2D Layer Arrangement of Solely [HS-HS] or [LS-LS] Molecules in the [HS-LS] State of a Dinuclear Fe(II) Spin Crossover Complex

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Received: 13 April 2020; Accepted: 8 May 2020; Published: 31 May 2020

Abstract: Herein we report the synthesis and characterization of three new dinuclear iron(II) complexes \([\text{Fe}^{\text{II}}_2(\text{I}^4\text{MTD})_2](\text{F}_3\text{CSO}_3)_4\) (C1), \([\text{Fe}^{\text{II}}_2(\text{I}^4\text{MTD})_2](\text{ClO}_4)_4\) (C2) and \([\text{Fe}^{\text{II}}_2(\text{I}^4\text{MTD})_2](\text{BF}_4)_4\) (C3) based on the novel ligand \((\text{I}^4\text{MTD}) = 2,5\text{-bis}[(1\text{H}-\text{imidazol-4-yl}\text{methyl})\text{amino}]\text{methyl}-1,3,4\text{-thiadiazole})\). Magnetic susceptibility measurements and single-crystal structure analysis show that the iron(II) spin centers for all complexes are in the high spin state at high temperatures. While the magnetic data of air-dried samples confirm the [HS-HS] state for C1 and C2 down to very low temperature, for C3, a gradual spin crossover is observed below 150 K. The crystal structure of C3·THF at 100 K shows that a spin transition from [HS-HS] to an intermediate state takes place, which is a 1:1 mixture of discrete [HS-HS] and [LS-LS] molecules, as identified unambiguously by crystallography. The different SCO properties of C1–C3 can be attributed to crystal packing effects in the solid state.

Keywords: spin crossover; dinuclear complex; [HS-LS]; 1,3,4-thiadiazole; iron(II); magnetism; single-crystal structure analysis

1. Introduction

The growing interest and the necessity of miniaturizing processes lead to multiple research areas in the past decades [1]. The ability to switch between different states at the molecular scale, thus exhibiting molecular bistability, renders spin crossover (SCO) compounds highly promising candidates for memory storage devices, sensors, actuators or displays [2–11]. Complexes of first-row transition metal ions with an electron configuration of \(d^4–d^7\) can either be in the high spin [HS] or in the low spin [LS] state, depending on the octahedral field splitting (\(\Delta_O\)) and the spin pairing energy (\(P\)). Switching between these two states by external stimuli such as the change of temperature, pressure or light is called SCO [12–14]. Iron(II) complexes in the \(N_6\) coordination environment are by far the most investigated SCO compounds. Their \(d^6\) electron configuration allows switching between a diamagnetic LS state (\(S = 0\)) and a paramagnetic HS state (\(S = 2\)). Occupying or, vice versa, complete depopulating of the antibonding \(e_g^*\) orbitals gives rise to a large change in the average Fe-N bond length. This allows the investigation of SCO in iron(II) compounds by standard methods such as temperature-dependent magnetic measurements and X-ray crystallography. Since the interest in SCO is mainly due to the possible application as a molecular switch in information storage or sensors, the research focus is on a complete, abrupt and hysteretic spin switch [1,15–17]. In the solid state, the abrupt change in the properties upon switching and even more, the occurrence of a thermal SCO hysteresis strongly depends on the cooperativity between the spin centers. This is highly favored by intermolecular hydrogen bridges and \(\pi–\pi\) interactions between the ligand backbones. However, an even better tool to improve cooperativity is to take advantage of intramolecular covalent linking.
of the metal centers in polymeric compounds [1,3,13,18–21]. Drawbacks are here the difficulties to control the polymerization that hampers crystallization. This can be overcome with oligonuclear compounds. Especially, dinuclear compounds are of particular interest due to the easier control of synthesis and characterization [19,22–25]; furthermore, dinuclear complexes offer the possibility of addressing three accessible states ([HS-HS], [HS-LS] and [LS-LS]) [26], which opens the chance for higher information storage capacities and mathematical operations based on trinary logic [27–29]. In 2005, Brooker reported the dinuclear triazole bridged iron(II) complex [FeII2(PMAT)2][BF4]4 (PMAT = 2,5-bis[[2-pyridylmethyl]amino]methyl-4-amino-4H-1,2,4-triazole) (Figure 1) that shows a spin switch from the [HS-HS] state at high temperature to an [HS-LS] state at lower temperatures [30].

Our group reported the synthesis and characterization of symmetric dinuclear complexes incorporating the PMTD (2,5-bis[(2-pyridylmethyl)amino]methyl-1,3,4-thiadiazole, Figure 1) and PMOD ligand (2,5-bis[(2-pyridylmethyl)amino]methyl-1,3,4-oxadiazole, Figure 1) which both show spin crossover in dependence of the solvent and non-coordinating counterions used [31–33]. Like the PMAT ligand, the bridging bis-tridentate ligands PMTD and PMOD provide six donor atoms, respectively, allowing for octahedral coordination of both iron(II) ions. Recently, we reported six new dinuclear iron(II) complexes based on two new 1,3,4-thiazole bridging ligands (I$^{\text{PMTD}} = 2,5$-bis[[1H-imidazol-2-ylmethyl]amino]methyl]-1,3,4-thiadiazole and TMTD = 2,5-bis[[thiazol-2-yl-methyl]amino]methyl]-1,3,4-thiadiazole, Figure 1). For the complex [FeII2(TMTD)2][ClO4]4·3MeCN a two-step spin crossover is observed that is accompanied by two distinct phase transitions. While slow cooling leads to distinguishable HS/LS pairs in the mixed [HS-LS] state, rapid cooling leads to a superposition of the HS and LS iron(II) ions in the [HS-LS] state. Thus, quenching prevents the phase transition to be observable crystallographically. In contrast, all complexes with the I$^{\text{PMTD}}$ ligand remain in the [HS-HS] state until very low temperatures [34].

We now report on the modification of the I$^{\text{PMTD}}$ ligand by changing the binding of the imidazolyl heteroaromatic ring to the thiadiazole backbone. The novel I$^{\text{TMTD}}$ (2,5-bis[[1H-imidazol-4-ylmethyl]amino]methyl]-1,3,4-thiadiazole, Figure 1) was synthesized and characterized. The purpose of this modification was to investigate the intermolecular cooperative interaction pathways of the dinuclear complexes bridged by the I$^{\text{PMTD}}$ ligand compared to the I$^{\text{TMTD}}$ based complexes. Since the position of the protonated nitrogen atom in the imidazolyl ring is changed, different hydrogen bonding is expected. We synthesized and characterized three new bimetallic iron(II) complexes [FeII2(I$^{\text{TMTD}}$)2](X)4 (with X = BF4$^-$, ClO4$^-$ and F3CSO3$^-$), which exhibit distinct different hydrogen bonding networks via the non-coordinating counterions, resulting in different magnetic properties.

![Figure 1. Summary of the ligand systems mentioned in the introduction.](image-url)
2. Experimental Section

**General Methods and Materials:** All chemicals were purchased as commercially available from Alfa Aesar (Thermo Fisher (Kandel) GmbH, Kandel, Germany), Deutero (Deutero GmbH, Kastellaun, Germany), TCI (TCI Deutschland GmbH, Eschborn, Germany), Sigma-Aldrich (Sigma-Aldrich Chemie GmbH, Munich, Germany) and Acros Organics (Thermo Fisher Scientific, Geel, Belgium) and used without further purification as described in the literature [35]. Variable-temperature magnetic susceptibility measurements and elemental analysis (C, H, N) were performed at the microanalytical laboratories of Johannes Gutenberg University Mainz. Single-crystal X-ray diffraction data were collected at 100 K, 173 K and 200 K with a STOE STADIVARI at the Johannes Gutenberg University Mainz. The structures were solved with ShelXT [37] and refined with ShelXL [38] implemented in the program Olex2 (OlexSys Ltd., Durham, United Kingdom) [39]. CCDC-1995090-1995093 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Caution!** The prepared perchlorate complexes are potentially explosive. Even though no explosions occurred, only small amounts should be prepared and handled with care.

**Ligand synthesis:** 1,2-Bis(chloroacetyl)hydrazine, 2,5-bis(chloromethyl)-1,3,4-thiadiazole, 2,5-bis(azidomethyl)-1,3,4-thiadiazole and 2,5-bis(aminomethyl)-1,3,4-thiadiazole (I) were prepared according to literature-known procedures [31,34]. The ligand \( \text{I}^{\text{MTD}} = 2,5\text{-Bis}[\{(1\text{H-imidazol-4-ylmethyl)amino}\text{methyl}\}-1,3,4\text{-thiadiazole} \) was synthesized based on similar reductive amination recently published by us [34].

2,5-Bis[\{(1H-imidazol-4-ylmethyl)amino]methyl\}-1,3,4-thiadiazole (I\(^{\text{MTD}}\)): A solution of 1H-Imidazol-4-carbaldehyde (2) (2.02 g, 21.00 mmol, 2.1 equiv.), 2,5-bis(aminomethyl)-1,3,4-thiadiazole (I) (1.44 g, 10.00 mmol, 1.0 equiv.), sodium cyanoborohydride (3.14 g, 50.00 mmol, 5.0 equiv.), and acetic acid (1.26 g, 21.00 mmol, 2.1 equiv.) in methanol (200 mL) was refluxed and followed with TLC (chloroform/methanol 2:1) until the disappearance of the ligand. After removal of the solvent under reduced pressure, the obtained oil was purified by column chromatography (SiO\(_2\), chloroform/methanol 2:1). The brown and oily product crystallized upon drying under reduced pressure. The product could not be separated from small impurities. Yield: 2.80 g (9.20 mmol, 92.0%).

**General complex synthesis of \([\text{Fe}^{II}(\text{I}^{\text{MTD}})\text{X}_4]\):** The complex syntheses were carried out in a glovebox under nitrogen atmosphere and exclusion of water and oxygen. After a solution of the ligand (I\(^{\text{MTD}}\), 0.10 mmol) in absolute acetonitrile/methanol (2:1, 2 mL) was added to a solution of the corresponding iron(II) salt (0.10 mmol, Fe(BF\(_4\))\(_{2}\)-6H\(_2\)O, Fe(CIO\(_4\))\(_2\)-xH\(_2\)O or Fe(F\(_3\)SO\(_3\))\(_2\)) in absolute acetonitrile (2 mL) the resulting yellowish to orange complex solutions were exposed to vapor diffusion of absolute diethyl ether or absolute tetrahydrofuran. After several days to weeks, crystals have formed, which were suitable for single-crystal X-ray studies.

\[\text{[Fe}^{\text{II}}(\text{I}^{\text{MTD}})\text{F}_3\text{SO}_3]_2\text{solvents} (\text{C1}): \text{Fe}(\text{F}_3\text{SO}_3)_2 (35 \text{ mg}) \text{ and } 2,5\text{-Bis}[\{(1\text{H-imidazol-4-ylmethyl)amino]methyl\}-1,3,4\text{-thiadiazole} (\text{I}^{\text{MTD}}, 30 \text{ mg}) \text{ were used to obtain C1 (23 mg, 33.6%)} \text{ as yellow crystals.} \] C\(_{25}\)H\(_{32}\)Fe\(_2\)F\(_{12}\)N\(_{16}\)O\(_{12}\)S\(_{6}\) \[\text{Fe}^{\text{II}}(\text{I}^{\text{MTD}})\text{F}_3\text{SO}_3]_2 (1316.50): \text{calcd. C 55.44 H 2.45 N 17.02; found (after air-drying) C 55.17 H 2.15 N 16.61.}\]

\[\text{[Fe}^{\text{II}}(\text{I}^{\text{MTD}})\text{ClO}_4]_2\text{THF (C2): Fe}(\text{ClO}_4)_2\text{xH}_2\text{O (27 mg)} \text{ and } 2,5\text{-Bis}[\{(1\text{H-imidazol-4-ylmethyl)amino]methyl\}-1,3,4\text{-thiadiazole} (\text{I}^{\text{MTD}}, 30 \text{ mg}) \text{ were used to obtain C2 (26 mg, 45.6%) as}\]
3. Results and Discussion

3.1. Synthesis

The synthesis of the ligand 

\[ \text{[Fe}^{	ext{II}}{\text{(I}^4\text{MTD})}_2{\text{C}_3\text{SO}_3}]_4 \] (C1) was previously reported by us [34]. The ligand \((\text{I}^4\text{MTD}) = 2,5\text{-bis}[(1\text{H-imidazol-4-ylmethyl})\text{amino[methyl]}]-1,3,4\text{-thiadiazole}\) was synthesized according to a published reductive amination [34] by reacting 1 with 1H-imidazole-4-carbaldehyde (2) followed by an in situ reduction of the formed imine to the respective amine with sodium cyanoborohydride. The reaction scheme for the synthesis of the ligand \((\text{I}^4\text{MTD})\) is shown in Scheme 1.

![Scheme 1. Synthesis of the ligand \((\text{I}^4\text{MTD})\) starting from 2,5-bis(aminomethyl)-1,3,4-thiadiazole (1).](image)

The complexes \([\text{Fe}^{	ext{II}}{\text{(I}^4\text{MTD})}_2{\text{C}_3\text{SO}_3}]_4\) (C1), \([\text{Fe}^{	ext{II}}{\text{(I}^4\text{MTD})}_2{\text{ClO}_4}]_4\) (C2) and \([\text{Fe}^{	ext{II}}{\text{(I}^4\text{MTD})}_2{\text{BF}_4}]_4\) (C3) were synthesized in stoichiometric reactions of the ligand \((\text{I}^4\text{MTD})\) with the respective iron(II) salt \([\text{Fe}^{	ext{II}}\text{ClO}_4]_2\), \([\text{Fe}^{	ext{II}}\text{ClO}_4]\text{H}_2\text{O}\) or \([\text{Fe}^{	ext{II}}\text{BF}_4]_2\text{H}_2\text{O}\). Single crystals suitable for X-ray diffraction have been obtained by vapor diffusion of diethyl ether or tetrahydrofuran into complex solutions of acetonitrile and methanol (5:1 volume ratio). The syntheses were performed under nitrogen atmosphere using absolute solvents to prevent oxidation of the iron(II) ions.

3.2. Crystal Structures

The crystal structures of the complexes \([\text{Fe}^{	ext{II}}{\text{(I}^4\text{MTD})}_2{\text{C}_3\text{SO}_3}]_4\) \(\text{Et}_2\text{O}/2\text{MeCN}\) (C1-Et2O/2MeCN, \@173 K), \([\text{Fe}^{	ext{II}}{\text{(I}^4\text{MTD})}_2{\text{ClO}_4}]_4\) THF (C2-THF, \@173 K) and \([\text{Fe}^{	ext{II}}{\text{(I}^4\text{MTD})}_2{\text{BF}_4}]_4\) THF (C3-THF, \@100 and 200 K) all have the centrosymmetric \([\text{Fe}_2\text{L}_2]^4\text{+}\) complex cation in common. The two iron(II) centers are bridged by two ligand molecules via the two nitrogen donor atoms of the thiadiazole moiety. The two ligands provide an \(\text{N}_6\) octahedral environment for each metal center. Despite the possibility of \(\text{cis-}\) or \(\text{trans-}\)-axial coordination of the ligand, as shown for compounds with related ligands [30,31,34,40], all here described complexes feature the \(\text{cis-}\)-axial coordination (see Figure 2). The crystal structures comprise four respective anions counterbalancing the charge. For C2 and C3, the non-coordinating solvent molecule included is tetrahydrofuran. For C1, the electron density can be interpreted as either one diethyl ether molecule or two acetonitrile molecules per cation. The highly disordered solvent molecules were treated with SQUEEZE [41] in the program Olex2 [39]. The formula \([\text{Fe}^{	ext{II}}{\text{(I}^4\text{MTD})}_2{\text{C}_3\text{SO}_3}]_4\) solvent (C1-solvent) is used throughout the paper. All crystallographic parameters are given in Table S1.

C1 is found to be in the monoclinic space group \(\text{C}2/c\) (\@173 K), C2 in the triclinic space group \(\text{P}\text{\bar{T}}\) (\@173 K) and C3 in the orthorhombic group \(\text{Pbca}\) (\@200 K). For all three structures, one half of the complex cation is part of the asymmetric unit and the full cation is symmetry generated by an inversion center located between the two metal centers in the bimetallic complex. The average Fe-N bond lengths of 2.188 Å (C1-solvents), 2.192 Å (C2-THF) and 2.187 Å (C3-THF, \@200 K), account for...
an iron(II) ion in the HS state, resulting in the [HS-HS] state for the whole complex molecule at the
given temperatures. This is further confirmed by the octahedral distortion parameters \( \Sigma \) (sum of the
devation from 90° of the 12 cis-N-Fe-N angles in the FeN₆ coordination sphere) of 108.0° (C1-solvents),
105.3° (C2-THF) and 116.5° (C3-THF, @200 K) [5,12,13,42]. Information on bond lengths and angles of
C1–C3 are summarized in Table 1.

![Figure 2. Sketch of the centrosymmetric complex cation \([\text{Fe}^{II}_{2}(t^4\text{MTD})_{2}]^{4+}\), showing the cis-coordina
tion of the ligand as well as octahedral coordination environment for the iron(II) ions.](image)

**Table 1.** Selected bond lengths (Å), N-Fe-N bond angles (°) and the octahedral distortion parameter \( \Sigma \) [°] for the compounds C1–C3. For compound C3 the values are given for different temperatures.

| Selected Parameters a b | C1 Solvents (@173 K) | C2 THF (@173 K) | C3 THF (@100 K) | C3 THF (@200 K) |
|-------------------------|----------------------|-----------------|-----------------|-----------------|
| Fe-N₁TDa(L1)            | 2.157(2)             | 2.150(2)        | LS 1.967(8)/     | 2.154(2)        |
|                         |                      |                 | HS 2.147(8)     |                 |
| Fe-N₁TDa(L2)            | 2.161(2)             | 2.174(2)        | LS 1.971(7)/     | 2.158(2)        |
|                         |                      |                 | HS 2.170(8)     |                 |
| Fe-N₁NH(L1)             | 2.298(2)             | 2.296(2)        | LS 2.055(8)/     | 2.255(2)        |
|                         |                      |                 | HS 2.239(7)     |                 |
| Fe-N₁NH(L2)             | 2.304(2)             | 2.297(2)        | LS 2.103(8)/     | 2.301(2)        |
|                         |                      |                 | HS 2.290(8)     |                 |
| Fe-N₁Imz(L1)            | 2.106(2)             | 2.114(2)        | LS 1.995(8)/     | 2.132(2)        |
|                         |                      |                 | HS 2.131(7)     |                 |
| Fe-N₁Imz(L2)            | 2.104(2)             | 2.120(2)        | LS 1.958(8)/     | 2.122(2)        |
|                         |                      |                 | HS 2.124(7)     |                 |
| av. Fe-N                | 2.188                | 2.192            | LS 2.008/        | 2.187           |
|                         |                      |                 | HS 2.184        |                 |
| av. cis N-Fe-N          | 90.2                 | 90.2             | LS 90.0/        | 90.2            |
|                         |                      |                 | HS 90.2         |                 |
| av. trans N-Fe-N        | 169.5                | 169.5            | LS 172.9/       | 168.2           |
|                         |                      |                 | HS 168.1        |                 |
| \( \Sigma \) c          | 108.0                | 105.3            | LS 69.5/        | 116.5           |
|                         |                      |                 | HS 115.6        |                 |

a \( N_{TDa} \) = donor atom on thiadiazole; \( N_{Imz} \) = donor atom on imidazole; \( N_{NH} \) = amine donor atom. b Fe₁/Fe₂. c Octahedral distortion parameter \( \Sigma \) (sum of the deviation from 90° of the 12 cis-N-Fe-N angles in the FeN₆ coordination sphere).
Variable-temperature magnetic susceptibility measurements have been performed for all complexes (see below). For C3, a partial spin state switching below 150 K was observed. To elucidate this finding, we decided to investigate the X-ray data at lower temperatures. Thus, the single-crystal X-ray data were collected for C3-THF at 100 K. The yellow crystal turned red during cooling, but also got fine cracks, which lowers the quality of the crystallographic data. However, a phase transition was seen unambiguously when lowering the temperature to 100 K. The space group changed from orthorhombic Pbcă (@200 K) to monoclinic P2₁/c (@100 K). The asymmetric unit of the monoclinic phase consists now of two half complex cations with two crystallographic independent iron(II) ions; one per cation (Figure 3).

For one complex cation in the asymmetric unit, the iron(II) ion (FeHS) stays in the HS state. The average Fe-N bond length of 2.184 Å and the octahedral distortion Σ of 115.6° remain almost the same as in the structure obtained at 200 K (2.187 Å and 116.3°), confirming a localized [HS-HS] dimer. For the other complex cation, the average Fe-N bond lengths and the octahedral distortion parameter Σ for the iron(II) ion (FeLS) decrease to 2.008 Å and 69.5°, which accounts for a localized [LS-LS] complex cation. Thus, a spin transition occurs between 200 and 100 K from the [HS-HS] to the mixed [HS/LS] state, which is a 1:1 mixture of localized dimers either in the [HS-HS] or in the [LS-LS] state (Figure 3). The crystallographic differentiation, whether the [HS-LS] state is realized by discrete [HS-LS] molecules or it composes from a 1:1 mixture of [HS-HS] and [LS-LS] molecules, is not possible in most cases due to higher symmetry in the space group. In centrosymmetric molecular structures, a superposition of the HS and LS iron(II) ions might be observed [43–49]. Fortunately, this is not the case for C3, where at low temperatures the dimeric spin crossover complexes can be clearly identified as either [HS-HS] or [LS-LS] molecules.

![Figure 3](image-url). Crystallographic independent complex cations for C3-THF at 200 (top) and 100 K (bottom). The asymmetric units are depicted in bold, while the second half of the cations (wireframe) are symmetry generated. The orientation of the molecules and the labeling is the same as for Figure 2. Hydrogens, solvent molecules and cations are omitted for clarity. Color code: Fe dark red, N blue, S yellow, C gray.
However, to get a better understanding of why C3-THF shows SCO while C1-solvents and C2-THF do not, we have to take a closer look at the crystal packing, which has a crucial influence on the SCO behavior \[3,25,42,50\].

Along the crystallographic c-axis in C3-THF (@200 K), the dinuclear [HS-HS] molecules are arranged in two-dimensional layers formed by hydrogen bonds between the amine protons and the fluorine atoms of the tetrafluoroborate ions (Figure 4, bottom). These layers are separated by 3.11 Å and non-coordinating tetrahydrofuran solvent molecules, as well as tetrafluoroborate counterions which are located between the layers (Figure 4, top). However, there is no cooperative interaction pathway via hydrogen bonding between the two layers. When lowering the temperature, the occurring SCO phenomenon, ([HS-HS] → [HS-LS]) is accompanied by a phase transition and the space group changes from \( \text{Pbca} \) to \( \text{P}2_1/c \). At low temperatures, the complex cations in every second layer are switched to the [LS-LS] state, resulting in alternating layers of either [LS-LS] or [HS-HS] molecules. This layered arrangement of molecules solely in the HS or in the LS is rare and we found only a few examples in the literature for which the spin crossover is accompanied by shrinking or expanding of one distinguished crystallographic axis \[51–56\]. Note that although the direction of the stacking does not change, the crystallographic c-axis of the high-temperature space group \( \text{Pbca} \) turns to be the \( a \)-axis in \( \text{P}2_1/c \) (Figures 4 and 5). While the intramolecular bond lengths and angles for the iron(II) centers change significantly when going from the HS to the LS state, the intermolecular hydrogen bridges between the dimers in each layer do not change significantly. Thus, to give way to the overall reduced required space for [LS-LS] dimers, compared to the [HS-HS] ones, the stacking changes. With the SCO the interlayer diameter reduces by 0.3 Å from 3.110 Å to 2.804 Å. This drastic impact of the phase transition on only one of the crystallographic axes results inevitably to the small cracks in the crystal.

![Figure 4](image_url)

**Figure 4.** Crystal packing and hydrogen bonding (black dashed lines) toward neighboring anions in C3-THF at 200 K (space group \( \text{Pbca} \)). **Top.** View along the crystallographic b-axis. **Bottom.** View along the crystallographic c-axis. Solvent molecules, as well as non-bridging counterions, have been omitted for clarity. Color code: Fe dark red, N blue, S yellow, C gray, B pink, F green and H white.
For C1 and C2, the dinuclear complex cations show hydrogen bonding between the amino or the imidazolyl groups and the respective counter ions triflate or perchlorate (Figures S8 and S10). While for C1, a three-dimensional network is realized for C2 intertwined layers are formed. In both cases, the molecules are quite densely packed in the solid state and there is basically no “space” to compensate for bond lengths and volume changes that come together with a spin transition. Thus, single-crystal structure analysis reveals that it is very unlikely that C1 and C2 show any SCO behavior.

3.3. Variable-Temperature Magnetic Susceptibility Measurements

Variable-temperature magnetic susceptibility measurements were performed on microcrystalline to powderous air-dried samples of C1–C3 in the temperature range of 2–300 K in an applied magnetic field of 1000 Oe (0.1 T) (Figure 6 and Figure S12). It is important to mention that the freshly prepared crystalline samples of C1–C3 almost immediately lose crystallinity, when exposed to air, explained by the loss of the volatile solvents (diethyl ether or tetrahydrofuran). Thus, we did not succeed to obtain magnetic data of freshly prepared crystalline samples. The magnetic studies were performed with a cooling/heating rate of 1.5 K/min and the $\chi_M T$ vs $T$ plots are indistinguishable for the measurements when heated or cooled. In all three compounds C1–C3, the dimers are in the [HS-HS] state at 300 K as indicated by $\chi_M T$ values between 6.54 and 6.96 cm$^3$Kmol$^{-1}$ per complex cation varying with the counterions. All measured values are slightly higher than the calculated one for an iron(II) dimer with two non-interacting HS iron(II) ions of 6.00 cm$^3$Kmol$^{-1}$ using the spin-only formalism. However, this
difference is expected, as the spin-only formula does not account for any orbital angular momentum. Upon lowering the temperature, the $\chi_MT$ values for C1 and C2 remain almost invariant, indicating that the iron(II) ions remain in the HS state down to low temperature. Below 50 K, for both complexes, the $\chi_MT$ value decreases which can be explained by the presence of weak anti-ferromagnetic exchange interactions between the iron(II) ions and/or by the zero-field splitting of the $S = 2$ state. For C3, the $\chi_MT$ value remains high until about 150 K before it drops to ~4.40 cm$^{-3}$Kmol$^{-1}$. The resulting small plateau between 70 and 50 K can be explained by a gradual spin transition of a major part of the dimers (calculated to 70%) from the [HS-HS] to the [HS-LS] state. The decrease of the $\chi_MT$ value for C3 below 50 K is again explained with the presence of weak anti-ferromagnetic exchange interactions between the HS iron(II) ions in the remaining [HS-HS] dimers and/or by the zero-field splitting of the $S = 2$ state. The difference between the magnetic data and the single-crystal structure analysis (described above) of C3 is explained by the loss of the volatile solvent molecules and thus by the loss of crystallinity upon air-drying of the sample. The effect of the solvent loss on the magnetic data is shown in Figure S13 in the supporting information.

4. Conclusions

Concluding, we synthesized the new bis-tridentate 1,3,4-thiadiazole bridging ligand ($^{11}$MTD = 2,5-Bis[[[1H-imidazol-4-ylmethyl]amino]methyl]-1,3,4-thiadiazole, from which we obtained a series of three potentially SCO active dinuclear iron(II) complexes ([Fe$^{II}$]$_2$($^{11}$MTD)$_2$]$^\text{X}$ with $X = F_3$CSO$_3^-$ (C1), ClO$_4^-$ (C2) and BF$_4^-$ (C3)). Magnetic susceptibility measurements and single-crystal structure analysis revealed a temperature-independent [HS-HS] state for C1 and C2. In contrast, magnetic data for C3 showed a gradual spin transition below 200 K suggesting an intermediate [HS-LS] state at low temperatures. However, single-crystal X-ray analysis proved the supposed intermediate spin state to be a 1:1 mixture of [HS-HS] and [LS-LS] molecules. While the local ligand field strength for the iron(II) ions is the same in all three complexes, very clearly, different crystal packing causes the different spin switching properties of the complexes. For C1 and C2, three-dimensional hydrogen bridged networks or strongly intertwined layers of iron(II) dimer molecules are found. In contrast, the dimers in C3 arrange in two-dimensional layers that are well separated by the non-coordinating counterions and
solvent molecules. The SCO is accompanied by a crystallographic phase transition that accounts for the molecular re-arrangement. With this, the interlayer spacing is already reduced by 0.3 Å although only the molecules in every second 2D layer change the spin state. At 100 K alternating layers of [HS-HS] and [LS-LS] dimers are observed in the crystal structure. In magnetic data obtained from the bulk sample, an average “[HS-LS]” state is featured. Thus, our results clearly underline the importance of investigations of SCO phenomena using complementary methods.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4352/10/6/448/s1, Figure S1. $^1$H-NMR of 2,5-bis[[(1H-imidazol-4-ylmethyl)amino]methyl]-1,3,4-thiadiazole (MTD). Figure S2. $^{13}$C-NMR of 2,5-bis[[(1H-imidazol-4-ylmethyl)amino]methyl]-1,3,4-thiadiazole (MTD). Figure S3. Field desorption mass spectrum of 2,5-bis[[(1H-imidazol-4-ylmethyl)amino]methyl]-1,3,4-thiadiazole (MTD). Figure S4. IR spectrum of air-dried [Fe$^{III}_2$(MTD)$_2$](F$_2$CSO$_3$)$_4$ (C1). Figure S5. IR spectrum of air-dried [Fe$^{III}_2$(MTD)$_2$](ClO$_4$)$_4$ (C2). Figure S6. IR spectrum of air-dried [Fe$^{III}_2$(MTD)$_2$]@[BF$_4$]$_4$ (C3). Figure S7. Molecular structure of [Fe$^{III}_2$(MTD)$_2$](F$_2$CSO$_3$)$_4$@[solvents] with thermal ellipsoids at 173 K. Solvent molecules could not be solved. Color code: Fe is dark red, N blue, S yellow, C grey, H white, O red and F light green. Figure S8. Crystal packing and hydrogen bonding (black dashed lines) via anions in [Fe$^{III}_2$(MTD)$_2$](F$_2$CSO$_3$)$_4$@[solvents] at 173 K. Non-bridging counter ions have been omitted for clarity. a) View along crystallographic b-axis. b) View along crystallographic a-axis. Color code: Fe is dark red, N blue, S yellow, C grey, H white, O red and F light green. Figure S9. Molecular structure of [Fe$^{III}_2$(MTD)$_2$](ClO$_4$)$_4$@[THF] (C2@[THF]) with thermal ellipsoids at 173 K. Color code: Fe is dark red, N blue, S yellow, C grey, H white, O red and Cl green. Figure S10. Crystal packing and hydrogen bonding (black dashed lines) via anions in [Fe$^{III}_2$(MTD)$_2$](ClO$_4$)$_4$@[THF] (C2@[THF]) at 173 K. Non-bridging counter ions and solvent molecules have been omitted for clarity. a) View along crystallographic a-axis. b) View along the angle bisector of the crystallographic a- and b-axis. Color code: Fe is dark red, N blue, S yellow, C grey, H white, O red and Cl green. Figure S11. Molecular structure of [Fe$^{III}_2$(MTD)$_2$]@[BF$_4$]$_4$@[THF]@solvents) with thermal ellipsoids at a) 200 K and b) 100 K. Color code: Fe is dark red, N blue, S yellow, C grey, H white, O red, B pink and F light green. Figure S12. $\chi_M$ T vs. T data for the air-dried compounds C1 (squares) and C2 (triangles). The data are given per dinuclear iron(II) molecule. Figure S13. $\chi_M$ T vs. T data for C3 for a freshly taken sample measured from 10–300 K after direct low-temperature freezing within the magnetometer (filled squares), subsequently measured from 300–10 K (empty squares) and for a dried sample from 10–300 K after heating the sample to 400 K for 2 h (filled circles). The data are given per dinuclear iron(II) molecule. Table S1. Crystallographic parameters for all discussed crystal structures of C1–C3.

Author Contributions: F.F. performed the synthesis and characterization of the ligand and the complexes. F.F. and L.M.C. performed the X-ray acquisition data and analysis. F.F. and E.R. finalized the manuscript with contributions from L.M.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflicts of interest.

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