# Dalton Transactions

An international journal of inorganic chemistry

www.rsc.org/dalton

Volume 41 | Number 17 | 7 May 2012 | Pages 5073–5420



ISSN 1477-9226

## RSCPublishing

**COVER ARTICLE** Ruben *et al.* The interplay of iron(II) spin transition and polymorphism



## Dalton Transactions

Cite this: Dalton Trans., 2012, 41, 5163

www.rsc.org/dalton

## PAPER

### The interplay of iron(II) spin transition and polymorphism<sup>†</sup>

Ivan Šalitroš,<sup>*a,b*</sup> Olaf Fuhr,<sup>*a*</sup> Andreas Eichhöfer,<sup>*a*</sup> Robert Kruk,<sup>*a*</sup> Ján Pavlik,<sup>*b*</sup> Lubor Dlháň,<sup>*b*</sup> Roman Boča<sup>*b*</sup> and Mario Ruben<sup>\**a,c*</sup>

*Received 10th October 2011, Accepted 8th December 2011* DOI: 10.1039/c2dt11906d

The mononuclear compound (1)  $[Fe^{II}(L)_2](BF_4)_2$  (L = 4-ethynyl-2,6-bis(pyrazol-1-yl)pyridine) was prepared and structurally as well as magnetically characterised. The crystallisation revealed the formation of two polymorphs – the orthorhombic **1A** and the tetragonal form **1B**. A third, intermediate phase **1C** was found exhibiting a different orthorhombic space group. Reversibility of the phase transition between **1A** and **1C** was studied by variable-temperature single-crystal and powder X-ray diffraction studies, while an irreversible phase transition was observed for the transition of **1B** $\rightarrow$ **1C**. The magnetic studies show that the **1A** $\leftrightarrow$ **1C** transition is accompanied by a very abrupt spin transition (ST) with 8 K hysteresis width ( $T_{1/2}(\downarrow) = 337$  K,  $T_{1/2}(\uparrow) = 345$  K). The ST was confirmed by Mössbauer spectroscopy as well as by DSC studies. In contrast, the **1B** polymorph remained low-spin up to 420 K. In conclusion, a full cycle of intertwined phase- and spin-conversions of three polymorphs could be proven following the general scheme **1B** $\rightarrow$ **1C** $\leftrightarrow$ **1A**.

#### 1. Introduction

The discovery of spin transition (ST) phenomenon<sup>1</sup> has raised a long-standing and increasing interest in molecular bistability. Bistability in ST materials is based on the crossover between the low-spin (LS) and high-spin (HS) state and the intra-atomic reorganisation of spin density causes changes of physical properties on the molecular as well as on the macroscopic level. The conversion of spin-states can be triggered by external parameters like temperature,<sup>2</sup> pressure,<sup>3</sup> magnetic<sup>4</sup> or electric fields,<sup>5,6</sup> as well as by electromagnetic excitation at visible<sup>7</sup> or X-ray<sup>8,9</sup> spectral wavelengths.

From the application point of view, materials which exhibit bistability target the exploitation of the change of magnetic moment<sup>10</sup> (data storage devices, contrast agents for MRI), the thermochromism<sup>11</sup> (displays technologies), or the spin-dependent change of conductivity.<sup>5,6</sup> However, the ST materials have to fulfil several important requirements like abruptness of the transition, room-temperature hysteresis loops or stability of the material against fatigue<sup>12</sup> With respect to this, the family of iron(II) complexes of the bispyrazolylpyridine type of ligands is

a promising candidate in view of the required technological requests.<sup>13–17</sup>

ST compounds are built from metallic ions with  $3d^4-3d^7$  electronic configurations, whereby most of the studies are dedicated to iron(II) metal ions ( $d^6$  configuration) exhibiting a paramagnetic-diamagnetic spin transition from the HS (S = 2) to the LS (S = 0) states. The central iron(II) atom is coordinated by six donor atoms (usually nitrogen or oxygen) organized in a pseudo-octahedral environment, which causes the break of spherical symmetry of d-orbitals into the  $e_g$  and  $t_{2g}$  orbital subsets. Therefore, the electron occupation of the d-orbitals can follow either the *Aufbau* principle (LS diamagnetic state) or Hund's rule (HS paramagnetic state) depending on the value of the ligand field splitting parameter.

Even though the ST phenomenon is a single molecule property based on the equilibrium between the ligand-field strength and the inter-electronic repulsion energy of electrons on d shells, the features of the transition properties are tuned strongly by the chemical or structural characteristics of ensembles of molecules. For instance, it is well known that abruptness of transition and presence of thermal hysteresis can be affected by the intermolecular cooperativity/connectivity between the ST moieties.<sup>18</sup> Such an idea was successfully proven by the synthesis of coordination ST polymers,<sup>19–21</sup> by introduction of substituents which are able to create hydrogen bonding networks,<sup>22</sup> or by the coordination of ligands with aromatic moieties in order to increase interconnection by  $\pi$ - $\pi$  contacts.<sup>23–24</sup>

Furthermore, the presence of counter anions and cations and of interstitial solvent molecules can influence the parameters of ST. Thus, the change of nature of the counter anions while maintaining the identity of the ST complex moiety is responsible for significant differences in the symmetry of the crystal structures

<sup>&</sup>lt;sup>a</sup>Institut für Nanotechnologie, Karlsruher Institut für Technologie, Postfach 3640, 76021 Karlsruhe, Germany. E-mail: mario.ruben@ kit.edu

<sup>&</sup>lt;sup>b</sup>Institute of Inorganic Chemistry, Technology and Materials, Faculty of Chemical and Food Technology, Slovak University of Technology, Bratislava, 812 37, Slovak Republic

<sup>&</sup>lt;sup>c</sup>Institute de Physique et Chimie des Matériaux de Strasbourg (IPCMS), CNRS-Université de Strasbourg, 23, rue du Loess, BP 43, 67034 Strasbourg cedex 2, France

<sup>†</sup> Electronic supplementary information (ESI) available. CCDC reference numbers 846470–846473. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt11906d

leading to different ST behaviour.<sup>25</sup> However, similar size and charge of isoelectronic counter anions can result in the formation of identical space group symmetries with very close unit cell parameters leading to very similar transition temperatures  $T_{1/2}$ .<sup>26–29</sup> It can be concluded that changes in the transition properties are mainly due to the change of crystal symmetry than to local density fluctuation within the unit cell.<sup>30</sup>

It has to be noticed that ST properties are very sensitive to changes of the crystal symmetry. In other words, the presence and the character of ST is strongly affected by the manner of placing/seating/localization of ST moieties within the crystal lattice, respectively, the unit cell. In this sense, the study and understanding of polymorphism is one of the pivotal challenges for the ST investigation and recent works concerning this topic have already shown the influence of this phenomenon.<sup>31–34</sup> On the other hand, the ST parameters can be actively tuned by manipulating the different polymorphic phases of iron(II) compounds.

Herein, we report on the synthesis, the structural determination, and the characterisation of the spectral, magnetic and thermodynamic properties of one polymorphic iron(II) ST system (1). The compound  $[Fe^{II}(L)_2](BF_4)_2$  crystallizes in two polymorphic forms 1A and 1B. Upon heating, the phase conversion into a third polymorph 1C was observed. Magnetic studies of 1A reveal an abrupt, combined spin/phase transition which was characterized by temperature dependent X-ray and Mössbauer spectroscopy as well as by DSC investigations. The polymorph 1B is low spin and shows at increased temperatures an irreversible phase transition into the dichotomous 1C/1A couple.

#### 2. Experimental

#### 2.1. General

Purchased chemicals and solvents (Fe<sup>II</sup>(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, acetone, hexane, ethyl acetate, acetonitrile and diethyl ether) were used as received. The ligand 4-ethynyl-2,6-bis(pyrazol-1-yl)pyridine (L) was prepared as described previously.<sup>35–37</sup> Elemental analysis on carbon, hydrogen, and nitrogen was carried out by Vario Micro Cube. FT-IR spectra were measured in KBr pellets (Magna FTIR 750, Nicolet) in the 4000–400 cm<sup>-1</sup> region. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker DPX 300 spectrometer with solvent proton and carbon atoms as an internal standard. Matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectrometric analytical data were acquired on a Voyager-DE PRO Bio spectrometry workstation. Electrospray ionization time of flight (ESI TOF) mass spectrometric analytical data were acquired on a micrOTOF -Q II Bruker.

#### 2.2. Synthesis

**Ligand preparation.** Ligand L, 4-ethynyl-2,6-bis(pyrazol-1yl)pyridine, was prepared according to a reported procedure<sup>35</sup> *via* a Sonoghashira coupling reaction of 4-iodo-2,6-bis(pyrazollyl)pyridine<sup>36–37</sup> with trimethylsilylacethylene followed by deprotection of the (CH<sub>3</sub>)<sub>3</sub>Si protecting group with methanol and sodium carbonate. The ligand preparation resulted in 79% yield in the form of a white powder.

Synthesis of polymorphic compound  $([Fe(L)_2]$ 1  $(BF_4)_2$ ). 70 mg (0.298 mmol) of 4-ethynyl-2,6-bis(pyrazol-1-yl) pyridine (L) was dissolved in 50 cm<sup>3</sup> of acetonitrile, stirred under a N<sub>2</sub> atmosphere at 70 °C for 30 min and 50 mg (0.149 mmol) of Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O as solid was added. The complexation of the ligand was immediately carried out exhibiting a colour change of the solution to red-orange. The reaction mixture was stirred for a further 4 h (70 °C, N<sub>2</sub> atmosphere), cooled down, filtered and left for crystallization by diffusion of diethyl ether under a N<sub>2</sub> atmosphere. After two weeks two types of dark-orange crystals - needles (polymorph 1A) and rhombic blocks (polymorph 1B) were collected, washed in a small amount of acetonitrile, rinsed with diethyl ether and dried under a N<sub>2</sub> atmosphere. Elemental analysis for C<sub>26</sub>H<sub>18</sub>N<sub>10</sub>B<sub>2</sub>F<sub>8</sub>Fe found% (calc.% for 1B and 1B): C 44.43 (44.61)%; H 2.75 (2.59)%; N 19.91 (20.01)%. MALDI ToF MS m/z (matrix nicotinic acid): found: 525.92 (C<sub>26</sub>H<sub>18</sub>N<sub>10</sub>B<sub>2</sub>F<sub>8</sub>Fe; 20%); calc. for  $(\{[Fe(L)_2]\}): 526.33. ESI-TOF MS: [Fe(L)_2]^{2+} (FeC_{26}H_{18}N_{10})$ at m/z = 263.05 (calc. m/z = 263.05);  $[Fe(L)_2(BF_4)]^+$  $(FeC_{26}H_{18}N_{10}BF_4))$  at m/z = 613.10 (calc. m/z = 613.14);  $[Fe(L)_2(BF_4)_2]Li^{1+}$  (FeC<sub>26</sub>H<sub>18</sub>N<sub>10</sub>B<sub>2</sub>F<sub>8</sub>Li) at m/z = 707.03 (calc. m/z = 707.13). <sup>1</sup>H NMR (CD<sub>3</sub>CN;  $\delta$  (ppm)): 57.53 (s, 2H), 52.76 (s, 2H), 34.90 (s, 2H<sub>r</sub>), 32.39 (s, 2H), 4.23 (s, acetylene). FT IR (KBr;  $\tilde{\nu}/cm^{-1}$ ): 3294 (ms, C–H<sub>ar</sub>); 3274 (ms, C–H<sub>ar</sub>); 3247 (ms, C-H<sub>ar</sub>); 3167 (ms, C-H<sub>ar</sub>); 3125 (ms, C-H<sub>ar</sub>); 3102 (ms, C-Har); 3 (ms, C-Har); 2116(ms, C=C). Yield 0.96 g (97%).

#### 2.3. Magnetic susceptibility measurement

All herein reported magnetic measurements were performed on a SQUID magnetometer (Quantum Design, model MPMS-XL-5). In all cases, the temperature dependence of the magnetic moment was recorded at B = 0.1 T as an external magnetic field. The temperature sweeping rate was 1 K  $min^{-1}$  and it was the same for cooling and heating modes. Gelatine capsules as sample containers for the measurement in the temperature range 5-380 K were used. In the case of high temperature magnetic measurements (300-460 K), the experiment was carried out using a special heating setup. A high temperature sample holder consisted of a quartz glass tube and Teflon filler. The very small diamagnetic contribution of the gelatine capsule and high temperature sample holder had a negligible contribution to the overall magnetization, which was dominated by the sample. The diamagnetic corrections of the molar magnetic susceptibilities were applied using Pascal's constants.<sup>38</sup>

#### 2.4. Diffraction experiments

Single crystal X-ray diffraction data were collected on a STOE IPDS II diffractometer with graphite monochromated Mo-K $\alpha$  radiation (0.71073 Å). The structures were solved by direct methods (SHELX-97). Refinement was performed with anisotropic temperature factors for all non-hydrogen atoms (disordered atoms were refined isotropically).<sup>39,40</sup> X-Ray powder diffraction patterns (XRD) were measured on a STOE STADI P diffractometer (Germanium monochromator, Debye–Scherrer geometry) with Cu-K $_{\alpha 1}$  radiation in glass capillaries. A theoretical powder

diffraction pattern were calculated on the basis of the atom coordinates obtained from single crystal X-ray analysis by using the program package STOE WinXPOW.<sup>41</sup>

#### 2.5. Mössbauer spectroscopy

The Mössbauer spectral absorber contained *ca.* 80 mg cm<sup>-2</sup> of polymorph **1A** of  $[Fe^{II}(L)_2](BF_4)_2$ , and the spectra were measured at 297 K and 350 K on a constant-acceleration spectrometer that utilized a room-temperature rhodium matrix <sup>57</sup>Co source and was calibrated at room temperature with  $\alpha$ -Fe foil. In order to avoid the presence of phase impurities from polymorph **1B**, the sample was overheated above 473 K before the Mössbauer experiment.

#### 2.6. DSC investigations

The calorimetric study of **1A** polymorph was performed on a Perkin Elmer Pyris Diamond DSC. The heating and cooling rates were both equal to 20 K min<sup>-1</sup>. The temperature scale was calibrated with the help of indium<sup>42,43</sup> and adamantane<sup>43</sup> standards and the heat flux values with a powder aluminium standard.<sup>44–45</sup>

#### 3. Results and discussion

#### 3.1. Synthesis and spectral properties

The ligand L, 4-ethynyl-2,6-bis(pyrazol-1-yl)pyridine, was prepared according to the procedure described elsewhere.<sup>35–37</sup> Compound [Fe<sup>II</sup>(L)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> was prepared by the reaction of 2 equivalents of L with one equivalent of Fe<sup>II</sup>(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in acetonitrile at 70 °C. Single crystals were obtained by diffusing diethyl ether into an acetonitrile solution of the complex under a N<sub>2</sub> atmosphere at room temperature. The crystallization resulted in two polymorphic forms – dark orange needles (polymorph **1A**) and dark orange rhombic blocks (polymorph **1B**). For magnetic, Mössbauer, and DSC studies the two polymorphs **1A** and **1B** were carefully separated under a microscope. The temperaturedependent X-ray diffraction studies elucidated the emergence of a third polymorph **1C** from both polymorphs, however only with phase transitions occurring at elevated temperatures above 340 K (Fig. 1a).

The UV/VIS absorption spectroscopy was recorded for **1A** and **1B** in solid state at room temperature (see ESI<sup>†</sup>). Both compounds are in low spin state at the temperature of the measurement. At 530 nm the  ${}^{1}A_{1}$ – ${}^{1}T_{1}$  d–d transition<sup>46</sup> was observed and MLCT bands<sup>14</sup> can be detected at 457 nm (**1A**) or 471 nm (**1B**) respectively. The spectra of the two polymorphs are distinguished by slight shifts of the absorption bands maxima, which may be caused by the presence of different short contact interactions in the crystal lattice of the related compounds (see chapter 3.2).

The comparison of the infrared spectra of **1A** and **1B** reveal differences in the area of stretching C–H vibrations (see ESI†). The most significant shift was observed for the C–H acetylene vibration modes. While the vibration wavenumber for **1A** is  $3245 \text{ cm}^{-1}$ , the polymorph **1B** shows this vibration at



Fig. 1 Schematic view of the three polymorphs and their temperaturedependent relationship: The room temperature crystallization of  $[Fe^{II}(L)_2](BF_4)_2$  leads to two different polymorphs – orthorhombic 1A and tetragonal 1B. 1A exhibits a reversible phase transition around 340 K into another orthorhombic phase – polymorph 1C. Above 420 K, tetragonal 1B undergoes irreversible phase transition into orthorhombic phase 1C.

3272 cm<sup>-1</sup>. **1A** shows C–H aromatic vibrations at 3173 cm<sup>-1</sup> and 3138 cm<sup>-1</sup>, but in **1B** the same peaks are slightly shifted to lower energies – 3166 and 3124 cm<sup>-1</sup> (see ESI<sup>†</sup>).

#### 3.2. X-Ray diffraction studies

The single-crystal X-ray analysis of polymorph **1A** (Fig. 2a), obtained at 180 K and 350 K, reveal at both temperatures an orthorhombic  $P2_12_12_1$  space group (Table 1). At 180 K, the unit cell parameters are a = 15.379(3) Å, b = 16.291(3) Å, c = 23.329(5) Å, V = 5845(2) Å<sup>3</sup>; slightly increased unit cell parameters are observed at 350 K (with a = 15.681(3) Å, b = 16.300(3) Å, c = 23.553(5) Å and V = 6020(2) Å<sup>3</sup>). The asymmetric unit consists of two dication moieties  $[Fe^{II}(L)_2]^{2+}$  and four  $BF_4^-$  counter anions, while the unit cell contains eight  $[Fe^{II}(L)_2](BF_4)_2$  species. No solvent molecules are present in the crystal lattice (Fig. 3a). The bond distances of the coordination polyhedra exhibit values typical for the low-spin state of iron(1) at 180 K as well as at 350 K (Table 2). The structural differences between the low temperature structure and structure at 350 K are negligible and they can be attributed to the thermal factor.

In parallel to polymorph **1A**, the polymorph **1B** (Fig. 2c) crystallizes from acetonitrile solution at room temperature being isostructural with its counter anion analogue  $[Fe^{II}(L)_2](ClO_4)_2$ .<sup>35</sup> The single crystal diffraction study reveals tetragonal  $I4_1/a$  symmetry with unit cell parameters a = b = 9.5513(14) Å, c = 29.315(6) Å, V = 2674.4(8) Å<sup>3</sup> (Table 1) and four molecular species can be found within the unit cell (Fig. 3c). There is a twofold crystallographic axis running through the atoms Fe1, N3, C6, C7, and C8 with the atom Fe1 located on the Wyckoff position 4a (site symmetry  $\bar{4}$ ); also the atom B1 of the counterion lies on a twofold axis. At the temperature of the measurement, the Fe<sup>II</sup>–N bond lengths have typically low-spin values – 1.975(14) Å and 1.881(19) Å (Table 2).

In order to investigate high-spin crystal structure and structural changes elicited by ST of polymorph 1A, single crystal X-ray



**Fig. 2** Overview of the molecular structures of polymorphic compound  $[Fe^{II}(L)_2](BF_4)_2$ . The independent units of (a) orthorhombic **1A** and (b) tetragonal **1B** polymorphs both being in the LS state (average of Fe–N bond lengths are 1.941 Å for **1A** and 1.928 Å for **1B**, respectively) and HS structure of (c) the orthorhombic polymorph **1C** (average value of Fe–N bond distances is 2.144 Å). The hydrogen atoms are omitted for clarity; ellipsoids are drawn for 40% probability.

diffraction studies were carried out on the orthorhombic phase at 370 K. The results of this experiment reveal a reversible crystallographic phase transition of polymorph **1A** ( $P2_12_12_1$  space group) into orthorhombic *Pbcn* (polymorph **1C**) phase, with the unit cell parameters a = 16.726(3) Å, b = 12.202(2) Å, c = 15.212(3) Å and a cell volume of 3104.6(11) Å<sup>3</sup> (Table 1). The comparison of unit cell parameters of the orthorhombic polymorphs allows us to conclude, that the transformation of **1A** into **1C** is caused by a formal splitting of the lattice parameter c(23.329(5) Å) of the acentric  $P2_12_12_1$  unit cell by approximately half in order to create centric *Pbcn* unit cell of **1C**. The corresponding lattice cell parameter in the **1C** crystal structure is b =12.202(2) Å. The other two parameters, a (15.681(3) Å), b(16.300(3) Å) in **1A** and c (15.212(3) Å), a (16.726(3) Å) in **1C**, are not affected by the **1A** $\leftrightarrow$ **C** phase transition exhibiting very similar values to each other. The asymmetric unit in **1C** consists of half a complex cation  $[Fe^{II}(L)_2]^{2+}$  (with Fe1 on a twofold axis) and one corresponding BF<sub>4</sub><sup>-</sup> counter anion; four formula units can be found within the unit cell (Fig. 3b). At 370 K, the bond distances acquire values typical for HS of iron(II) and vary in the range 2.129(4)–2.161(5) Å (Table 2, see ESI†). All three polymorphs of  $[Fe^{II}(L)_2](BF_4)_2$  show weak interactions between the ligand atoms and BF<sub>4</sub><sup>-</sup> counter anions.<sup>47</sup>

The comparison of the structural features of 1A and 1B reveals some dramatic changes induced by the spin transition. The average of the Fe–N bond lengths of 1A is 1.941 Å at 180 K and 1.969 Å at 350 K and so close to the distances found in 1B (1.8813(19) and 1.9755(14) Å; Table 2) indicating the

**Table 1** Crystal and structure refinement data of three crystallographic phases 1A, 1B and 1C of compound  $[Fe^{II}(L)_2](BF_4)_2$ 

	Polymorph 1A		Polymorph <b>1B</b>	Polymorph 1C
Formula Formula weight/g mol <sup>-1</sup> Crystal colour	$C_{26}H_{18}B_2F_8FeN_{10}$ 699.97 Orange	$C_{26}H_{18}B_2F_8FeN_{10}$ 699.97 Orange	$C_{26}H_{18}B_2F_8FeN_{10}$ 699.97 Orange	$C_{26}H_{18}B_2F_8FeN_{10}$ 699.97 Light orange
T/K	180(2)	350(2)	180(2)	370(2)
Wavelength/Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Tetragonal	Orthorhombic
Space group	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$	$I4_1/a$	Pbcn
a/Å	15.379(3)	15.681(3)	9.5513(14)	16.726(3)
b/Å	16.291(3)	16.300(3)	9.5513(14)	12.202(2)
c/Å	23.329(5)	23.553(5)	29.315(6)	15.212(3)
$\alpha$ (°)	90.00	90.00	90.00	90.00
$\beta$ (°)	90.00	90.00	90.00	90.00
$\gamma$ (°)	90.00	90.00	90.00	90.00
V/Å <sup>3</sup>	5845(2)	6020(2)	2674.4(8)	3104.6(11)
$Z, \rho_{\rm c}/{\rm g~cm^{-3}}$	8, 1.591	8, 1.545	4, 1.738	4, 1.498
$\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>	0.605	0.588	0.661	0.570
F(000)	2816	2816	1408	1408
Crystal size/mm	$0.35 \times 0.08 \times 0.07$	$0.39 \times 0.13 \times 0.12$	$0.40 \times 0.30 \times 0.28$	$0.25 \times 0.22 \times 0.19$
$\theta$ range for the data collection (°)	1.52 to 25.65	1.51 to 24.84	1.37 to 26.09	2.46 to 25.77
Abs. structure parameter	0.019(18)	0.06(2)	_	
Final <i>R</i> indices $[I > 2\sigma(I)]^a$	$R_1 = 0.0498$ w $R_2 = 0.0709$	$R_1 = 0.0593$ w $R_2 = 0.1535$	$R_1 = 0.0289$ w $R_2 = 0.0749$	$R_1 = 0.0652$ w $R_2 = 0.1646$
R indices (all data) <sup><math>a</math></sup>	$R_1 = 0.0820$ w $R_2 = 0.0709$	$R_1 = 0.0929$ w $R_2 = 0.1713$	$R_1 = 0.0298$ w $R_2 = 0.0756$	$R_1 = 0.1529$ w $R_2 = 0.2137$
Extinction coefficient	0.00014(4)		0.0026(5)	0.0063(18)
GoF on $F^2$	0.874	0.954	1.046	0.937
CCDC number	846470	846471	846472	846473
<sup><i>a</i></sup> $R1 = \sum (F_{o} - F_{c}) / \sum (F_{o}); wR2 =$	$= \sqrt{\sum \left[w\left(F_{o}^{2} - F_{c}^{2}\right)^{2}\right]/\sum \left[w\left(F_{o}^{2} - F_{c}^{2}\right)^{2}\right]}$	$\overline{\left(F_{o}^{2}\right)^{2}}$ ]		

presence of the LS state for both polymorphs. However, the polymorph **1C** shows typical HS bond lengths at 370 K which scatter in the range of 2.129(4)-2.161(5) Å at 370 K (Table 2).

During the concomitant  $1A \leftrightarrow 1C$  phase/spin transition the most significant growth of bond lengths (*ca.* 13%) was observed along the *b* direction, in particular along the axial Fe–N<sub>pyridine</sub> bonds (Fe1–N3, Fe1–N8, Fe2–N13, Fe2–N18 for **1A** and Fe1–N3, Fe1–N3' for **1C** polymorph), while the increase of the equatorial Fe–N<sub>pyrazole</sub> bond distances was determined to be about 9.5%.

The structural changes induced by ST also usually affect the plasticity of the coordination polyhedron. The change of the spin state causes either an increase or decrease in N-Fe-N angles (Table 3). The angle deviation from the optimum coordination sphere can be reflected by the parameter  $\Sigma$ , which is derived from the 12 octahedral angles.<sup>48</sup> This parameter has been successfully used for the detection of the spin state in the group of  $[Fe^{II}(L)_n(SCN)_2]$  ST complexes, where the difference between  $\Sigma_{\rm LS}$  and  $\Sigma_{\rm HS}$  was around 32° on average.<sup>49</sup> Consequently, the low-spin  $\Sigma$  values for 1A and 1B structures are about 87° and the  $\Sigma$  parameter for the high-spin state is almost two times higher in [Fe(L)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> reaching 161.18° (Table 3). The careful comparison of LS and HS structures reveals several other angles whose values differ according to the respective spin state (Table 3). While in the LS state of 1A and 1B the analogous angles scatter between 159.914 (180)°-160.610(4)°, the HS N1-Fe–N5 angle of 1C polymorph is significantly smaller exhibiting a value 145.675(179)° at 370 K.

A polycrystalline sample of 1B was additionally submitted to variable temperature X-ray powder diffraction investigations (see

ESI<sup>†</sup>). The powder diffraction pattern at room temperature is highly comparable with the calculated reflection pattern from single-crystal X-ray data measured at 180 K (Fig. S3<sup>†</sup>). Upon increasing the temperature above 450 K the sharp reflections of the tetragonal **1B** phase gradually decrease while new and broader peaks appear. This phase change is almost complete at 490 K. The resulting powder pattern at this temperature is in agreement with those two calculated for the two orthorhombic phases (**1A** and **1C**), whereas the broadness of the peaks does not allow for further differentiation (Fig. S4<sup>†</sup>). Upon cooling and heating the shape of the pattern remains nearly unchanged apart from small variations of the peak positions. The interpretation of the powder patterns proves the irreversibility of the **1B**→**1C** phase transition.

#### 3.4. Magnetic properties

Temperature-dependent measurements of the magnetic susceptibility of the crystalline sample of polymorph **1A** were carried out in heating and cooling modes. This investigation elucidates a reversible, very abrupt transition of the spin states accompanied with a thermal hysteresis (Fig. 4a). In the temperature range of 5-310 K the  $\chi T$  product possesses a typical behaviour of diamagnetic low spin (S = 0) compound – its values are negative and close to zero in the heating as well as in the cooling mode. Above this temperature, the product function starts slightly to increase and reaches 0.57 cm<sup>3</sup> K mol<sup>-1</sup> at 343 K, which corresponds to 19% of iron(II) in HS state. However, above this temperature, the product function rises dramatically to a saturated HS value of 3.48 cm<sup>3</sup> K mol<sup>-1</sup> at 370 K. Upon cooling, the



Fig. 3 The presentation of molecular packing within a-c plane of unit cell in crystal structure of the (a) orthorhombic 1A (Z = 8), (b) tetragonal 1B (Z = 4) and (c) orthorhombic 1C (Z = 4) polymorphs (hydrogen atoms are omitted for clarity).

Table 2 Fe–N bond lengths of the polymorphs 1A, 1B and 1C at different temperatures

Fe1-N1 Fe1-N3 Fe1-N5 Fe1-N6 Fe1-N8	Polymorph <b>1A</b> 180(2) 350(2)			180(2)	350(2)	Polymorph <b>1B</b> 180(2) K	Polymorph <b>1C</b> 370(2) K
	1.968(5) 1.904(5) 1.956(5) 1.958(5) 1.883(5)	1.999(5) 1.941(4) 1.960(5) 1.980(5) 1.948(5)	Fe2–N11 Fe2–N13 Fe2–N15 Fe2–N16 Fe2–N18	1.950(5) 1.901(5) 1.967(4) 1.950(5) 1.913(5) 1.976(4)	$ \begin{array}{r} 1.991(5) \\ 1.907(4) \\ 1.990(5) \\ 1.990(5) \\ 1.925(5) \\ 2.011(5) \\ \end{array} $	Fe1–N1 1.9755(14) Fe1–N3 1.8813(19)	Fe1–N1 2.142(5) Fe1–N3 2.129(4) Fe1–N5 2.161(5)

measured sample is paramagnetic and high-spin between 370 K and 341 K. Below 340 K, an abrupt ST takes a place, and the value of  $\chi T$  product drops to 0.34 cm<sup>3</sup> K mol<sup>-1</sup> at 335 K which corresponds to the 13% high spin fraction of iron(II). It is interesting to note, that more than 80% of iron(II) atoms undergoes reversible ST within 4 K in heating as well as within 5 K in cooling mode and transition temperatures are only slightly above the room temperature –  $T_{1/2}(\uparrow) = 345$  K for heating,  $T_{1/2}(\downarrow) = 337$  K for cooling mode ( $\Delta T_{1/2} = 8$  K).

Due to the LS behaviour of the **1B** polymorph, magnetic properties of this compound were investigated in the high temperature regime and the results are presented in Fig. 4b. At first, the sample was studied in the heating mode. The small paramagnetic values of  $\chi T$  product can be attributed to the paramagnetic impurities only, and **1B** exhibits diamagnetic low spin behaviour up to 400 K where it obeys  $\chi T = 0.42$  cm<sup>3</sup> K mol<sup>-1</sup>. Above this temperature, the product function starts to grow significantly and it achieves 3.30 cm<sup>3</sup> K mol<sup>-1</sup> at the highest temperature of measurement (470 K) – a typical value for the high spin state of iron(II) mononuclear compounds. The growth of the product function is irreversible and upon cooling the  $\chi T$  product stays constant up to 350 K. However, at  $T_{1/2} = 340$  K a reversible ST centred accompanied with 5 K hysteresis width is observed. Since the rise of the product function in the first heating mode is

Published on 30 January 2012 on http://pubs.rsc.org | doi:10.1039/C2DT11906D

Downloaded by KIT on 16 April 2012

Polymorph 1A (180 K) Polymorph 1B Polymorph 1C LS state LS state HS state 160.3 145.7 N1Fe1N5 N1FeN1 160.61 N1FeN5 (2)(8)(2)160.0 N11Fe2N15 (2)N6Fe1N10 160.7 N1'FeN1' 160.61 N1'FeN5' 145.7 (2)(8)(2)N16Fe2N20 159.9 (2)N3-Fe1-N8 N3-Fe-N3-Fe-N3' N3′ N13-Fe1-N18 N1Fe1N3 80.3(2)N1FeN3 80.30(7)N1FeN3 73.0(2) N11Fe2N13 79.5(2) N3Fe1N5 80.1(2) N1FeN3 80.30(7)N3FeN5 72.9(2)N13Fe2N15 80.5(2) N6Fe1N8 80.6(2) N1'FeN3 80.30(7) N1'FeN3' 73.0(2) N16Fe2N18 80.0(2) N8Fe1N10 80.1(2) N1'FeN3 80.30(7) N3'FeN5' 72.9(2) N18FeN20 80.1(2) N1Fe1N8 98.5(2) N1FeN3' 80.30(7) N1FeN3 113.0 (2)N11Fe2N18 99.1(2) N3Fe1N6 101.3 N1'FeN3 99.70(7) N1'FeN3 113.0 (2) (2) 102.5 N13Fe2N16 (2)89.1(2) N1FeN1' 100.8 N5Fe1N6 91.63(5) N5FeN1 (2)N16Fe2N15 93.0(2) N1FeN1' 91.63(5) N1FeN5' 100.8 N1Fe1N10 90.3(2) (2)94.5(5) N11Fe2N20  $\Sigma_1$ 86.20 Σ 161.18 Σ 84.04  $\Sigma_2^1$ 87.94

Table 3 Comparison of selected bond angels of the coordination polyhedral of the three crystallographic phases 1A, 1B and 1C of the compound  $[{\rm Fe}^{1l}(L)_2]~({\rm BF}_4)_2$ 

irreversible, and the observed ST in the cooling and the second heating mode is placed exactly in the region, where polymorph **1A** shows its spin transition, it can be concluded that this transition corresponds to the previously observed ST of **1A** $\leftrightarrow$ **1C**. The history-dependent slight differences between the ST properties of the two observed **1A** $\leftrightarrow$ **1C** transitions (8 K against 5 K thermal hysteresis width, slightly different saturation value of  $\chi T$ in high spin-plateau of HS state) can be attributed to the different degree of crystallinity of measured materials as well as to the lower sensitivity of high-temperature SQUID set-up.

#### 3.5. Temperature dependent Mössbauer spectroscopy of 1A

The Mössbauer spectroscopy measurements for a powdered, <sup>57</sup>Fe enriched sample of polymorph **1A** were performed at two different temperatures 297 K and 350 K. The spectroscopic parameters obtained by the least-squares fitting of the experimental data are given in the Table in Fig. 5. The spectra recorded at room temperature showed the presence of a single component iron(II) phase. The parameters of the doublet [A/% = 100;  $E_Q/$  mm s<sup>-1</sup> = 0.643;  $\delta/$ mm s<sup>-1</sup> = 0.310] indicate iron(II) in a low spin state. The change of an iron spin state at higher temperature is clearly reflected in Mössbauer spectra. The least-squares



Fig. 4 (a) Magnetic susceptibility data of polymorph 1A: the sample was cooled from 300 K to 5 K and the  $\chi T$  was first measured upon warming from 5 K to 370 K followed by the cooling mode. (b) Magnetic data for polymorph 1B. Since 1B polymorph was low spin up to 370 K, the magnetic investigation was performed in high temperature mode in the following manner: (i) heating from 330 K up to 460 K (red circles); (ii) cooling from 460 K up to 300 K (blue triangles); (iii) heating from 300 K up to 400 K (red triangles). In total, a conversion cycle 1B→1C↔1A is performed.

analysis of spectra collected at 350 K shows two components which indicate coexistence of the spin states. The component which is assigned to the low spin state has parameters very similar to the doublet at room temperature [A/% = 37;  $E_Q/mm s^{-1} = 0.565$ ;  $\delta/mm s^{-1} = 0.276$ ] while the second component yields parameters characteristic of the high spin state of iron(II) [A/% = 63;  $E_Q/mm s^{-1} = 1.132$ ;  $\delta/mm s^{-1} = 0.927$ . The results obtained from Mössbauer spectroscopy are in a good agreement with high spin molar ratio extracted from the magnetic measurements. Presence of a low-spin remnant at 350 K is indicative of an incomplete **1A** $\rightarrow$ **1C** transition at this temperature.

#### 3.6. DSC study of polymorphic compound 1A

The ST of 1A was also investigated by DSC. The transition temperatures were identified from the resulting heat flux as



Fig. 5 Mössbauer spectra with parameters for 1A obtained at 300 K and 350 K and comparison of high-spin molar fraction obtained from Mössbauer investigation (red dots) with the data from the SQUID measurement.

intersections of the peak onset with the corresponding baseline (Fig. 6). Their respective values are 343.5 K on heating and 338.2 K on cooling in satisfying agreement with the values obtained from susceptibility measurements. During the experiment the heat flux between filled and empty containers was measured. The raw data were corrected for the apparatus zeroline and scaled by comparing the measured and referenced aluminium heat capacity. The resulting function (ideally the heat capacity if no kinetic effects are present) was integrated<sup>50</sup> providing the value of molar enthalpy of transition  $\Delta H = 7.74$  kJ  $mol^{-1}$ . The change of entropy was obtained in an analogous way the only difference being that every single point of the function in question was divided by respective absolute temperature before its integration<sup>51</sup> The final molar entropy change is  $\Delta S =$ 22.2 J  $K^{-1}$  mol<sup>-1</sup>. The ratio of these two quantities is equal to  $T_{\rm c} \sim \Delta H / \Delta S = 348.6$  K and in an ideal reversible conduction of the experiment it matches the transition temperature.

#### 4. Conclusion

In conclusion, the results presented illustrate the effect of polymorphism on the magnetic ST parameters. Three different polymorphic phases of one mononuclear iron(II) compound were structurally and magnetically characterized. Structurally, three different crystallographic systems were detected. The first two polymorphs were obtained by parallel crystallization and the difference in their magnetic properties illustrates the consequence of changes of the symmetry of the crystal lattice on the spin transition properties. While in the first case an abrupt and hysteretic low-spin/high-spin transition is observed, the second polymorph stays low-spin and magnetically silent. The



Fig. 6 DSC curve for orthorhombic phase 1A. The heat flow for 1A was recorded in the heating mode (upper curve) and subsequently in the cooling mode (lower curve).

significant differences in magnetic behaviour for three different crystallographic phases of the same compound can be explained by the different level of cooperativity in each of the polymorphs. At the bottom line, this can be attributed to a different alignment of molecular species within the crystal lattice opening slightly different communication pathways between the complex units with the consequence of scattering of the Fe(II) spin transition parameters (*e.g.* temperature and abruptness of transition, presence of hysteresis loop). Our findings highlight the importance of polymorphism in ST systems; a problem to be considered in the design of molecular devices based on ST materials.<sup>5,6,52</sup>

#### Acknowledgements

Grant agencies (Slovakia: VEGA 1/0052/11, APVV-VVCE 0004-07, STU support grant for young scientists 6402/2011; NanoSciERA-DFG "Internet"; and DFG Interregio "3Met") are acknowledged for the financial support.

#### References

- 1 L. Cambi and L. Szeg, Ber. Dtsch. Chem. Ges. A, 1931, 64, 167.
- 2 L. Cambi and L. Malatesta, *Ber. Dtsch. Chem. Ges. B*, 1937, **70**, 2067.
- 3 V. Ksenofontov, A. B. Gaspar and P. Gütlich, *Top. Curr. Chem.*, 2004, 235, 23.
- 4 A. Bousseksou, F. Varret, M. Goiran, K. Boukheddaden and J. P. Tuchagues, *Top. Curr. Chem.*, 2004, **235**, 65.
- 5 V. Meded, A. Bagrets, K. Fink, R. Chandrasekar, M. Ruben, F. Evers, A. Bernand-Mantel, J. S. Seldenthuis, A. Beukman and H. S. J. van der Zant, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, 83, 245415.
- 6 F. Prins, M. Monrabal-Capilla, E. A. Osorio, E. Coronado and H. S. J. van der Zant, *Adv. Mater.*, 2011, 23, 1545.
- 7 A. Hauser, Top. Curr. Chem., 2004, 234, 155.
- 8 D. Collison, C. D. Garner, C. M. McGrath, J. F. W. Mosselmans, M. D. Roper, J. M. W. Seddon, E. Sinn and N. A. Young, *J. Chem. Soc., Dalton Trans.*, 1997, 4371.
- 9 G. Vanko, F. Renz, G. Molnar, T. Neisius and S. Karpati, *Angew. Chem.*, *Int. Ed.*, 2007, 46, 5306.
- 10 O. Kahn and C. Jay-Martinez, Science, 1998, 279, 44.
- 11 J.-F. Létard, P. Guionneau and L. Goux-Capes, *Top. Curr. Chem.*, 2004, 235, 221.
- 12 O. Kahn, J. Krober and C. Jay, Adv. Mater., 1992, 4 (11), 718.
- 13 I. Šalitroš, N. T. Madhu, R. Boča, J. Pavlik and M. Ruben, *Monatsh. Chem.*, 2009, 140, 695.
- 14 J. Elhaïk, V. A. Money, S. A. Barrett, C. A. Kilner, I. Radosavljevic, A. Evans and M. A. Halcrow, *Dalton Trans.*, 2003, 2053.
- 15 J. M. Holland, J. A. McAllister, C. A. Kilner, M. Thornton-Pett, A. J. Bridgeman and M. A. Halcrow, J. Chem. Soc., Dalton Trans., 2002, 548.
- 16 C. Rajadurai, O. Fuhr, R. Kruk, M. Ghafari, H. Hahn and M. Ruben, *Chem. Commun.*, 2007, 2636.
- 17 M. Clemente-León, E. Coronado, M. Carmen Giménez-López and F. M. Romero, *Inorg. Chem.*, 2007, 46, 11266.
- 18 K. S. Murray and C. J. Kepert, Top. Curr. Chem., 2004, 233, 195.
- 19 J. Kröber, E. Codjovi, O. Kahn, F. Grolibre and C. Jay, J. Am. Chem. Soc., 1993, 115, 9810.
- 20 J. Kröber, J.-P. Audibre, R. Claude, E. Codjovi and O. Kahn, *Chem. Mater.*, 1994, 6, 1404.
- 21 V. Niel, J. M. Martinez-Agudo, M. Carmen Munoz, A. B. Gaspar and J. A. Real, *Inorg. Chem.*, 2001, **40**, 3838.
- 22 B. Weber, W. Bauer and J. Obel, Angew. Chem., Int. Ed., 2008, 47 (52), 10098.
- 23 S. Hayami, K. Hiki, T. Kawahara, Y. Maeda, D. Urakami, K. Inoue, M. Ohama, S. Kawata and O. Sato, *Chem.-Eur. J.*, 2009, 15, 3497.
- 24 R. Boča, M. Boča, L. Dlháň, K. Falk, H. Fuess, W. Haase, R. Jaroščiak, B. Papánková, F. Renz, M. Vrbová and R. Werner, *Inorg. Chem.*, 2001, 40, 3025.

- 25 M. Quesada, F. Prins, E. Bill,H. Kooijiman, P. Gamez, O. Roubeau, A. L. Spek, J. G. Haasnoot and J. Reedijk, *Chem.-Eur. J.*, 2008, 14, 8486.
- 26 I. Šalitroš, J. Pavlík, R. Boča, O. Fuhr, C. Rajadurai and M. Ruben, *CrystEngComm*, 2010, 12, 2361.
- 27 M. Yamada, H. Hagiwara, H. Torigoe, N. Matsumoto, M. Kojima, F. Dahan, J. P. Tuchagues and N. R. S. Iijima, *Chem.-Eur. J.*, 2006, **12**, 4536.
- 28 H. Hagiwara, N. Matsumoto, S. Iijima and M. Kojima, *Inorg. Chim. Acta*, 2011, 366, 283.
- 29 C. Rajadurai, Z. Qu, O. Fuhr, B. Gopalan, R. Kruk, M. Ghafari and M. Ruben, *Dalton Trans.*, 2007, 3531.
- 30 J. Elhaik, D. J. Evans, C. A. Kilner and M. A. Halcrow, *Dalton Trans.*, 2005, 1693.
- 31 M. Haryono, F. W. Heinemann, K. Petukhov, K. Gieb, P. Müller and A. Grohmann, *Eur. J. Inorg. Chem.*, 2009, 2136.
- 32 A. Galet, A. B. Gaspar, M. C. Munoz, G. Levchenko and J. A. Real, *Inorg. Chem.*, 2006, 45, 9670.
- 33 C. Faulmann, P. Á. Szilágyi, K. J. Chahine and L. Valade, New J. Chem., 2009, 33, 1268.
- 34 G. S. Matouzenko, E. Jeanneau, A. Yu. Verat and Azzedine Bousseksou, *Dalton Trans.*, 2011, 40, 9608.
- 35 N. T. Madhu, I. Salitros, F. Schramm, S. Klyatskaya, O. Fuhr and M. Ruben, C. R. Chim., 2008, 11, 1166.
- 36 C. Rajadurai, F. Schramm, S. Brink, O. Fuhr, M. Ghafari, R. Kruk and M. Ruben, *Inorg. Chem.*, 2006, 45, 10019.
- 37 C. Rajadurai, F. Schramm, O. Fuhr and M. Ruben, *Eur. J. Inorg. Chem.*, 2008, **17**, 2649.
- 38 O. Kahn, Molecular Magnetism, 1993, VCH Publishers, New York.
- 39 G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 1990, 46, 467.
- 40 G. M. Sheldrick, SHELXL-97 (Release 97-2) Program for the refinement of Crystal Structures, University of Göttingen, Germany, 1997
- 41 STOE, WinXPOW, STOE & Cie GmbH, Darmstadt, 2000.
- 42 G. Della Gatta, M. J. Richardson, S. M Sarge and S. Stolen, Pure Appl. Chem., 2006, 78, 1455.
- 43 P. J. van Ekeren, A. C. D. van Genderen and G. J. K. van den Berg, *Thermochim. Acta*, 2006, 446, 33.
- 44 Y. Takahashi, T. Azumi and Y. Sekine, *Thermochim. Acta*, 1989, 139, 133.
- 45 D. B. Downie and J. F. Martin, J. Chem. Thermodyn., 1980, 12, 779.
- 46 K. H. Sugiyarto and H. A. Goodwin, Aust. J. Chem., 1988, 41, 1645.
- 47 G. R. Desiraju and T. Steiner, *The weak hydrogen bond*, 1999, IUCr Oxford Science Publication.
- 48  $\sum_{i=1}^{12} (|\varphi_i 90|)$ ; where  $\varphi_i$  is value of N-Fe-N octahedron angle.
- 49 P. Guionneau, M. Marchivie, G. Bravic, J. F. Létard and D. Chasseau, *Top. Curr. Chem.*, 2004, 234, 97.
- 50 G. W. H. Hoehne, W. Hemminger and H. J. Flammersheim, *Differential Scanning Calorimetry: An Introduction for Practitioners*, 2003, Springer Verlag, Berlin.
- 51 A. Kondepudi and I. Prigogine, *Modern Thermodynamics*, 1998, Viley-VCH, Weinheim.
- 52 E. A. Osorio, T. Bjornholm, J.-M. Lehn, M. Ruben and H. S. J. van der Zant, J. Phys.: Condens. Matter, 2008, 20, 374121.