High-Temperature Spin Crossover in Iron(II) Complexes with 2,6-Bis(1H-imidazol-2-yl)pyridine

Ludmila G. Lavrenova 1,*, Olga G. Shakirova 1,2,*, Evgeniy V. Korotaev 1, Svetlana V. Trubina 1, Alexsei Ya. Tikhonov 3, Irina A. Os’kina 3, Sergey A. Petrov 4, Konstantin Yu. Zhizhin 5 and Nikolay T. Kuznetsov 5

Abstract: Novel iron(II) coordination compounds containing a ligand 2,6-bis(1H-imidazol-2-yl)pyridine (L), having such a composition as [FeL2SO4·0.5H2O], [FeL2Br2·H2O], [FeL2][ReO4]12, [FeL2]B10H10·H2O, [FeL2]B12H12·1.5H2O had been synthesized and studied using UV-Vis (diffuse reflectance), infrared, extended X-ray absorption fine structure (EXAFS), and Mössbauer spectroscopy methods, as well as X-ray diffraction and static magnetic susceptibility methods. The analysis of the $\mu_{eff}(T)$ dependence in the temperature range of 80–600 K have shown that all the obtained complexes exhibit a high-temperature spin crossover $^1A_1 \leftrightarrow ^5T_2$.

Keywords: iron(II) complexes; 2,6-bis(1H-imidazol-2-yl)pyridine; X-ray diffraction analysis; EXAFS; Mössbauer; IR; UV-Vis (diffuse reflectance) spectroscopy methods; spin crossover

1. Introduction

Searching for novel coordination compounds wherein the spin state of the central atom can be switched by an external action is an urgent problem. This is indicated by regularly appearing publications in the literature devoted to this topic [1–8]. These compounds include iron(II) complexes with spin crossover (SCO) $^1A_1 \leftrightarrow ^5T_2$. The change in spin multiplicity occurs owing to affecting temperature, pressure, irradiation with light of a certain wavelength (LIESST effect), high-frequency magnetic or electric field, and other factors. The transition from a low-spin (LS) to a high-spin (HS) state causes a change in the magnetic, optical, and vibrational properties of the complexes. An important property associated with the spin transition consists in changing metal–donor interatomic distance amounting to 0.2 Å in the case of Fe(II) complexes. Owing to the universal properties of complexes with SCO they have a wide range of potential applications in making optoelectronic, molecular electronic, and spintronic devices [9–15]. At present, polyfunctional materials combining SCO and other properties are under active study [16–19].

2,6-Bis(1H-imidazol-2-yl)pyridines represent a promising class of potential ligands for the synthesis of complexes with SCO [20]. Earlier, we have reported the studies on iron(II) complexes with 2,6-bis(benzimidazol-2-yl)- and 2,6-bis(4,5-dimethyl-1H-imidazol-2-yl)pyridine [21–24], wherein SCO is exhibited. It seemed worthwhile to continue these
investigations into synthesizing and studying Fe(II) complexes with 2,6-bis(1H-imidazol-2-yl)pyridine (Scheme 1), which does not contain substituents at the imidazole fragment. Earlier, this ligand was used in order to synthesize complexes with Ru(II), and with a number of metals belonging to the first transition series [25–29]. The X-ray diffraction data have shown that L is coordinated to the metal ion in a tridentate-cyclic manner by two nitrogen atoms belonging to two imidazole rings and one nitrogen atom belonging to pyridine.

![Scheme 1. 2,6-Bis(1H-imidazol-2-yl)pyridine (L).](image)

2. Materials and Methods

2.1. Materials

Commercial metal salts and solvents without further purification were used in the synthesis. 2,6-Bis(imidazol-2-yl)pyridine was synthesized as described in [30] (NMR spectra of ligand given in the Supplementary Materials, Figures S1–S4); K$_2$B$_{10}$H$_{12}$·2H$_2$O, K$_2$B$_{12}$H$_{12}$ were obtained according to the procedure [31].

2.2. Synthesis of [FeL]SO$_4$·0.5H$_2$O (1·0.5H$_2$O)

A 0.28 g (1 mmol) sample of FeSO$_4$·7H$_2$O with the addition of 0.1 g of ascorbic acid was dissolved in 10 mL of water under heating; a 0.51 g (2 mmol) L was dissolved in 10 mL of ethanol, and the solutions were then heated and mixed. The resulting solution was evaporated until a red-violet precipitate began to form. After the solution with the precipitate was cooled in a crystallizer with ice, the precipitate was filtered off, washed twice with small portions of water, and dried in air. Yield: 70%. Anal. Calc. for C$_{22}$H$_{20}$FeN$_{10}$O$_8$ (614.5): C, 43.0; H, 4.9; N, 20.9. Found: C, 42.5; H, 4.9; N, 21.5.

2.3. Synthesis of [FeL]Br$_2$·H$_2$O (2·H$_2$O) and [FeL]ReO$_4$·H$_2$O (3)

A 0.28 g (1 mmol) sample of FeSO$_4$·7H$_2$O was dissolved in 5 mL of distilled water acidified with 0.1 g of ascorbic acid. An excess (0.43 g, 1.5 mmol) of KReO$_4$ or KBr (0.36 g, 3.0 mmol) in 10 mL of water and a solution of L (0.51 g, 2 mmol) in 10 mL of ethanol were successively added to the resulting solution under stirring. The resulting solution was evaporated until a red-violet precipitate began to form. After the solution with the precipitate was cooled in a crystallizer with ice, the precipitate was filtered off, washed twice with small portions of water, and dried in air. Yield: 55%. Anal. Calc. for C$_{22}$H$_{19}$FeN$_{10}$O$_{9/2}$S$_x$ (583.4): C, 45.3; H, 3.3; N, 14.6. Found: C, 46.2; H, 3.5; N, 14.6.

2.4. Synthesis of [FeL]B$_{10}$H$_{12}$·H$_2$O (4·H$_2$O) and [FeL]B$_{12}$H$_{12}$·1.5H$_2$O (5·1.5H$_2$O)

A 0.14 g (0.5 mmol) sample of FeSO$_4$·7H$_2$O was dissolved in 3 mL of distilled water acidified with 0.05 g of ascorbic acid. An excess (0.23 g, 1 mmol) of K$_2$B$_{10}$H$_{12}$·2H$_2$O or K$_2$B$_{12}$H$_{12}$·2H$_2$O (0.22 g, 1 mmol) in 10 mL of water and a solution of L (0.21 g, 1 mmol) in 5 mL of ethanol were added to the resulting solution under stirring. Red-brown precipitates began to form immediately. Each precipitate was filtered off, washed twice with small portions of water and ethanol, and dried in air. Yield: 45% (4·H$_2$O), 68% (5·1.5H$_2$O). Anal. Calc. for C$_{22}$H$_{30}$B$_{10}$FeN$_{10}$O$_x$ (614.5): C, 43.0; H, 4.9; N, 22.8. Found: C, 42.5; H, 5.0; N, 22.1. Anal. Calc. for C$_{22}$H$_{33}$B$_{12}$FeN$_{10}$O$_{3/2}$ (647.1): C, 40.8; H, 5.1; N, 21.6. Found: C, 40.6; H, 5.3; N, 20.9.
2.5. Measurement and Characterization

The data for elemental analysis of the complexes was acquired on a EURO EA 3000 analyzer (EuroVector, Pavia, Italy).

X-ray absorption spectra (XAS) in the Fe K edge region (150 eV before and 800 eV after) were measured in the transmission mode with the use of synchrotron radiation on the 8 beamline, VEPP-3 storage ring at the Siberian Synchrotron and Terahertz Radiation Center (Budker Institute of Nuclear Physics, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia) [32]. A Si(111) cut-off crystal was used as a two-crystal monochromator. The operating mode of the storage ring during measurement: energy—2 GeV; current—70–140 mA. For measurements, the samples were mixed with cellulose powder as a filler and pressed into tablets. The mass of the sample was calculated so that the absorption jump at the Fe K-edge was 0.8–1. The preprocessing of the absorption spectra (selection of the oscillating part—EXAFS spectra) was performed with the use of the VIPER 10.17 program [33]. The “radial pair distribution function” (Figure 1) was obtained by the Fourier transform of the $k^3$-weighted EXAFS function in the range of wave vectors $k = 2.0–11.0 \, \text{Å}^{-1}$.

![Figure 1. Fe K-edge EXAFS spectra (left) and their Fourier transform modules without consideration of the phase shift (right) of complexes 1–5.](image)

The local environment of the Fe ion [interatomic distances ($R_i$) and angles ($\Theta_i$), coordination numbers ($N_i$), and Debye–Waller factors ($\sigma_i^2$)] was modeled using the EXCURVE 98 code [34]. In this program phase and amplitude characteristics were calculated in the von-Bart and Hedin approximation. The amplitude suppression factor $S_0^2$ due to multielectron processes was determined for the crystallographically characterized compound ($S_0^2 = 0.85$) and fixed during further modeling of the studied compounds spectra. The Debye–Waller factor was the same separately for nitrogen and carbon atoms.

IR spectra were taken on a Scimitar FTS 2000 in the range of 4000–400 cm$^{-1}$ and a Vertex 80 in the range of 600–100 cm$^{-1}$. Compound samples were prepared as suspensions in vaseline and fluorinated oils and in polyethylene.

The Kubelka-Munk diffuse reflectance spectra were obtained on a Shimadzu UV-3101 PC scanning spectrometer.

The XRD investigation of polycrystalline samples was performed using a Shimadzu XRD 7000 diffractometer (CuK$\alpha_\text{L}$ radiation).

The static magnetic susceptibility was measured using Faraday balance type setup equipped with electromagnetic compensating torsion quartz microbalance. The Delta DTB9696 temperature controller (Delta Electronics Inc., Taipei, Taiwan) was used for the investigated compounds temperature stabilization (~1 K) in the range of temperatures...
80–600 K. The temperature scanning rate for the process of heating or cooling samples was ~1 K/min. The magnetic field strength (7300 Oe) stabilization precision was ~2%. The compounds studied were sealed in quartz cellules filled with atmospheric air at 760 Torr. In order to study the effect of crystallization water, the samples were placed in open quartz ampoules and vacuumed at 10\(^{-2}\) Torr, after which the helium atmosphere at 5 Torr was formed.

The effective magnetic moment of studied compounds was calculated as:

\[
\mu_{\text{eff}} = \left( \frac{3k}{N_A \mu_B^2} \cdot \chi T \right)^{1/2} \approx (8\chi T)^{1/2},
\]

\(k\)—Boltzmann constant, \(N_A\)—Avogadro constant, and \(\mu_B\)—Bohr magneton. In the above formula, the diamagnetic contribution in total magnetic susceptibility (\(\chi\)) was taken into account using the method of Pascal’s constants. The direct (\(T \uparrow\)) and reverse (\(T \downarrow\)) transitions temperatures were obtained using condition the magnetic moment second derivative zero value (\(d^2(\mu_{\text{eff}}(T))/dT^2 = 0\)).

The Mössbauer spectra were collected with a spectrometer NP-610 (KFKI, Budapest, Hungary), using \(^{57}\)Co in a metal Rh matrix as a radioactive source. The spectra were measured at a room temperature. The spectra were processed to find the values of isomer shift \(\delta\) and quadrupole splitting \(\varepsilon\). The isomer shifts are given relative to metal iron.

### 3. Results and Discussion

Iron(II) complexes with 2,6-bis(1H-imidazol-2-yl)pyridine were isolated from aqueous-ethanol solutions. To maintain the oxidation state of iron(II), ascorbic acid was added to the solution.

Complex **1-0.5H\(_2\)O** was synthesized by reacting stoichiometric amounts of FeSO\(_4\) and L. Syntheses **2-H\(_2\)O, 3, 4-H\(_2\)O, 5-1.5H\(_2\)O** were carried out in two stages. At the first stage, the corresponding iron(II) salts were obtained by adding a 1.5- or 2-fold excess of KBr, KReO\(_4\), K\(_2\)B\(_{10}\)H\(_{10}\) or K\(_2\)B\(_{12}\)H\(_{12}\) into a solution of FeSO\(_4\) salt. At the second stage, a solution of the ligand in ethanol was added to the resulting salt solution. The obtained diffraction patterns show that the synthesized compounds are crystalline, while [FeL\(_2\)]SO\(_4\)-0.5H\(_2\)O and [FeL\(_2\)]Br\(_2\)-H\(_2\)O, as well as [FeL\(_2\)]B\(_{10}\)H\(_{10}\)-H\(_2\)O and [FeL\(_2\)]B\(_{12}\)H\(_{12}\)-1.5H\(_2\)O are isotypical.

The structure of the whole molecule for all complexes in the LS state (T = 297 °C) was established from the EXAFS data using the multiple scattering approximation within the software package EXCURV (except for [FeL\(_2\)](ReO\(_4\))\(_2\) (3)) excluding hydrogen atoms, and anions that exert only a weak effect on the shape of the EXAFS spectrum owing to their spatial separation from the central iron ion. For complex 3, the signal-to-noise ratio in the EXAFS spectrum is worse than that for the spectra of other complexes owing to the presence of a heavy anion ReO\(_4\)^{2−}. Simulation of the whole molecule in the multiple scattering approximation gives too large errors in determining the parameters. Therefore, the simulation of the EXAFS spectrum for complex 3 could be carried out only in a single scattering approximation. The structure of the complexes in the LS state (by the example of complex **4-H\(_2\)O**) obtained by means of EXAFS spectra simulation is presented in Figure 2.

Table 1 lists the microstructure parameters of the coordination site for complexes **1-0.5H\(_2\)O, 2-H\(_2\)O, 4-H\(_2\)O, 5-1.5H\(_2\)O**.

The structure of the coordination site of complex [FeL\(_2\)](ReO\(_4\))\(_2\) (3) in the LS state was obtained from modeling the spectrum filtered in real space (\(\Delta R = 0.9\) to 3.0 Å). The simulation data are presented in Table 2. The coordination numbers of the nearest spheres of the iron ion environment were fixed in accordance with the data obtained in the simulation of complexes in the LS state in the multiple scattering approximation.
Figure 2. General view of the structure of the coordination core obtained by means of EXAFS spectra simulation for such complexes as 1·0.5H₂O, 2·H₂O, 4·H₂O, 5·1.5H₂O.

Table 1. Microstructure parameters of the Fe coordination site for the complexes at T = 300 K (LS) obtained by EXAFS fitting with multiple scattering approximation (Rᵢ—interatomic distance, 2σᵢ²—Debye–Waller factor, Fᵢ—the statistical error of the fitting).

| Bonds                  | 1·0.5H₂O | 2·H₂O | 4·H₂O | 5·1.5H₂O | Angles                  | 1·0.5H₂O | 2·H₂O | 4·H₂O | 5·1.5H₂O | Ω, Deg.               |
|------------------------|----------|-------|-------|----------|------------------------|----------|-------|-------|----------|------------------------|
| Fe(1)-N(1)             | 1.96     | 1.97  | 1.98  | 1.94     | N(1)Fe(1)N(8)          | 107.9    | 102.6 | 105.9 | 102.6    |                        |
| Fe(1)-N(3)             | 1.96     | 1.91  | 1.93  | 1.95     | N(1)Fe(1)N(6)          | 95.3     | 92.5  | 95.1  | 100.1    |                        |
| Fe(1)-N(4)             | 1.95     | 1.97  | 1.98  | 1.93     | N(1)Fe(1)N(9)          | 97.1     | 92.1  | 96.6  | 102.2    |                        |
| Fe(1)-N(6)             | 1.95     | 1.96  | 1.98  | 1.96     | N(1)Fe(1)N(3)          | 75.2     | 79.8  | 75.6  | 85.3      |                        |
| Fe(1)-N(8)             | 1.86     | 1.88  | 1.90  | 1.86     | N(3)Fe(1)N(9)          | 97.8     | 102.1 | 100.3 | 102.9    |                        |
| Fe(1)-N(9)             | 1.96     | 1.95  | 1.96  | 1.96     | N(3)Fe(1)N(4)          | 75.8     | 81.2  | 80.6  | 73.7      |                        |
| 2σᵢ² (Fe-N), Å²        | 0.014    | 0.013 | 0.013 | 0.012    |                        | 2.7      | 2.5   | 1.8   | 1.6       |                        |

* The determination accuracy for parameters (interatomic distances and angles) based on the EXAFS data is ±1% (for the nearest sphere of the environment). $F_i = \sum w_i^2 (\lambda_i^\text{exp}(k) - \lambda_i^\text{th}(k))^2$, $w_i = \frac{k_i^4}{\sum 1/k_j^4}$.

Table 2. Microstructure parameters for complex [FeL₂(ReO₄)₂] in the LS state obtained by single-scattering EXAFS data fitting.

| Compound         | Central Ion–Scattering Atom | Nᵢ | Rᵢ, Å | 2σᵢ², Å² | Fᵢ |
|------------------|-----------------------------|-----|-------|----------|-----|
| [FeL₂(ReO₄)₂]    | Fe–N                        | 6   | 1.96  | 0.010    |     |
|                  | Fe–C                        | 8   | 2.78  | 0.014    | 2.7 |
|                  | Fe–C                        | 4   | 3.20  |          |     |

*Figure 3 illustrates a comparison of the experimental and simulated radial distribution function for [FeL₂]B₁₀H₁₀·H₂O. The simulation was carried out using a multiple scattering approximation.*
Therefore, the 5·1.5H2O and Fe(II) complexes. In the high-frequency spectral region for 
the presence of non-split bands inherent in stretching vibrations characteristic of the SO42-
ions indicates the coordination of nitrogen atoms of the rings to Fe(II) ions. The presence of 
non-split bands inherent in stretching vibrations characteristic of the SO42- anions is typical for 
the spectra of low-spin octahedral iron(II) complexes [35].

Table 3 and Figures S5–S7 show the main vibration frequencies in the spectra of L 
and Fe(II) complexes. In the high-frequency spectral region for 1-0.5H2O, 2-H2O, 4-H2O, 
5-1.5H2O, ν(OH) vibrations are observed; in the wave number range of 3200–3250 cm^{-1} 
for all the complexes there are stretching vibrations of NH-groups, and in the range of 3100–2850 cm^{-1} 
there are vibrations of ν(CH). In the wave number range of 1650–1450 cm^{-1}, 
there are stretching and bending vibration bands inherent in heterocyclic rings. The spectra 
of the complexes in the range of ring vibrations exhibit a change in the number and 
position of the imidazole and pyridine bands in comparison with the spectrum of the ligand, 
which indicates the coordination of nitrogen atoms of the rings to Fe(II) ions. The presence of 
non-split bands inherent in stretching vibrations characteristic of the SO42- and ReO4- 
anions indicates the fact that they are in outer-sphere position. The vibration bands of the 
B–H bonds of the outer-sphere anions B10H102- and B12H122- are centered at the wave 
numbers of 2470 (ν(BH)) and 1075 cm^{-1} (δ(BBH)). In the case of the spectra for 4-H2O, 
5-1.5H2O they are shifted with respect to those observed in the spectra of the initial salts, 
which could be, to all appearance, caused by the formation of H2Oδ-⋯δ+H–B bonds. 
In the far region of the spectra of all the complexes, Fe(3dδ)—ligand(π) charge-transfer 
transition bands and vibration bands (M-N) are observed. The position of these bands is 
typical for the spectra of low-spin octahedral iron(II) complexes [35].

The diffuse reflectance spectra (DRS, Figures S8–S12) of all the obtained complexes 
exhibit intense metal-ligand charge transfer bands ν1(εg → π0^+^) in the wavelength range of 
300–350 nm (λ_{max} ≈ 324–326 nm). The DRS of 4-H2O and 5-1.5H2O exhibit three absorption 
bands, too, (see Table 4); they correspond to the 1A_1 → 1T_2, 1A_1 → 1T_1 and 1A_1 → 1A_2 
transitions in the strong octahedral field of the ligands. For low-spin axially distorted 
octahedral iron(II) complexes, the term 1T_1 is transformed according to the representation 
of 1E + 1A_2, whereas term 1T_2 is transformed according to the representation of 1E + 1B_2 [36]. 
Therefore, the 1A_1 → 1B_2, 1A_1 → 1A_2 and 1A_1 → 1E wide transition bands (see Table 4) 
observed in the spectra of 1-0.5H2O, 2-H2O and 3, indicate the fact that an axial distortion 
of the octahedral coordination of these complexes occur. Low-intensity transitions and 
overlapping three wide bands do not make it possible to perform reliable quantitative 
calculations of crystal field parameters in this case. The spectra of all the complexes do 
not exhibit the 5T_2 → 5E band, which is caused by the HS state of iron(II). We were able to 
calculate the splitting parameters based on the difference between 1A_1 → 1T_2 and 1A_1 → 1T_1 
absorption frequencies [36] for low-spin (LS) forms of complexes with closo-borate anions. 
The B values were computed using the formula 16B = [ν(1A_1 → 1T_2) − ν(1A_1 → 1T_1)]. The

![Figure 3](image_url)
values C and $\Delta_{LS}$ (Table 4) were calculated using the equations: $\nu_{LS} = \Delta_{LS} - C + 86B^2 / \Delta_{LS}$ and $C = 4.41 \cdot B$ [36–38]. The obtained data show that 2,6-bis(1H-imidazol-2-yl)pyridine is a strong field ligand. In addition, these data, as well as the values obtained for a number of previously synthesized Fe(II) complexes with 2,6-bis(benzimidazol-2-yl)pyridine and 2,6-bis(4,5-dimethyl-1H-imidazole) [22–24], obey the inequality that reflects the condition for the manifestation of SCO [37]: $19.000 \, \text{cm}^{-1} \leq \Delta_{LS} \leq 22.000 \, \text{cm}^{-1}$.

Table 3. The main vibrational frequencies (cm$^{-1}$) in the spectra of L and complexes.

| L       | 1·0.5H$_2$O | 2·H$_2$O | 3        | 4·H$_2$O | 5·1.5H$_2$O | Assignment   |
|---------|-------------|----------|----------|----------|-------------|--------------|
|         | 3485        | 3433     | 3225     | 3269     |             | $\nu$(OH)    |
| 3100$_w$| 3020$_w$    | 3147     | 3050$_w$ | 3047     | 3151        | $\nu$(NH)    |
| 3079    | 3060        | 3021     | 3067     | 2954     | 2988        | $\nu$(CH)    |
| 3035    |             |          | 3067     | 2924     | 2040        |              |
|         |             |          |          | 2854     | 2849        |              |
| 1598    | 1595        | 1569     | 1593     | 1622     | 1622        | $R_{\text{ring}}$ |
| 1573    | 1570        | 1551     | 1566     | 1558     | 1558        |              |
| 1552    | 1550        | 1479     | 1552     | 1490     | 1490        |              |
|         | 1118        | 1085     | 1070     | 1143     |             | $\nu$(SO$_4$) |
|         |             |          |          | 903      |             | $\nu$(ReO$_4$) |
|         |             |          |          | 2473     | 2493        |              |
|         |             |          |          | 1086     | 1105        |              |
|         |             |          |          | 1036     | 1054        | $\delta$(BBH) |
|         |             |          |          | 496      | 491         | 488          | 484         | Fe(3d$^6$)–ligand ($\pi$) charge-transfer transition |
|         |             |          |          | 385      | 376         | 381          | 334         | 333         | $\nu$(M-N)    |

Table 4. Parameters of diffuse reflectance spectra.

| Complex     | $\lambda(^1A_1 \rightarrow ^1T_2)$ | $\lambda(^1A_1 \rightarrow ^1B_2)$ | $\lambda(^1A_1 \rightarrow ^1T_1)$ | $\lambda(^1A_1 \rightarrow ^1A_2)$ | $\lambda(^1A_1 \rightarrow ^1E)$ | Calculated Parameter |
|-------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------|
|             | B                                 | C                                 | $\Delta_{LS}$                     |                                  |                                  |                      |
| 1·0.5H$_2$O | 454                               | 613                               | 536                               |                                  |                                  |                      |
| 2·H$_2$O    | 454                               | 624                               | 539                               |                                  |                                  |                      |
| 3           | 432                               | 603                               | 503                               |                                  |                                  |                      |
| 4·H$_2$O    | 475                               | 518                               | 620                               | 109.3                            | 482.0                            | 1.97 $\times 10^4$  |
| 5·1.5H$_2$O | 465                               | 518                               | 620                               | 137.5                            | 606.5                            | 1.98 $\times 10^4$  |

The Mössbauer spectra of complexes 1·0.5H$_2$O, 2·H$_2$O, 3 and 5·1.5H$_2$O represent quadrupole doublets whose parameters correspond to the LS state of iron(II) (Figure 4). The spectrum of 4·H$_2$O also exhibits a broadened doublet related to the HS form of the complex (36%). The parameters of the Mössbauer spectra are presented in Table 5.
Table 4. Parameters of diffuse reflectance spectra.

| Complex     | δ, mm/s | ε, mm/s | Γ, mm/s |
|-------------|---------|---------|---------|
| 1·0.5H2O    | 0.269   | 0.364   | 0.33    |
| 2·H2O       | 0.266   | 0.342   | 0.25    |
| 3           | 0.288   | 0.464   | 0.28    |
| 4·H2O       | 0.278 (64%) | 0.420 | 0.26    |
|             | 0.925 (36%) | 2.224 | 0.80    |
| 5·1.5H2O    | 0.282   | 0.465   | 0.25    |

The temperature dependences of the effective magnetic moment for the analyzed complexes are shown in Figure 5. Spin crossover (SCO) is observed for all the compounds under investigation. In the case of complexes 1·0.5H2O, 2·H2O, 3, 4·H2O, 5·1.5H2O (1–5).

Table 5. Mössbauer spectra parameters of the complexes.

| Complex     | δ, mm/s | ε, mm/s | Γ, mm/s |
|-------------|---------|---------|---------|
| 1·0.5H2O    | 0.269   | 0.364   | 0.33    |
| 2·H2O       | 0.266   | 0.342   | 0.25    |
| 3           | 0.288   | 0.464   | 0.28    |
| 4·H2O       | 0.278 (64%) | 0.420 | 0.26    |
|             | 0.925 (36%) | 2.224 | 0.80    |
| 5·1.5H2O    | 0.282   | 0.465   | 0.25    |

Figure 4. Mössbauer spectra of complexes 1·0.5H2O, 2·H2O, 3, 4·H2O, 5·1.5H2O (1–5).
should be noted that the experimental $\mu_{\text{eff}}$ values for 4·H$_2$O and 5·1.5H$_2$O complexes lead to appearing residual $\mu_{\text{eff}}$ value and to an increase in the temperature of SCO.

Figure 5. Dependences of $\mu_{\text{eff}}(T)$ (a–e) and $d^2(\mu_{\text{eff}}(T))/dT^2$ (f–j) for 1·0.5H$_2$O (a,f), 2·H$_2$O (b,g), 3 (c,h), 4·H$_2$O (d,i), 5·1.5H$_2$O (e,j). The white and black triangles in the figure correspond to the samples cooling and heating processes respectively.
Table 6. The temperatures of direct (Tc↑) and inverse (Tc↓) SCO for the studied complexes.

| Complex                     | Tc↑, K | Tc↓, K |
|-----------------------------|--------|--------|
| [FeL₂]SO₄·0.5H₂O            | >420   | 409    |
| [FeL₂]Br₂·H₂O               | >420   | >420   |
| [FeL₂](ReO₄)₂               | 340    | 340    |
| [FeL₂]B₁₀H₁₀·H₂O            | 436    | 436    |
| [FeL₂]B₁₂H₁₂·1.5H₂O         | 455    | 455    |
| [FeL₂]B₁₀H₁₀                 | 447    | 440    |
| [FeL₂]B₁₂H₁₂                 | 458    | 458    |

The effect of the crystallization of water has been studied for 4·H₂O and 5·1.5H₂O complexes (Figure 6). It should be noted that in the case of rarefied atmosphere the decomposition of the dehydrated complexes occurs in a lower temperature range than it is observed for initial compounds. Nevertheless, the SCO has been observed in this case, too. The μeff value of 4.65 μB achieved in HS state for 4 corresponds to the value observed for the initial complex. In the case of 5 complex, the μeff value (4.6 μB) exhibits an increase after dehydration. Residual μeff values (~1–1.5 μB) have been registered to occur for both complexes in the LS state. The SCO temperature increases after dehydration; however, the 5 complex demonstrates the highest SCO temperature values as it is observed in the case of the initial compound. Thus, the dehydration of 4·H₂O and 5·1.5H₂O complexes lead to appearing residual μeff value and to an increase in the temperature of SCO.

Figure 6. Dependences of μeff(T) (a,b) and d²(μeff(T))/dT² (c,d) for dehydrated complexes 4 (a,c), 5 (b,d). The white and black triangles in the figure correspond to the samples cooling and heating processes respectively.

4. Conclusions

In this work, we have synthesized and investigated five novel coordination compounds of various iron(II) salts with 2,6-bis(1H-imidazol-2-yl)pyridine (L). The structure of the coordination core of the complexes has been determined by means of EXAFS spectra simulation. Two ligand molecules are coordinated to the iron(II) ion in a tridentate-cyclic fashion by the nitrogen atom belonging to pyridine and two nitrogen atoms belonging to
imidazole rings. Thus, the complexes have the distorted-octahedral structure of the coordination polyhedron, the FeN₆ core. The studies on the \( T_{\text{eff}} \) dependence have shown that complexes having such a composition as \([\text{FeL}]\text{SO}_4\cdot 0.5\text{H}_2\text{O}, [\text{FeL}]\text{Br}_2\cdot \text{H}_2\text{O}, [\text{FeL}]\text{(ReO}_4)_2\), \([\text{FeL}]_2\text{B}_{10}\text{H}_{12}\cdot 1.5\text{H}_2\text{O}, [\text{FeL}]_2\text{B}_{12}\text{H}_{12}\cdot 1.5\text{H}_2\text{O}\) exhibit an \(^1A_1 \leftrightarrow ^3T_2\) high-temperature spin crossover. A comparison of the data obtained for the synthesized compounds with those obtained by us earlier [21–24] shows that spin-crossover \(^1A_1 \leftrightarrow ^3T_2\) is observed in all complexes of Fe(II) with 2,6-bis(imidazole-2-yl)pyridines. The temperatures of direct SCO, \( T_c \), in most compounds are significantly higher than room temperature.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules27165093/s1, Figure S1: NMR \(^1\text{H}\) of 2,6-di(1H-imidazol-2-yl)pyridine, 100 MHz, NS 24; Figure S2: NMR \(^13\text{C}\) of 2,6-di(1H-imidazol-2-yl)pyridine, 100 MHz, NS 96; Figure S3: NMR \(^13\text{C}\) of 2,6-di(1H-imidazol-2-yl)pyridine, 100 MHz, NS 7376; Figure S4: NMR \(^13\text{C}\) of 2,6-di(1H-imidazol-2-yl)pyridine, 100 MHz, NS 176; Figure S5: IR spectrum of 2,6-bis(1H-imidazol-2-yl)pyridine (I); Figure S6: IR spectrum of [FeL]_2\text{SO}_4\cdot 0.5\text{H}_2\text{O}; Figure S7: IR spectrum of [FeL]_2\text{B}_{12}\text{H}_{12}\cdot 1.5\text{H}_2\text{O} (5\cdot 1.5\text{H}_2\text{O}); Figure S8: Comparison of the experimental DRS and model for complex [FeL]_2\text{B}_{12}\text{H}_{12}\cdot 1.5\text{H}_2\text{O}; Figure S9: Comparison of the experimental DRS and model for complex [FeL]_2\text{B}_{12}\text{H}_{12}\cdot 2\text{H}_2\text{O}; Figure S10: Comparison of the experimental DRS and model for complex [FeL]_2\text{(ReO}_4)_2\; \text{; Figure S11: DRS for complex [FeL]_2\text{B}_{10}\text{H}_{10}\cdot \text{H}_2\text{O}; Figure S12: DRS for complex [FeL]_2\text{B}_{12}\text{H}_{12}\cdot 1.5\text{H}_2\text{O.}

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**Sample Availability:** Samples of the compounds are available from the authors on request.

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