applied to the single crystal of $[Fe(1\text{-}Bpp)_2][BF_4]_2$ does not change the temperature of the magnetostructural transition determined in the conducted experiments with an accuracy of 0.2 K.

According to the earlier presented Eq. (1), the absence of the effect of an external electrostatic field on the spin transition temperature can stem from the

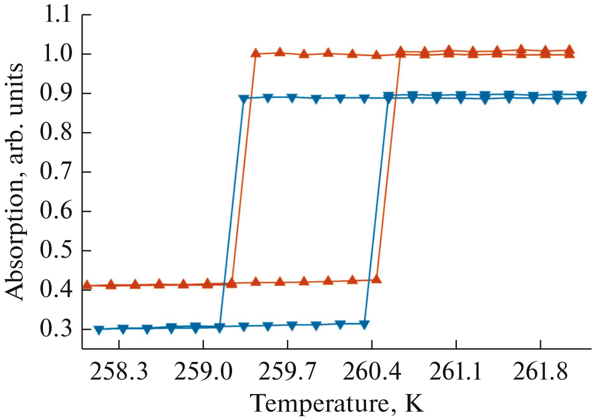

Fig. 3. Temperature dependence of the absorption line intensity at 1223 cm^{-1} in two ranges: ▼ is 258.1–261.5 K with an increment of 0.2 K, and ▲ is 258.0–261.4 K with an increment of 0.2 K. The plot of the temperature dependence detected in a range of 258.0–261.4 K is shifted by 0.1 arb. units for clarity.

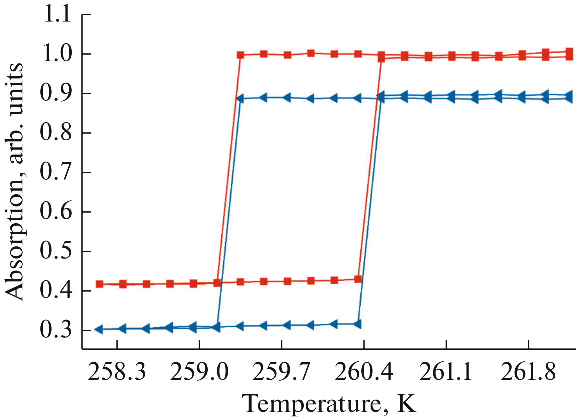

Fig. 4. Temperature dependence of the absorption line intensity at 1223 cm^{-1}: ◀ is the external electric field intensity equal to 0 kV/cm, and ■ is the external electric field intensity equal to 13 kV/cm. The plot of the temperature dependence with the electric field application is shifted by 0.1 arb. units for clarity.

low difference between the squared dipole moments ($p_{HS}^2 - p_{LS}^2$). Thus, if the dipole moments of the sample in the HS and LS states are fairly close, then this correction leads to a low shift of the spin transition temperature. This shift not exceed the reproducibility of TSCO taking into account the final intensity of the external electric field (13 kV/cm in the current experiments).

In future, it seems reasonable to study the external electric field influence on the spin transition temperature of the SCO complexes in fields of higher intensity thus achieving an increase in the breakdown voltage by the replacement of the nitrogen gas in the internal volume of the temperature stage by the sulfur hexafluoride gas (elegas SF_6). We are also planning to study the compounds that potentially would have higher $p_{HS}^2 - p_{LS}^2$ values compared to that of the $[Fe(1\text{-}Bpp)_2][BF_4]_2$ complex, for example, the SCO compounds based on cobalt(II) demonstrating the valence tautomerism phenomenon [9, 10].

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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