



## Article

# High-Temperature Wide Thermal Hysteresis of an Iron(II) Dinuclear Double Helicate

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**Abstract:** Two new dinuclear iron(II) complexes (**1**·PF<sub>6</sub> and **1**·AsF<sub>6</sub>) of the general formula [Fe<sup>II</sup><sub>2</sub>(L<sup>2C3</sup>)<sub>2</sub>](X)<sub>4</sub>·nH<sub>2</sub>O·mMeCN (X = PF<sub>6</sub>, n = m = 1.5 for **1**·PF<sub>6</sub> and X = AsF<sub>6</sub>, n = 3, m = 1 for **1**·AsF<sub>6</sub>) have been prepared and structurally characterized, where L<sup>2C3</sup> is a bis-1,2,3-triazolimine type Schiff-base ligand, 1,1'-[propane-1,3-diylbis(1*H*-1,2,3-triazole-1,4-diyl)]bis{N-[2-(pyridin-2-yl)ethyl]methanimine}. Single crystal X-ray structure analyses revealed that **1**·PF<sub>6</sub> and **1**·AsF<sub>6</sub> are isostructural. The complexation [Fe<sup>II</sup><sub>2</sub>(L<sup>2C3</sup>)<sub>2</sub>]<sup>4+</sup> of both has the same dinuclear double helicate architecture, in which each iron(II) center has an N<sub>6</sub> octahedral coordination environment. Neighboring helicates are connected by intermolecular  $\pi$ – $\pi$  interactions to give a chiral one-dimensional (1D) structure, and cationic 1D chains with the opposite chirality exist in the crystal lattice to give a heterochiral crystal. Magnetic and differential scanning calorimetry (DSC) studies were performed only for **1**·AsF<sub>6</sub>, since the thermal stability in a high-temperature spin crossover (SCO) region of **1**·PF<sub>6</sub> is poorer than that of **1**·AsF<sub>6</sub>. **1**·AsF<sub>6</sub> shows an unsymmetrical hysteretic SCO between the low-spin–low-spin (LS–LS) and high-spin–high-spin (HS–HS) states at above room temperature. The critical temperatures of warming ( $T_c \uparrow$ ) and cooling ( $T_c \downarrow$ ) modes in the abrupt spin transition area are 485 and 401 K, respectively, indicating the occurrence of 84 K-wide thermal hysteresis in the first thermal cycle.

**Keywords:** double helicate; hysteresis; spin crossover; iron; 1,2,3-triazolimine;  $\pi$ – $\pi$  interaction

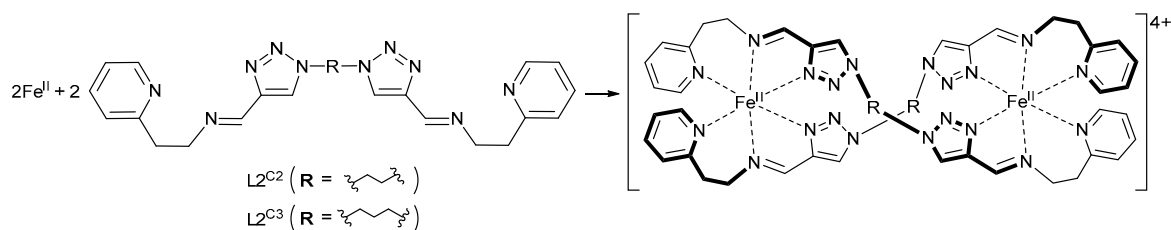
## 1. Introduction

The interconversion between a high-spin (HS) and a low-spin (LS) state, the so-called “spin crossover” (SCO), is one of the most attractive phenomena in the field of molecular bistability [1–3]. This phenomenon is observed in 3d<sup>4</sup>–3d<sup>7</sup> transition metal complexes with various coordination geometries (e.g., octahedral, square-pyramidal, trigonal-bipyramidal, tetrahedral, etc.) [1,4–7], and is triggered by an external stimulus such as temperature, pressure, light irradiation, or a magnetic field [1–3]. While SCO originates from an individual metal center, a spin transition profile, for example, abruptness and multi-steps with or without hysteresis, is provided from the cooperative effect between SCO metal sites through intra- or intermolecular pathways [1–3]. There is a need for SCO materials which are capable of abrupt and complete HS–LS interconversion at around room temperature (RT) with wide thermal hysteresis width ( $\Delta T$ ) for potential applications in molecular memories, switches, and display devices. As such, various cooperative SCO compounds have been produced with supramolecular assembly via intermolecular hydrogen bonding [8–10] and  $\pi$ – $\pi$  stacking [11–13], or coordination polymeric architecture by using bridging ligands [14–18]. Multinuclear clusters have also been widely studied in the hope of developing multistable compounds with more accessible spin states towards denser information storage, or hybrid SCO materials with multifunctional properties (e.g., SCO with charge transfer, magnetic coupling, luminescence, etc.) arising from the combination of the SCO metal center and other metal centers

[2,19–24]. In particular, dinuclear species have received much attention since they are a simple model for revealing intra- and intermolecular interactions for enhancing cooperativity [25–34]. From a more practical point of view, the importance of studying the reproducible nature and scan rate dependence of the hysteresis loop and high-temperature SCO with sufficient thermal stability has recently been pointed out in order to define the limiting characteristics of SCO materials [33,35–39].

Recently, we have focused on SCO molecules with 1-*R*-1*H*-1,2,3-triazole-containing Schiff-base (1-*R*-1*H*-1,2,3-triazolimine; *R* = Me and Ph) ligands since the ligand system can easily modify its structure with the choice of a substituent *R* of a precursor, 1-*R*-1*H*-1,2,3-triazole-4-carbaldehyde, and another amino precursor by simple click reaction [40–42], Schiff-base reaction [43] and replacement of *R* using the method reported by L'abbé and coworkers [44,45]. The iron(II) complexes with multidentate 1-*R*-1*H*-1,2,3-triazolimine ligand show a variety of SCO properties such as gradual, abrupt, and two-step transition with (or without) hysteresis in a wide temperature range (around RT, below RT and above RT over ca. 100 °C) [34,46,47]. In one of these studies, we reported the SCO iron(II) dinuclear double helicate for the first time [34]. This compound, with the formula  $[\text{Fe}^{\text{II}}_2(\text{L}2^{\text{C}2})_2](\text{PF}_6)_4 \cdot 5\text{H}_2\text{O} \cdot \text{MeCN}$ , has two bis-tridentate type ligand strands ( $\text{L}2^{\text{C}2}$ ) in which two 1,2,3-triazolimine moieties of the ligand strand are bridged by an ethylene chain (Scheme 1), and shows an anomalous two-step SCO with 11 K-wide hysteresis in a second step centered at 432 K, which is the highest hysteretic transition temperature in the dinuclear SCO system reported so far [26–29,33,48].

From the fascinating structure and function of the  $[\text{Fe}^{\text{II}}_2(\text{L}2^{\text{C}2})_2]^{4+}$  system, our own interest in the system has increasingly concerned the effect of the bridging alkyl chain length. We report here the synthesis, thermal stability, and structure of the corresponding propylene-bridged iron(II) dinuclear double helicate complexes  $[\text{Fe}^{\text{II}}_2(\text{L}2^{\text{C}3})_2](\text{PF}_6)_4 \cdot 1.5\text{H}_2\text{O} \cdot 1.5\text{MeCN}$  (**1**·**PF**<sub>6</sub>) and  $[\text{Fe}^{\text{II}}_2(\text{L}2^{\text{C}3})_2](\text{AsF}_6)_4 \cdot 3\text{H}_2\text{O} \cdot \text{MeCN}$  (**1**·**AsF**<sub>6</sub>), where  $\text{L}2^{\text{C}3} = 1,1'$ -[propane-1,3-diylbis(1*H*-1,2,3-triazole-1,4-diyl)]bis{*N*-[2-(pyridin-2-yl)ethyl]methanimine} (Scheme 1), and the high-temperature hysteretic SCO of **1**·**AsF**<sub>6</sub>.



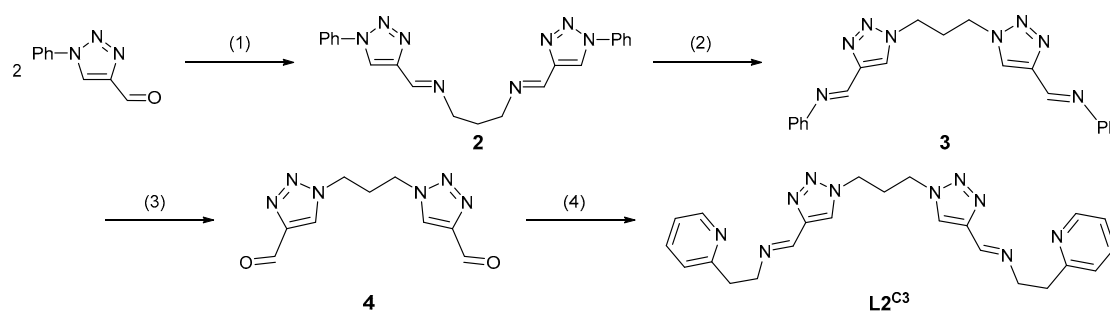
**Scheme 1.** Synthesis of the dinuclear double helicate complex-cation  $[\text{Fe}^{\text{II}}_2(\text{L}2^{\text{R}})_2]^{4+}$  (*R* = C2 = ethylene [34], *R* = C3 = propylene (this work)).

## 2. Results and Discussion

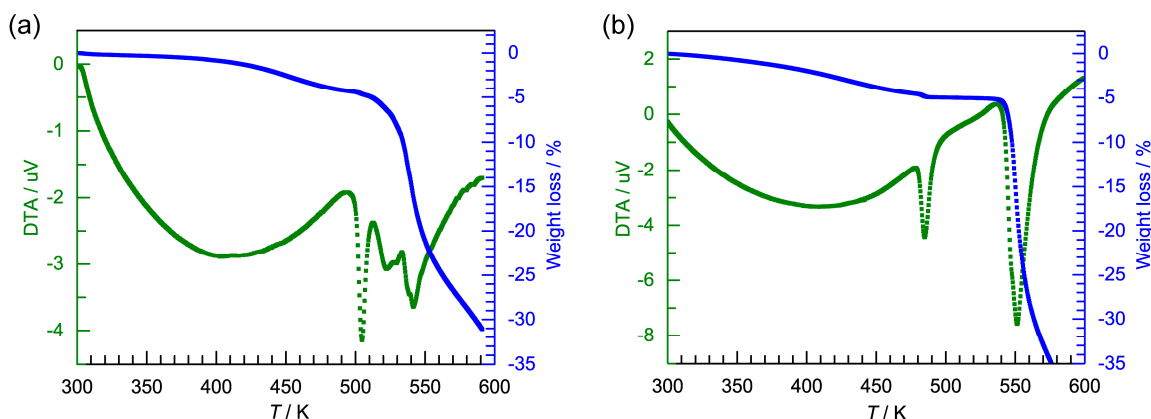
### 2.1. Synthesis and Characterization of $[\text{Fe}^{\text{II}}_2(\text{L}2^{\text{C}3})_2](\text{PF}_6)_4 \cdot 1.5\text{H}_2\text{O} \cdot 1.5\text{MeCN}$ (**1**·**PF**<sub>6</sub>) and $[\text{Fe}^{\text{II}}_2(\text{L}2^{\text{C}3})_2](\text{AsF}_6)_4 \cdot 3\text{H}_2\text{O} \cdot \text{MeCN}$ (**1**·**AsF**<sub>6</sub>)

The ligand  $\text{L}2^{\text{C}3}$  was prepared stoichiometric by the 1:2 condensation reaction of 1,1'-(propane-1,3-diyl)bis(1*H*-1,2,3-triazole-4-carbaldehyde) (**4**) and 2-(2-aminoethyl)pyridine. **4** was synthesized starting from 1-phenyl-1*H*-1,2,3-triazole-4-carbaldehyde and 1,3-diaminopropane (Scheme 2) based on the previously reported procedure of a related ethylene-bridged compound [34]. The dinuclear **1**·**PF**<sub>6</sub> and **1**·**AsF**<sub>6</sub> were prepared by mixing the ligand  $\text{L}2^{\text{C}3}$ ,  $\text{Fe}^{\text{II}}\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ , and *KX* (*X* =  $\text{PF}_6^-$  and  $\text{AsF}_6^-$  for **1**·**PF**<sub>6</sub> and **1**·**AsF**<sub>6</sub>, respectively) with a 1:1:2 molar ratio in MeOH/H<sub>2</sub>O mixed solution, which was then recrystallized from the MeCN/MeOH mixed solution. All the synthetic procedures were performed in air and both complexes were obtained as dark-red block crystals. The infrared spectra of both showed a characteristic band at ca. 1609 cm<sup>−1</sup>, corresponding to the C=N stretching vibration of the Schiff-base ligand [34,49]. In addition, characteristic bands at ca. 844 and 701 cm<sup>−1</sup> were observed, corresponding to the counter anions,  $\text{PF}_6^-$  and  $\text{AsF}_6^-$  for **1**·**PF**<sub>6</sub> and **1**·**AsF**<sub>6</sub>, respectively [34,49,50]. The formula of both complexes was confirmed by elemental analyses and thermogravimetric analyses. Thermogravimetry and differential thermal analysis (TG/DTA) curves

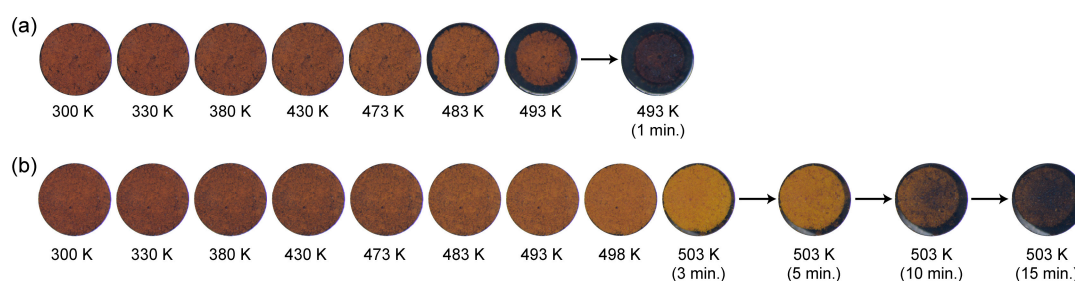
of both are shown in Figure 1. As shown in Figure 1a, when the powdered sample of **1**·**PF**<sub>6</sub> was heated from 30 °C (303 K) at a rate of 10 °C·min<sup>−1</sup>, the sample weight decreased gradually and a weight loss of 4.3% at 224 °C (497 K) was observed, which corresponds to the calculated weight percentages of 0.5H<sub>2</sub>O and 1.5MeCN molecules per [Fe<sup>II</sup><sub>2</sub>(L2<sup>C3</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub>·1.5H<sub>2</sub>O·1.5MeCN (**1**·**PF**<sub>6</sub>) (4.2%). Above this temperature, the weight loss became abrupt, and then the weight loss of the remaining one H<sub>2</sub>O molecule (1.1%) was observed at 242 °C (515 K). In this region, a sharp thermal anomaly in DTA appeared ( $T_{\max}$  = 232 °C (505 K)). Finally, above 242 °C (515 K), the weight loss became more and more abrupt, indicating the decomposition of **1**·**PF**<sub>6</sub>. In the same way, as shown in Figure 1b, when the powdered sample of **1**·**AsF**<sub>6</sub> was heated from 30 °C (303 K) at a rate of 10 °C·min<sup>−1</sup>, the sample weight decreased gradually and the total weight loss was 5.0% at 215 °C (488 K) in agreement with the calculated weight percentage of 3H<sub>2</sub>O and one MeCN molecule per [Fe<sup>II</sup><sub>2</sub>(L2<sup>C3</sup>)<sub>2</sub>](AsF<sub>6</sub>)<sub>4</sub>·3H<sub>2</sub>O·MeCN (**1**·**AsF**<sub>6</sub>) (5.1%). On further increasing the temperature from 215 °C (488 K), the desolvated sample of **1**·**AsF**<sub>6</sub> was stable up to ca. 263 °C (536 K), and began to decompose above this temperature. Although a sharp thermal anomaly in DTA was also observed at  $T_{\max}$  = 212 °C (485 K) in **1**·**AsF**<sub>6</sub>, this peak was far from the decomposition temperature (ca. 263 °C), which is obviously different from that of **1**·**PF**<sub>6</sub>. To access the reason for exhibiting a sharp thermal anomaly in DTA around 485–505 K, thermochromic properties of both compounds were also investigated (Figure 2). Although the orange-brown color of powdered samples of **1**·**PF**<sub>6</sub> becomes slightly lighter from 300 K to ca. 483 K, possibly due to the partial SCO, further elevation of the temperature to 493 K induces rapid black coloration, suggesting the decomposition of the compound (Figure 2a). This thermochromic tendency and TG/DTA results suggest that the decomposition temperature overlaps the spin transition temperature in **1**·**PF**<sub>6</sub>. On the other hand, powdered samples of **1**·**AsF**<sub>6</sub> showed a clearly distinguishable thermochromism from orange-brown at 300 K to orange-yellow at ca. 498 K, suggesting the occurrence of SCO (Figure 2b). Then, further increasing the temperature to 503 K induces slight yellowish coloration, and ca. 5 min. later, a black coloration related to decomposition proceeds. This color change of **1**·**AsF**<sub>6</sub> in a step-by-step-manner is comparable to the clear distinction between sharp thermal anomaly at  $T_{\max}$  = 485 K and decomposition temperature observed in TG/DTA curves. Consequently, we decided to investigate SCO properties only for **1**·**AsF**<sub>6</sub> which is more stable than **1**·**PF**<sub>6</sub> in a high-temperature SCO region.



**Scheme 2.** Synthetic scheme of the ligand L2<sup>C2</sup>. Reagents and conditions: (1) 1,3-diaminopropane, MeOH, 1 h, 60 °C; 78%; (2) 1-PrOH, 16 h, 80 °C; 78%; (3) HCl (aq), 2 h, room temperature (RT); 86%; (4) 2-(2-aminoethyl)pyridine (2 equiv), MeOH, 1 h, RT.



**Figure 1.** Thermogravimetry and differential thermal analysis (TG/DTA) curves of **1·PF<sub>6</sub>** (a) and **1·AsF<sub>6</sub>** (b).



**Figure 2.** Temperature-dependent optical microscope images of grinding samples of **1·PF<sub>6</sub>** (a) and **1·AsF<sub>6</sub>** (b) deposited on a heating stage. Unless otherwise noted, after increasing the sample temperature at each target point, the sample was held for 5 min, and then an image was taken at each temperature.

## 2.2. Crystal Structure of **1·PF<sub>6</sub>** and **1·AsF<sub>6</sub>**

The crystal structure of **1·PF<sub>6</sub>** and **1·AsF<sub>6</sub>** was determined at 120 K (low-spin–low-spin (LS–LS) state). As shown in Table 1, both complexes crystallize in the same monoclinic space group type *C2/c* (number 15) with *Z* = 4 and are isostructural. The structure consists of a  $[\text{Fe}^{\text{II}}_2(\text{L}^{\text{C}3})_2]^{4+}$  complex-cation, two disordered monovalent counterions ( $\text{PF}_6^-$  and  $\text{AsF}_6^-$  for **1·PF<sub>6</sub>** and **1·AsF<sub>6</sub>**, respectively), and  $\text{H}_2\text{O}$  and MeCN molecules as lattice solvents. In the crystal lattice, both solvent molecules are in the one solvent site in a severely disordered manner in both compounds. Thus, these regions, including solvent molecules, are treated with the *PLATON SQUEEZE* program [51] (see Experimental Section 3.3 including the details about analyses of disordered counter anions and solvent molecules).

Figure 3 shows the molecular structure of the complex-cation  $[\text{Fe}^{\text{II}}_2(\text{L}^{\text{C}3})_2]^{4+}$  of **1·AsF<sub>6</sub>** at 120 K. As shown in Table 2, the structural feature of the complex-cation of **1·PF<sub>6</sub>** is similar to that of **1·AsF<sub>6</sub>**. Thus, we only discuss the structure of **1·AsF<sub>6</sub>** below. The complex-cation has a dinuclear double-helical architecture, in which each ligand  $\text{L}^{\text{C}3}$  bound as a bis-tridentate ligand to two different iron centers, and conversely, the  $\text{Fe}^{\text{II}}$  centers are N6-coordinated pseudo-octahedral coordination environments bound to two different ligand strands. The intra-helical metal–metal distance is 10.894(3) Å, which is much longer than that of the related ethylene-bridged helicate  $[\text{Fe}^{\text{II}}_2(\text{L}^{\text{C}2})_2]^{4+}$  (7.855(3) Å) [34] due to the elongation of the alkyl chain from two to three C atoms. Each metal site is chiral, with either a  $\Delta$  or a  $\Lambda$  configuration, and the complex-cation depicted in Figure 3 has a homochiral  $\Lambda$ – $\Lambda$  pair. In the crystal, complex-cations with the  $\Delta$ – $\Delta$  and  $\Lambda$ – $\Lambda$  pairs coexist to form a racemic crystal since the complex crystallizes in a centrosymmetric space group, *C2/c*. The Fe–N coordination bond distances (1.954(3)–2.007(3) and 1.945(3)–2.007(3) Å for Fe1–N and Fe2–N, respectively) indicate that both centers are in the LS  $\text{Fe}^{\text{II}}$  state. While the average Fe–N bond distance and octahedral volume of LS–LS  $[\text{Fe}^{\text{II}}_2(\text{L}^{\text{C}3})_2]^{4+}$  are similar to those of LS–LS  $[\text{Fe}^{\text{II}}_2(\text{L}^{\text{C}2})_2]^{4+}$ , the  $\Theta$  [52]

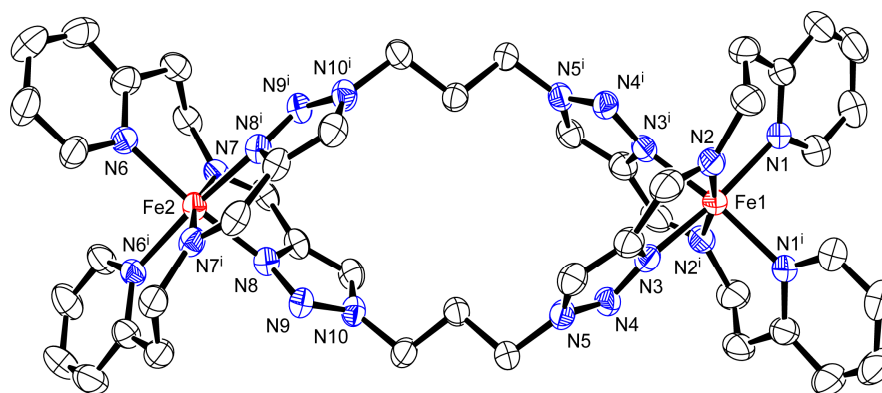
and continuous shape measures (CShMs) relative to the regular octahedron with the center as the reference shape [53] of LS–LS  $[\text{Fe}^{\text{II}}_2(\text{L}2^{\text{C}3})_2]^{4+}$  are lower than those of LS–LS  $[\text{Fe}^{\text{II}}_2(\text{L}2^{\text{C}2})_2]^{4+}$ , indicating that the  $\text{Fe}^{\text{II}}$  centers of LS–LS  $[\text{Fe}^{\text{II}}_2(\text{L}2^{\text{C}3})_2]^{4+}$  have a more regular octahedral geometry than those of LS–LS  $[\text{Fe}^{\text{II}}_2(\text{L}2^{\text{C}2})_2]^{4+}$  with the one minor exception of the  $\Sigma$  [54] of LS–LS  $[\text{Fe}^{\text{II}}_2(\text{L}2^{\text{C}2})_2]^{4+}$ , which is slightly lower than that of LS–LS  $[\text{Fe}^{\text{II}}_2(\text{L}2^{\text{C}3})_2]^{4+}$  (average Fe–N bond distance,  $\Sigma$ ,  $\Theta$ , CShMs and octahedral volume of the LS–LS  $[\text{Fe}^{\text{II}}_2(\text{L}2^{\text{C}2})_2]^{4+}$  for  $[\text{Fe}^{\text{II}}_2(\text{L}2^{\text{C}2})_2](\text{PF}_6)_4 \cdot 5\text{H}_2\text{O} \cdot \text{MeCN}$  [34] are 1.971 Å, 42.5°, 133.7°, 0.696 and 10.096 Å<sup>3</sup>, respectively).

**Table 1.** X-ray crystallographic data for **1·PF<sub>6</sub>** and **1·AsF<sub>6</sub>** at 120 K.

	$[\text{Fe}^{\text{II}}_2\text{L}2^{\text{C}3}]_2(\text{PF}_6)_4 \cdot 1.5\text{H}_2\text{O} \cdot 1.5\text{MeCN}$ ( <b>1·PF<sub>6</sub></b> ) <sup>a</sup>	$[\text{Fe}^{\text{II}}_2\text{L}2^{\text{C}3}]_2(\text{AsF}_6)_4 \cdot 3\text{H}_2\text{O} \cdot \text{MeCN}$ ( <b>1·AsF<sub>6</sub></b> ) <sup>a</sup>
Formula	$\text{C}_{49}\text{H}_{59.5}\text{N}_{21.5}\text{O}_{1.5}\text{P}_4\text{F}_{24}\text{Fe}_2$	$\text{C}_{48}\text{H}_{61}\text{N}_{21}\text{O}_3\text{As}_4\text{F}_{24}\text{Fe}_2$
Formula weight	1665.26	1847.55
Crystal system	monoclinic	monoclinic
Space group	$\text{C}2/c$ (No. 15)	$\text{C}2/c$ (No.15)
$a/\text{Å}$	19.049(6)	19.410(3)
$b/\text{Å}$	19.056(5)	19.034(3)
$c/\text{Å}$	20.600(9)	20.772(5)
$\beta/\text{deg.}$	115.832(3)	115.723(2)
$V/\text{Å}^3$	6731(4)	6914(2)
$Z$	4	4
$d_{\text{calcd.}}/\text{g}\cdot\text{cm}^{-3}$	1.643	1.775
$\mu$ (Mo $\text{K}\alpha$ )/ $\text{mm}^{-1}$	0.649	2.441
$R_1^b$ ( $I > 2\sigma(I)$ )	0.0879	0.0520
$wR_2^c$ ( $I > 2\sigma(I)$ )	0.2141	0.1167
$R_1^b$ (all data)	0.1054	0.0626
$wR_2^c$ (all data)	0.2286	0.1236
$u^c$	0.0791	0.0425
$v^c$	27.4133	16.3374
$S$	1.142	1.112
CCDC number	1544125	1544126

<sup>a</sup> The PLATON SQUEEZE program [51] was used to treat regions with highly disordered solvent molecules which could not be sensibly modeled in terms of atomic sites; <sup>b</sup>  $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ ; <sup>c</sup>  $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2 / \Sigma w|F_o|^2]^{1/2}$ ,  $w = 1/[\sigma^2(|F_o|^2) + (uP)^2 + vP]$  where  $P = (|F_o|^2 + 2|F_c|^2)/3$ .

The assembly structure of **1·AsF<sub>6</sub>** is shown in Figure 4. As shown in Figure 4a, a cationic one-dimensional (1D) structure is formed along the  $b$ -axis by slightly inclined intermolecular  $\pi$ – $\pi$  interactions between all pyridyl rings of neighboring complex-cations with  $\text{Cg}1 \cdots \text{Cg}2^{\text{ii}} = 4.123(3)$  Å.



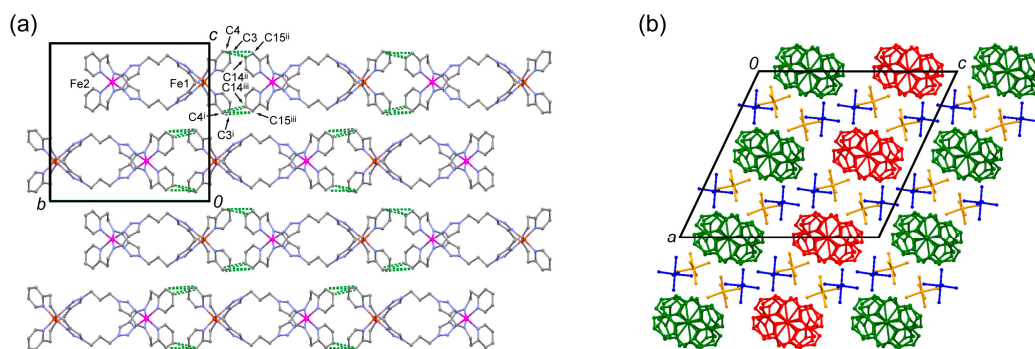
**Figure 3.** ORTEP drawing of the dinuclear double helicate complex-cation  $[\text{Fe}^{\text{II}}_2(\text{L}2^{\text{C}3})_2]^{4+}$  of **1·AsF<sub>6</sub>** at 120 K with the atom numbering scheme except for carbon atoms, where the thermal ellipsoids are drawn with a 50% probability level. H atoms have been omitted for clarity. Symmetry operation: (i)  $-x, y, 3/2 - z$ .

(Cg1 = centroid of the N1–C1–C2–C3–C4–C5 ring, Cg2 = centroid of the N6–C12–C13–C14–C15–C16 ring; symmetry operation: (ii)  $x, -1 + y, z$ ; Table 3). In the light of chiral assembly, homochiral complex-cations are linked together in the  $\pi$ -stacked 1D structure to give a homochiral 1D chain ( $\Delta\cdots\Delta\cdots\Delta\cdots\Delta\cdots$  or  $\Lambda\cdots\Lambda\cdots\Lambda\cdots\Lambda\cdots$ ). Figure 4b shows the stacking observed between adjacent cationic 1D chains viewed along the  $ac$  plane. One-dimensional chains of opposite chirality are alternately arrayed along the  $c$ -axis to give a heterochiral crystal. Each cationic 1D chain is separated by  $\text{AsF}_6^-$  ions and solvent molecules occupying the space between the 1D chains in a strongly disordered manner even at 120 K. Although the assembly structure of **1**·**PF**<sub>6</sub> is almost same as that of **1**·**AsF**<sub>6</sub>, these 1D-based structures are remarkably different from the two-dimensional (2D) assembly of the related ethylene-bridged helicate  $[\text{Fe}^{\text{II}}_2(\text{L}^{2\text{C}})_2](\text{PF}_6)_4 \cdot 5\text{H}_2\text{O} \cdot \text{MeCN}$  by intermolecular  $\pi$ - $\pi$  and CH/ $\pi$  interactions [34].

**Table 2.** Coordination bond lengths, angles, and structural parameters for **1**·**PF**<sub>6</sub> and **1**·**AsF**<sub>6</sub> at 120 K. CShMs: continuous shape measures.

Fe1 Site	1·PF <sub>6</sub>	1·AsF <sub>6</sub>	Fe2 Site	1·PF <sub>6</sub>	1·AsF <sub>6</sub>
Fe1–N Bond Lengths (Å)			Fe2–N Bond Lengths (Å)		
Fe1–N1	1.998(4)	2.007(3)	Fe2–N6	2.033(4)	2.007(3)
Fe1–N2	1.990(4)	1.970(4)	Fe2–N7	1.911(4)	1.962(3)
Fe1–N3	1.931(4)	1.954(3)	Fe2–N8	1.957(4)	1.945(3)
Fe1–N1 <sup>i</sup>	1.998(4)	2.007(3)	Fe2–N6 <sup>i</sup>	2.034(4)	2.007(3)
Fe1–N2 <sup>i</sup>	1.990(5)	1.970(4)	Fe2–N7 <sup>i</sup>	1.911(4)	1.962(3)
Fe1–N3 <sup>i</sup>	1.931(4)	1.954(3)	Fe2–N8 <sup>i</sup>	1.957(4)	1.945(3)
Average Fe1–N	1.973	1.977	Average Fe2–N	1.967	1.971
N–Fe1–N Bond Angles (°)			N–Fe2–N Bond Angles (°)		
N1–Fe1–N2	89.1(2)	91.35(15)	N6–Fe2–N7	93.38(17)	92.63(12)
N1–Fe1–N3	171.26(19)	170.93(14)	N6–Fe2–N8	172.89(15)	172.40(12)
N1–Fe1–N1 <sup>i</sup>	91.4(2)	92.67(18)	N6–Fe2–N6 <sup>i</sup>	93.9(2)	92.05(17)
N1–Fe1–N2 <sup>i</sup>	98.00(19)	95.70(14)	N6–Fe2–N7 <sup>i</sup>	95.50(16)	96.18(12)
N1–Fe1–N3 <sup>i</sup>	92.58(16)	91.47(12)	N6–Fe2–N8 <sup>i</sup>	89.72(17)	91.84(12)
N2–Fe1–N3	82.65(18)	80.20(13)	N7–Fe2–N8	80.17(17)	80.47(12)
N2–Fe1–N1 <sup>i</sup>	98.00(19)	95.69(15)	N7–Fe2–N6 <sup>i</sup>	95.50(16)	96.17(12)
N2–Fe1–N2 <sup>i</sup>	169.9(3)	169.79(18)	N7–Fe2–N7 <sup>i</sup>	167.0(3)	167.32(16)
N2–Fe1–N3 <sup>i</sup>	89.86(17)	92.27(13)	N7–Fe2–N8 <sup>i</sup>	90.38(16)	90.16(12)
N3–Fe1–N1 <sup>i</sup>	92.58(16)	91.47(12)	N8–Fe2–N6 <sup>i</sup>	89.72(17)	91.84(12)
N3–Fe1–N2 <sup>i</sup>	89.85(17)	92.27(13)	N8–Fe2–N7 <sup>i</sup>	90.38(16)	90.16(12)
N3–Fe1–N3 <sup>i</sup>	84.6(2)	85.61(17)	N8–Fe2–N8 <sup>i</sup>	87.3(3)	85.07(17)
N1 <sup>i</sup> –Fe1–N2 <sup>i</sup>	89.1(2)	91.36(15)	N6 <sup>i</sup> –Fe2–N7 <sup>i</sup>	93.38(17)	92.63(12)
N1 <sup>i</sup> –Fe1–N3 <sup>i</sup>	171.26(19)	170.93(14)	N6 <sup>i</sup> –Fe2–N8 <sup>i</sup>	172.89(15)	172.41(12)
N2 <sup>i</sup> –Fe1–N3 <sup>i</sup>	82.65(18)	80.20(14)	N7 <sup>i</sup> –Fe2–N8 <sup>i</sup>	80.17(17)	80.47(12)
$\Sigma$ (°) [54]	44.8	48.2		45.3	47.7
$\Theta$ (°) [52]	113.9	120.1		106.9	108.1
CShMs <sup>c</sup> [53]	0.594	0.616		0.636	0.590
Octahedral volume (Å <sup>3</sup> )	10.132	10.183		10.029	10.098

Symmetry operation: (i)  $-x, y, 3/2 - z$ ; <sup>c</sup> The reference shape is the regular octahedron with center.



**Figure 4.** (a) Intermolecular interactions of **1·AsF<sub>6</sub>** at 120 K. Adjacent complex-cations  $[\text{Fe}^{\text{II}}_2(\text{L2C}^3)_2]^{4+}$  with the same chirality are connected by intermolecular  $\pi$ - $\pi$  interactions (green dotted line) to form the homochiral 1D chain structure along the *b*-axis. Symmetry operations: (i)  $-x, y, 3/2 - z$ ; (ii)  $x, -1 + y, z$ ; (iii)  $-x, -1 + y, 3/2 - z$ ; (b) Packing diagram of **1·AsF<sub>6</sub>** at 120 K viewed along the *ac* plane.  $\Delta$ - $\Delta$ - $[\text{Fe}^{\text{II}}_2(\text{L2C}^3)_2]^{4+}$  and  $\Lambda$ - $\Lambda$ - $[\text{Fe}^{\text{II}}_2(\text{L2C}^3)_2]^{4+}$  enantiomers are represented by green and red colors, respectively. Cationic 1D chains with the opposite chirality running along the *b*-axis exist in a crystal lattice to give a heterochiral crystal. Each cationic chain is separated by the space-occupying two disordered  $\text{AsF}_6^-$  ions (blue and orange; only the major component is indicated) and solvent molecules such as  $3\text{H}_2\text{O}$  and one MeCN molecule (not indicated), which could not be sensibly modeled due to the strong disorder and regions including these solvent molecules being treated with the PLATON SQUEEZE program. H atoms have been omitted for clarity.

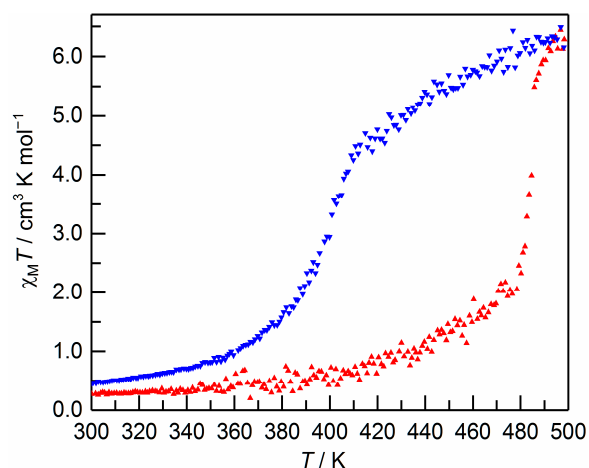
**Table 3.** Intermolecular contacts (Å) of  $\pi$ - $\pi$  interaction for **1·PF<sub>6</sub>** and **1·AsF<sub>6</sub>** at 120 K.

	<b>1·PF<sub>6</sub></b>	<b>1·AsF<sub>6</sub></b>
Cg1 <sup>a</sup> ...Cg2 <sup>b,ii</sup>	4.139(4)	4.123(3)
C3...C14 <sup>ii</sup>	3.582(13)	3.610(9)
C3...C15 <sup>ii</sup>	3.403(12)	3.423(8)
C4...C14 <sup>ii</sup>	3.432(11)	3.421(7)
C4...C15 <sup>ii</sup>	3.711(11)	3.703(6)

<sup>a</sup> Cg1 = centroid of the N1–C1–C2–C3–C4–C5 ring; <sup>b</sup> Cg2 = centroid of the N6–C12–C13–C14–C15–C16 ring. Symmetry operation: (ii)  $x, 1 + y, z$  for **1·PF<sub>6</sub>** and  $x, -1 + y, z$  for **1·AsF<sub>6</sub>**.

### 2.3. Magnetic Property of **1·AsF<sub>6</sub>**

The magnetic susceptibilities for polycrystalline samples of **1·AsF<sub>6</sub>** were measured upon heating from 300 to 498 K and subsequent cooling to 300 K at a sweep rate of  $0.5 \text{ K} \cdot \text{min}^{-1}$  under an applied magnetic field of 1 T using a superconducting quantum interference device (SQUID) magnetometer with a special heating setup. The  $\chi_{\text{M}}T$  vs.  $T$  plots are shown in Figure 5, where  $\chi_{\text{M}}$  is the molar magnetic susceptibility per Fe and  $T$  is the absolute temperature. As shown in Figure 5, **1·AsF<sub>6</sub>** showed an unsymmetrical hysteretic SCO above room temperature. The initial  $\chi_{\text{M}}T$  value is  $0.3 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$  at 300 K, which is consistent with the theoretical value for a LS–LS  $\text{Fe}^{\text{II}}$  system. On raising the temperature from 300 K, the  $\chi_{\text{M}}T$  value increases gradually to reach ca.  $2.1 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$  at 478 K, and then increases abruptly to reach ca.  $6.3 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$  at 498 K, which is consistent with the theoretical value for a high-spin–high-spin (HS–HS)  $\text{Fe}^{\text{II}}$  system ( $\chi_{\text{M}}T = 6.0 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ ). On lowering the temperature from 498 K, the  $\chi_{\text{M}}T$  value decreases gradually, reaching ca.  $4.3 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$  at 409 K, and then decreases abruptly to reach ca.  $1.5 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$  at 379 K. Then, the  $\chi_{\text{M}}T$  value further decreases gradually to reach ca.  $0.5 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$  at 300 K. The critical temperatures of the warming ( $T_{\text{c}} \uparrow$ ) and cooling ( $T_{\text{c}} \downarrow$ ) modes in the abrupt spin transition area are 485 and 401 K, respectively, indicating the occurrence of  $\Delta T = 84 \text{ K}$ , which is the widest thermal hysteresis loop in the dinuclear system reported so far [26–29,33,34,48]. It is also noteworthy that the  $T_{\text{c}} \uparrow$  of **1·AsF<sub>6</sub>** is considerably higher than that of the related ethylene-bridged helicate  $[\text{Fe}^{\text{II}}_2(\text{L2C}^2)_2](\text{PF}_6)_4 \cdot 5\text{H}_2\text{O} \cdot \text{MeCN}$  ( $T_{\text{c}} \uparrow = 437 \text{ K}$ ) [34] by about 48 K.

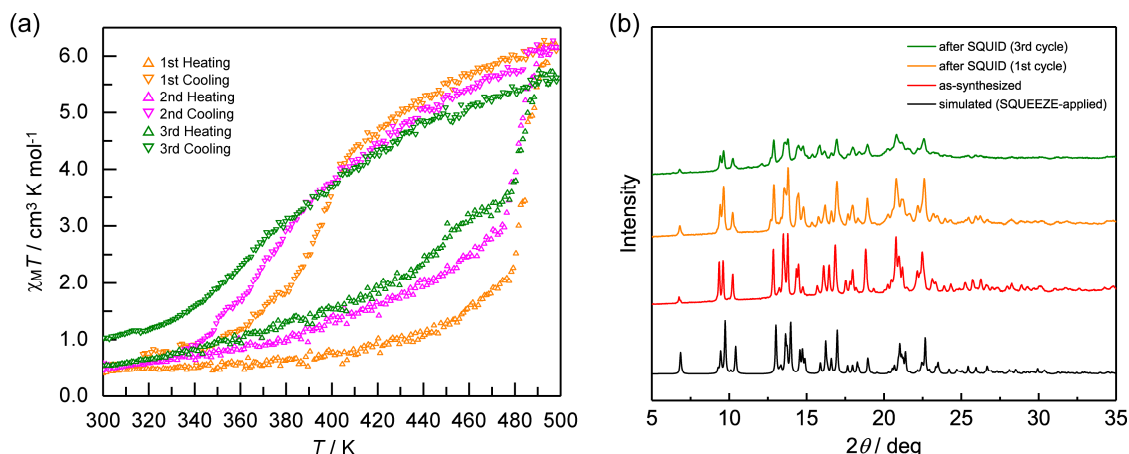


**Figure 5.** The magnetic behavior of **1·AsF<sub>6</sub>** in the form of the  $\chi_M T$  vs.  $T$  plots. **1·AsF<sub>6</sub>** was warmed from 300 to 498 K (filled triangles; red), and then cooled from 498 to 300 K (filled inverted triangles; blue) at a sweep rate of 0.5 K·min<sup>−1</sup>.

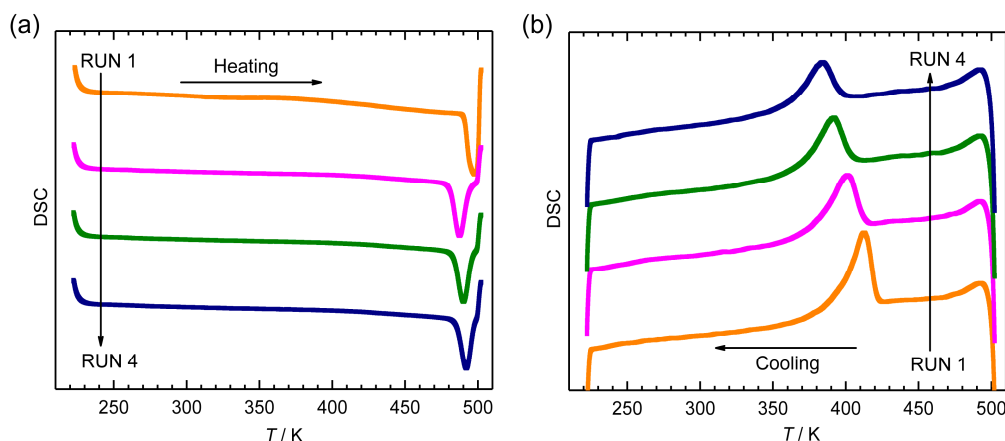
#### 2.4. Reproducibility of Hysteretic SCO of **1·AsF<sub>6</sub>**

To reveal the desolvation effect and reproducibility of hysteretic SCO of **1·AsF<sub>6</sub>**, temperature-dependent magnetic susceptibilities were also measured over three consecutive cycles. As shown in Figure 6a, although **1·AsF<sub>6</sub>** shows a more gradual spin transition in the second cycle than in the first cycle, probably due to the in situ solvent liberation in the first heating, an asymmetric wide hysteresis loop is then still observed. Further thermal cycling (third cycle) causes the spin transition pattern to have a much more gradual and partial SCO fashion, which does not occur in the related ethylene-bridged helicate [Fe<sup>II</sup><sub>2</sub>(L2<sup>C2</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub>·5H<sub>2</sub>O·MeCN [34]. Comparing powder X-ray diffraction (PXRD) patterns of as-synthesized **1·AsF<sub>6</sub>** and after first thermal cycle of SQUID measurement confirms that there is no structural phase transition associated with the desolvation, because the peak patterns of the sample are not changed, although the peak positions increase slightly possibly due to the removal of solvent molecules and concomitant lattice contraction (Figure 6b). However, an intensity decrease and peak broadening are observed after three thermal cycles of SQUID measurement, presumably due to a loss of crystallinity and/or partial decomposition.

These properties were also confirmed by differential scanning calorimetry (DSC) experiments of four consecutive thermal cycles at a sweep rate of 10 K·min<sup>−1</sup>, in the temperature range of 222–502 K (Figure 7). As shown in Figure 7, from the first cycle in heating and following cooling modes, a thermal hysteresis of ca. 85 K was detected ( $T_{\max\uparrow}$  and  $T_{\max\downarrow}$  are 498 and 413 K, respectively) and the hysteresis width is consistent with the  $\Delta T$  value observed by the magnetic measurement. As the thermal cycling is repeated, the shape of DSC peaks becomes broader and smaller, and the position of the peak shifts to a lower temperature in both the heating and cooling modes of the second cycle due to the solvent loss in the first heating ( $T_{\max\uparrow}$  and  $T_{\max\downarrow}$  are 487 and 401 K, respectively, in the second cycle). However, further thermal cycling from the second cycle induces the peak shift to the opposite directions, in which the temperature variation in cooling modes is larger than that in heating modes ( $T_{\max\uparrow}$  and  $T_{\max\downarrow}$  are 490 and 392 K, respectively, in the third cycle, and 492 and 384 K, respectively, in the fourth cycle). In addition, peak broadening and reduction also continue in the third and fourth cycles. As a whole, thermal hysteresis of **1·AsF<sub>6</sub>** is retained for at least four cycles, although the spin transition becomes gradual and incomplete with shifting the transition temperature due to the solvent liberation in the first cycle and a loss of crystallinity and/or partial decomposition upon further thermal cycling.



**Figure 6.** (a) Temperature dependence of the  $\chi MT$  product of **1·AsF<sub>6</sub>** in the heating (empty triangles) and cooling (empty inverted triangles) modes over three successive thermal cycles at a sweep rate of  $0.5 \text{ K} \cdot \text{min}^{-1}$ . Orange: first cycle; magenta: second cycle; olive: third cycle; (b) Powder X-ray diffraction (PXRD) patterns of **1·AsF<sub>6</sub>** at RT in different states. Black: simulated from the SQUEEZE-applied single crystal X-ray data at 120 K; red: as-synthesized **1·AsF<sub>6</sub>**; orange: **1·AsF<sub>6</sub>** after the first thermal cycle of superconducting quantum interference device (SQUID) measurement; olive: **1·AsF<sub>6</sub>** after a third thermal cycle of SQUID measurement.



**Figure 7.** Differential scanning calorimetry (DSC) curves of **1·AsF<sub>6</sub>** in the heating mode (a) and cooling mode (b) recorded over four successive thermal cycles at a sweep rate of  $10 \text{ K} \cdot \text{min}^{-1}$ , in the temperature range of 222–502 K. Orange: first cycle; magenta: second cycle; olive: third cycle; navy blue: fourth cycle.

### 3. Materials and Methods

#### 3.1. Synthesis of $\text{Fe}^{\text{II}}$ Complexes

##### 3.1.1. General

All reagents and solvents were purchased from commercial sources and used for the syntheses without further purification. The 1-Phenyl-1*H*-1,2,3-triazole-4-carbaldehyde was prepared according to methods in the literature [47]. The synthetic procedure of 1,1'-(propane-1,3-diyl)bis(1*H*-1,2,3-triazole-4-carbaldehyde) (**4**) was constructed by modifying the reported procedures [34]. All the synthetic procedures were carried out in air.

##### 3.1.2. Preparation of 1,1'-(propane-1,3-diyl)bis(1*H*-1,2,3-triazole-4-carbaldehyde) (**4**)

To a warm pale yellow solution of 1-phenyl-1*H*-1,2,3-triazole-4-carbaldehyde (3.464 g, 20 mmol) in MeOH (30 mL), 1,3-diaminopropane (0.741 g, 10 mmol) in MeOH (1 mL) was added. The resulting

solution was stirred for 1 h at 60 °C, and was then cooled in a fridge. The precipitated white powders were collected by suction filtration, washed with Et<sub>2</sub>O (10 mL × 3), and dried in vacuo. White solid of *N,N'*-(propane-1,3-diyl)bis[1-(1-phenyl-1*H*-1,2,3-triazol-4-yl)methanimine] (**2**). Yield: 3.005 g (78%). Mp 127–128 °C (from MeOH), <sup>1</sup>H NMR (600 MHz; DMSO-*d*<sub>6</sub>; TMS): δ 9.24 (s, 2H), 8.55 (s, 2H), 8.00–7.98 (m, 4H), 7.63–7.60 (m, 4H), 7.53–7.51 (m, 2H), 3.72 (t, *J* = 6.5 Hz, 4H), 2.05–2.00 (m, 2H). Anal. Calcd. for 2·0.2H<sub>2</sub>O = C<sub>21</sub>H<sub>20.4</sub>N<sub>8</sub>O<sub>0.2</sub>: C, 65.00; H, 5.30; N, 28.88%. Found: C, 65.05; H, 5.19; N, 29.01%.

A suspension of **2** (2.898 g, 7.5 mmol) in 1-PrOH (25 mL) was heated at 80 °C for 16 h, turning into a pale yellow solution, and the resulting solution was then cooled in a fridge. The precipitated white powders were collected by suction filtration, washed with Et<sub>2</sub>O (10 mL), and dried in vacuo. White solid of 1,1'-[propane-1,3-diylbis(1*H*-1,2,3-triazole-1,4-diyl)]bis(*N*-phenylmethanimine) (**3**). Yield: 2.260 g (78%). m.p. 192–193 °C (from 1-PrOH), <sup>1</sup>H NMR (600 MHz; DMSO-*d*<sub>6</sub>; TMS): δ 8.78 (s, 2H), 8.67 (s, 2H), 7.43–7.41 (m, 4H), 7.28–7.25 (m, 6H), 4.52 (t, *J* = 6.9 Hz, 4H), 2.59–2.55 (m, 2H). Anal. Calcd. for 3·0.35H<sub>2</sub>O = C<sub>21</sub>H<sub>20.7</sub>N<sub>8</sub>O<sub>0.35</sub>: C, 64.55; H, 5.34; N, 28.68%. Found: C, 64.15; H, 5.20; N, 29.06%.

Hydrochloric acid (36%) (1.671 g, 16.5 mmol) in H<sub>2</sub>O (28 mL) was added to white powders of **3** (2.125 g, 5.5 mmol), and the mixture was stirred for 2 h at room temperature. After turning the mixture into a yellowish-white suspension, the residual white solids of **4** were collected by suction filtration, washed with H<sub>2</sub>O (10 mL) and then Et<sub>2</sub>O (10 mL), and dried in vacuo. Yield: 1.103 g (86%). m.p. 124–125 °C (from H<sub>2</sub>O), <sup>1</sup>H NMR (600 MHz; DMSO-*d*<sub>6</sub>; TMS): δ 10.03 (s, 2H), 8.89 (s, 2H), 4.52 (t, *J* = 6.9 Hz, 4H), 2.55–2.51 (m, 2H). Anal. Calcd. for C<sub>9</sub>H<sub>10</sub>N<sub>6</sub>O<sub>2</sub>: C, 46.15; H, 4.30; N, 35.88%. Found: C, 45.87; H, 4.19; N, 35.56%.

### 3.1.3. Synthesis of the Bis-Tridentate Ligand L2<sup>C3</sup> = 1,1'-[propane-1,3-diylbis(1*H*-1,2,3-triazole-1,4-diyl)]bis[*N*-[2-(pyridin-2-yl)ethyl]methanimine]

The ligand L2<sup>C3</sup> was prepared by mixing **4** and 2-(2-aminoethyl)pyridine with 1:2 molar ratio in MeOH. The ligand solution thus prepared was used for the synthesis of Fe<sup>II</sup> complexes without further purification and isolation.

#### 3.1.4. Preparation of [Fe<sup>II</sup><sub>2</sub>(L2<sup>C3</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub>·1.5H<sub>2</sub>O·1.5MeCN (**1**·PF<sub>6</sub>)

2-(2-Aminoethyl)pyridine (0.122 g, 1 mmol) in MeOH (1 mL) was added to a solution of **4** (0.118 g, 0.5 mmol) in MeOH (20 mL), and the resulting mixture was stirred at ambient temperature for 1 h. A pale yellow solution of the ligand (0.5 mmol) thus prepared was treated first with a solution of Fe<sup>II</sup>Cl<sub>2</sub>·4H<sub>2</sub>O (0.099 g, 0.5 mmol) in MeOH (1 mL), turning into a dark orange-red solution, and then with KPF<sub>6</sub> (0.184 g, 1 mmol) in 4 mL of a mixed solution of MeOH and H<sub>2</sub>O (1/1 by volume). The resulting mixture was stirred at ambient temperature for 1 h, during which time the precipitated orange-brown crude product was collected by suction filtration. The collected precipitate was dissolved in MeCN (4 mL) and then filtered. Dark-red block crystals were obtained by slow diffusion of MeOH (8 mL) into the filtrate (liquid–liquid diffusion) for a day. Yield: 0.154 g (37%). Anal. Calcd. for [Fe<sup>II</sup><sub>2</sub>(L2<sup>C3</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub>·1.5MeCN·1.5MeOH = C<sub>49</sub>H<sub>59.5</sub>N<sub>21.5</sub>O<sub>1.5</sub>P<sub>4</sub>F<sub>24</sub>Fe<sub>2</sub>: C, 35.34; H, 3.60; N, 18.08%. Found: C, 35.48; H, 3.37; N, 18.06%. IR (KBr): ν<sub>C=N</sub> 1609 cm<sup>-1</sup>, ν<sub>P-F</sub>(PF<sub>6</sub><sup>-</sup>) 844 cm<sup>-1</sup>.

#### 3.1.5. Preparation of [Fe<sup>II</sup><sub>2</sub>(L2<sup>C3</sup>)<sub>2</sub>](AsF<sub>6</sub>)<sub>4</sub>·3H<sub>2</sub>O·MeCN (**1**·AsF<sub>6</sub>)

2-(2-Aminoethyl)pyridine (0.122 g, 1 mmol) in MeOH (2 mL) was added to a solution of **4** (0.118 g, 0.5 mmol) in MeOH (20 mL), and the resulting mixture was stirred at ambient temperature for 1 h. A pale yellow solution of the ligand (0.5 mmol) thus prepared was treated first with a solution of Fe<sup>II</sup>Cl<sub>2</sub>·4H<sub>2</sub>O (0.099 g, 0.5 mmol) in MeOH (2 mL), turning into a dark orange-red solution, and then with KAsF<sub>6</sub> (0.228 g, 1 mmol) in 4 mL of a mixed solution of MeOH and H<sub>2</sub>O (1/1 by volume). The resulting mixture was stirred at ambient temperature for 30 min, during which time the precipitated red-orange crude product was collected by suction filtration. The collected precipitate was dissolved in MeCN (3 mL) and then filtered. Dark-red block crystals were obtained by slow diffusion of MeOH (7 mL) into the filtrate (liquid–liquid diffusion) for a day. Yield: 0.155 g (33%). Anal. Calcd. for

$[\text{Fe}^{\text{II}}_2(\text{L}_2\text{C}_3)_2](\text{AsF}_6)_4 \cdot 3\text{H}_2\text{O} \cdot \text{MeCN} = \text{C}_{48}\text{H}_{61}\text{N}_{21}\text{O}_3\text{As}_4\text{F}_{24}\text{Fe}_2$ : C, 31.21; H, 3.33; N, 15.92%. Found: C, 31.46; H, 3.04; N, 16.25%. IR (KBr):  $\nu_{\text{C}=\text{N}}$  1609  $\text{cm}^{-1}$ ,  $\nu_{\text{As}-\text{F}}(\text{AsF}_6^-)$  701  $\text{cm}^{-1}$ .

### 3.2. Physical Measurements

Elemental C, H, and N analyses were performed on a J-Science Lab (Kyoto, Japan) MICRO CORDER JM-10. IR spectra were recorded at room temperature using a JASCO (Tokyo, Japan) FT/IR 460Plus spectrophotometer or a PerkinElmer (Waltham, MA, USA) Spectrum100 FT-IR spectrometer with the samples prepared as KBr disks.  $^1\text{H}$  NMR spectra were recorded on a JEOL (Tokyo, Japan) ECA-600 spectrometer. The melting point was measured through a Yanaco (Kyoto, Japan) MP-S3 micro melting point meter and was uncorrected. Thermogravimetric data were collected on a TG/DTA6300 (SII Nano Technology Inc., Chiba, Japan) instrument in the temperature range of 30–318 °C (303–591 K) for **1**·**PF**<sub>6</sub> and 30–381 °C (303–654 K) for **1**·**AsF**<sub>6</sub> at a rate of 10 K·min<sup>−1</sup> under a nitrogen atmosphere. DSC measurements for **1**·**AsF**<sub>6</sub> were performed with a DSC6200 (SII Nano Technology Inc., Chiba, Japan) over the temperature range of 222–502 K, at a sweep rate of 10 K·min<sup>−1</sup> under a nitrogen atmosphere using aluminum hermetic pans with an empty pan as reference. Magnetic susceptibilities of **1**·**AsF**<sub>6</sub> were measured in the temperature range of 300–498 K at a sweep rate of 0.5 K·min<sup>−1</sup> under an applied magnetic field of 1 T using a Quantum Design (San Diego, CA, USA) MPMS-7 SQUID magnetometer with a special heating setup of a sample space oven option. The sample was wrapped in an aluminum foil and was then inserted into a quartz glass tube with a small amount of glass wool filler. Corrections for diamagnetism of the sample were made using Pascal's constants [55] and a background correction for the sample holder was applied. PXRD patterns were recorded at room temperature on a portion of polycrystalline powders placed on a non-reflecting silicon plate, using a Rigaku (Tokyo, Japan) MiniFlex600 diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å) operated at 0.4 kW power (40 kV, 10 mA). Images of grinding samples were recorded under an optical microscope SMZ800N (Nikon, Tokyo, Japan). The sample temperature was controlled by using a Linkam (Tadworth, UK) THMS 600 heating and freezing stage.

### 3.3. Crystallographic Data Collection and Structure Analyses

X-ray diffraction data of **1**·**PF**<sub>6</sub> and **1**·**AsF**<sub>6</sub> were collected by a Rigaku (Tokyo, Japan) AFC7R Mercury CCD diffractometer using graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71075$  Å) operated at 5 kW power (50 kV, 100 mA). A single crystal was mounted on a MiTeGen (Ithaca, NY, USA) MicroMount (200  $\mu\text{m}$ ) with liquid paraffin, then rapidly frozen in a nitrogen-gas stream at 120 K to avoid the loss of crystal solvents and the diffraction data were collected at 120 K. The temperature of the crystal was maintained by means of a Rigaku cooling device to within an accuracy of  $\pm 2$  K. The data were corrected for Lorentz, polarization, and absorption effects. The structures were solved by the direct method [56] and refined on  $F^2$  data using the full-matrix least-squares algorithm using SHELXL-2014 [57]. Non-hydrogen atoms were refined anisotropically. The structure of **1**·**PF**<sub>6</sub> contains two disordered PF<sub>6</sub><sup>−</sup> ions. Both PF<sub>6</sub><sup>−</sup> ions were disordered over two positions and the occupancy factors for the possible two positions of F atoms (F1A–F6A:F1B–F6B = 0.518(15):0.482(15) for P(1)F<sub>6</sub><sup>−</sup> and F7A–F12A:F7B–F12B = 0.635(16):0.365(16) for P(2)F<sub>6</sub><sup>−</sup>) were refined using the tools available from the SHELXL-2014 program package. In the refinement of these disordered PF<sub>6</sub><sup>−</sup> ions, the SADI command for all P–F bonds and F...F distances and the RIGU command for all P and F atoms were also applied. In addition, diffraction quality of the crystal of **1**·**PF**<sub>6</sub> was not sufficient to model highly disordered solvent molecules. The PLATON SQUEEZE program (290617, A.L. Spek, Utrecht, NL-UT, The Netherlands) [51] was used to treat regions with disordered solvent molecules which could not be sensibly modelled in terms of atomic sites. Available void volume was 892 Å<sup>3</sup>. Then, 196 electrons per unit cell were located and these were assigned to 1.5 H<sub>2</sub>O and 1.5 MeCN molecules per complex (196/4 = 49 e per complex; 1.5 H<sub>2</sub>O (15) + 1.5 MeCN (33) = 48 electrons). In the same way, the structure of **1**·**AsF**<sub>6</sub> contains two disordered AsF<sub>6</sub><sup>−</sup> ions and severely disordered solvent molecules. In **1**·**AsF**<sub>6</sub>, both AsF<sub>6</sub><sup>−</sup> ions were disordered over three positions and the occupancy factors for the possible three positions of F atoms (F1A–F6A:F1B–F6B:F1C–F6C = 0.434(3):0.291(3):0.275(3) for As(1)F<sub>6</sub><sup>−</sup> and F7A–F12A:F7B–F12B:F7C–F12C = 0.513(3):0.219(3):0.268(3) for As(2)F<sub>6</sub><sup>−</sup>) were refined using the SUMP

command to keep the sum of three occupancy factors of each ion as 1.0. In the refinement of these disordered  $\text{AsF}_6^-$  ions, the SADI command for all As–F bonds and F...F distances, the RIGU command for all As and F atoms, and the EADP command for F5A, F5B, F5C and F6A, F6B, F6C were also applied. The PLATON SQUEEZE program was also used to treat regions with disordered solvent molecules in the structure of **1·AsF<sub>6</sub>**. Available void volume was 926 Å<sup>3</sup>, and 220 electrons per unit cell were located. These were assigned to 3 H<sub>2</sub>O and 1 MeCN molecules per complex ( $220/4 = 55$  e per complex; 3 H<sub>2</sub>O (30) + 1 MeCN (22) = 52 electrons). All H atoms were placed in geometrically calculated positions, with the distances of C–H = 0.95 (aromatic) and 0.99 (CH<sub>2</sub>) Å, and refined as riding atoms, with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ . All calculations were performed by using the Yadokari-XG software package [58]. The CShMs of the Fe<sup>II</sup> centers relative to the ideal octahedron were calculated by SHAPE 2.1 [53]. The octahedral volumes of the Fe<sup>II</sup> centers were calculated by OLEX2 [59]. CCDC 1544125–1544126 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the CCDC (12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

#### 4. Conclusions

In conclusion, the present work reveals the effects of the extension of the bridging alkyl chain length (from C2 to C3) on the structure and SCO properties of the iron(II) dinuclear double helicate  $[\text{Fe}^{\text{II}}_2(\text{L}2^{\text{R}})_2](\text{X})_4 \cdot \text{solvent}$ , with the concomitant effects of the coexistent counter anions and lattice solvents. While propylene-bridged dinuclear complexes  $[\text{Fe}^{\text{II}}_2(\text{L}2^{\text{C3}})_2](\text{PF}_6)_4 \cdot 1.5\text{H}_2\text{O} \cdot 1.5\text{MeCN}$  (**1·PF<sub>6</sub>**) and  $[\text{Fe}^{\text{II}}_2(\text{L}2^{\text{C3}})_2](\text{AsF}_6)_4 \cdot 3\text{H}_2\text{O} \cdot \text{MeCN}$  (**1·AsF<sub>6</sub>**) are isostructural, the thermal stability of **1·PF<sub>6</sub>** is lower than that of **1·AsF<sub>6</sub>** in a high-temperature SCO region. **1·AsF<sub>6</sub>** shows an unsymmetrical hysteretic SCO between the LS–LS and HS–HS states at above room temperature with  $\Delta T = 84$  K ( $T_{\text{c}} \uparrow = 485$  K and  $T_{\text{c}} \downarrow = 401$  K in the abrupt spin transition area) in the first thermal cycle, which is the widest hysteresis loop in the dinuclear system reported so far. In addition, the  $T_{\text{c}} \uparrow$  of **1·AsF<sub>6</sub>** is considerably higher than that of the related ethylene-bridged compound, by about 48 K. This high-temperature wide thermal hysteresis may be related to the 1D assembly structure composed of inter-helicate  $\pi$ – $\pi$  interactions, which is obviously different from the 2D assembly of the related ethylene-bridged compound. Although the desolvation of **1·AsF<sub>6</sub>** does not directly affect the assembly structure, consecutive thermal cycles cause a loss of crystallinity and/or partial decomposition, and subsequent modification of the hysteretic SCO loop to a more gradual and partial fashion. As a consequence, the extension of the bridging alkyl chain length (from C2 to C3) and subsequent elongation of the dinuclear cation makes the 2D supramolecular assembly one-dimensional, and enhances the width of the hysteresis loop. Simultaneous raising of the  $T_{\text{c}} \uparrow$  may also cause the overlapping between spin transition temperature and decomposition temperature, which is related to the thermal durability upon SCO.

**Supplementary Materials:** The following are available online at [www.mdpi.com/2304-6740/5/3/49/s1](http://www.mdpi.com/2304-6740/5/3/49/s1). Cif and cif-checked files.

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