

Communication

Structures and Magnetic Properties of Iron(III) Complexes with Long Alkyl Chains

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Abstract: Iron(III) compounds with long alkyl chains, $[\text{Fe}(\text{C}_n\text{-pap})_2]\text{ClO}_4$ ($\text{C}_n\text{-pap}$: alkoxy-2-(2-pyridylmethyleneamino)phenol, $n = 8$ (**1**), 10 (**2**), 12 (**3**), 14 (**4**), 16 (**5**)) have been synthesized. The compounds were characterized by single crystal X-ray structure analysis and temperature dependent magnetic susceptibility in order to research the relationship between magnetic properties and the presence of long alkyl chains in soft molecules of the present type. The compounds **1**, **2**, **3** and **4** are in the high-spin (HS) state over the temperature range of 5 to 400 K. On the other hand, compound **5** is low-spin (LS) showing that the difference in magnetic properties depends on the length of the alkyl chain in the respective compounds.

Keywords: iron(III); soft material; spin crossover

1. Introduction

Metal proteins and enzymes consist of flexible structures typified by peptide links surrounding active centers giving rise to “flexible space” which may play an important role in the biochemical function of such systems [1]. In soft materials such as liquid crystals, gels and polymers, the presence of “flexible space” can be an important influence controlling the properties of such materials [2–10]. This motivated us to construct metal complexes with attached long alkyl chains that would result in flexible space in conjunction with the presence of metal complex centers. Positioning a spin-crossover (SCO) metal complex within the flexible space formed by the long alkyl chains is expected to result in altered properties based on synergic interactions occurring between the SCO and its environment reflecting external stimuli. A variety of d^n ($n = 4-7$) transition metal compounds exhibiting SCO between the high-spin (HS) and low-spin (LS) states have been reported [10]. Gradual or abrupt SCO may be observed in the solid state, depending on the degree of intermolecular cooperativity present. Flexibility in molecular assemblies based on molecular units has been shown to be an important factor in achieving synergy and resulting in various interesting physical properties among advanced materials [2–10].

Generally, SCO iron(III) compounds exhibit a $1/2 \leftrightarrow 5/2$ spin change. It has been known that the iron(III) compounds $[\text{Fe}(\text{pap})_2]\text{X}\cdot\text{H}_2\text{O}$ ($\text{Hpap} = 2$ -(2-pyridylmethyleneamino)phenol, $\text{X} = \text{BF}_4^-$ or ClO_4^-) exhibit abrupt SCO behavior [11–15]. We suggested that the strong intermolecular interactions (π - π stacking, hydrogen bonding and so on) are important for cooperativity. Although the π -conjugated system clearly plays an important role, in some cases the presence of long alkyl chains may also influence the magnetic behavior through intermolecular interaction. We have attempted to add long alkyl chains to iron(III) compounds with pap ligands. In this paper, we report about the iron(III) compounds $[\text{Fe}(\text{C}_n\text{-pap})_2]\text{ClO}_4$ ($n = 8$ (1), 10 (2), 12 (3), 14 (4), 16 (5)).

2. Results and Discussion

The preparation of the ligands **L1–L5** and the complexes **1–5** were essentially carried out according to the literature with minor modifications (Scheme 1) [14].

The compounds **1–5** were prepared and characterized by elemental analysis. Single crystals of **4** suitable for X-ray structural analysis were obtained by slow recrystallization of the initial product from $\text{MeOH}:\text{CHCl}_3$ (1:1). Single-crystal X-ray analysis of **4** was successfully carried out at 143 K (Figure 1) [16]. An ORTEP view of compound **4** is shown in Figure 1a. X-ray crystallographic data for **4** are given in Table 1. Complex **4** crystallizes in the space group P-1. The iron(III) ions are octahedrally coordinated by four nitrogen atoms and two oxygen atoms from two C14-pap ligands, *i.e.*, an N_4O_2 donor set. The Fe–N distances, the Fe–O distances, the N–Fe–N angles, the N–Fe–O angles and the O–Fe–O angles for **4** are shown in Table 1. The Fe(1)–N(1) and Fe(1)–N(3) axial bond distances, 2.109(2) and 2.112(2) Å, are shorter than the Fe(1)–N(2) and Fe(1)–N(4) distances, 2.207(2) and 2.2213(17) Å. The Fe(1)–O(1) and Fe(1)–O(3) bond distances, 1.935(1) and 1.9364(16) Å

are the shortest because of their ionic character. These bond lengths are typical for HS iron(III) compounds. The N–Fe–N angles and the N–Fe–O angles are N(1)–Fe(1)–N(3) = 167.26(6)°, N(2)–Fe(1)–O(1) = 152.76(8)° N(4)–Fe(1)–O(3) = 152.42(7)°, respectively, indicating that the [FeN₄O₂] octahedron core is distorted. Compound **4** forms an angled Z-shaped structure with the two coordinated C14-pap donor fragments nearly perpendicular to one another. A view of the packing for **4** is shown in Figure 1b. It shows that the arrangement of the long alkyl chains is not affected by the ClO₄[−] counter ions. There are two strong intermolecular interactions between each molecule. One is a π – π interaction between pap ligands, and the second is a “fastener” effect between the long alkyl chains which align adjacent to each other in the lattice.

Scheme 1. Synthesis of the C_n-pap ligand ($n = 8$ (**L1**), 10 (**L2**), 12 (**L3**), 14 (**L4**), 16 (**L5**)). Reagents and solvents: *a*: 30% H₂O₂ in CH₃COOH; *b*: (CH₃COO)₂O at 110 °C, EtOH at 140 °C, NaHCO₃/CHCl₃; *c*: HCl, NaHCO₃/CHCl₃; *d*: MnO₂ in *iso*-PrOH; *e*: K₂CO₃, *n*-alkylbromide in DMF at 100 °C; *f*: MeOH; *g*: Fe(ClO₄)₃ in MeOH/CHCl₃.

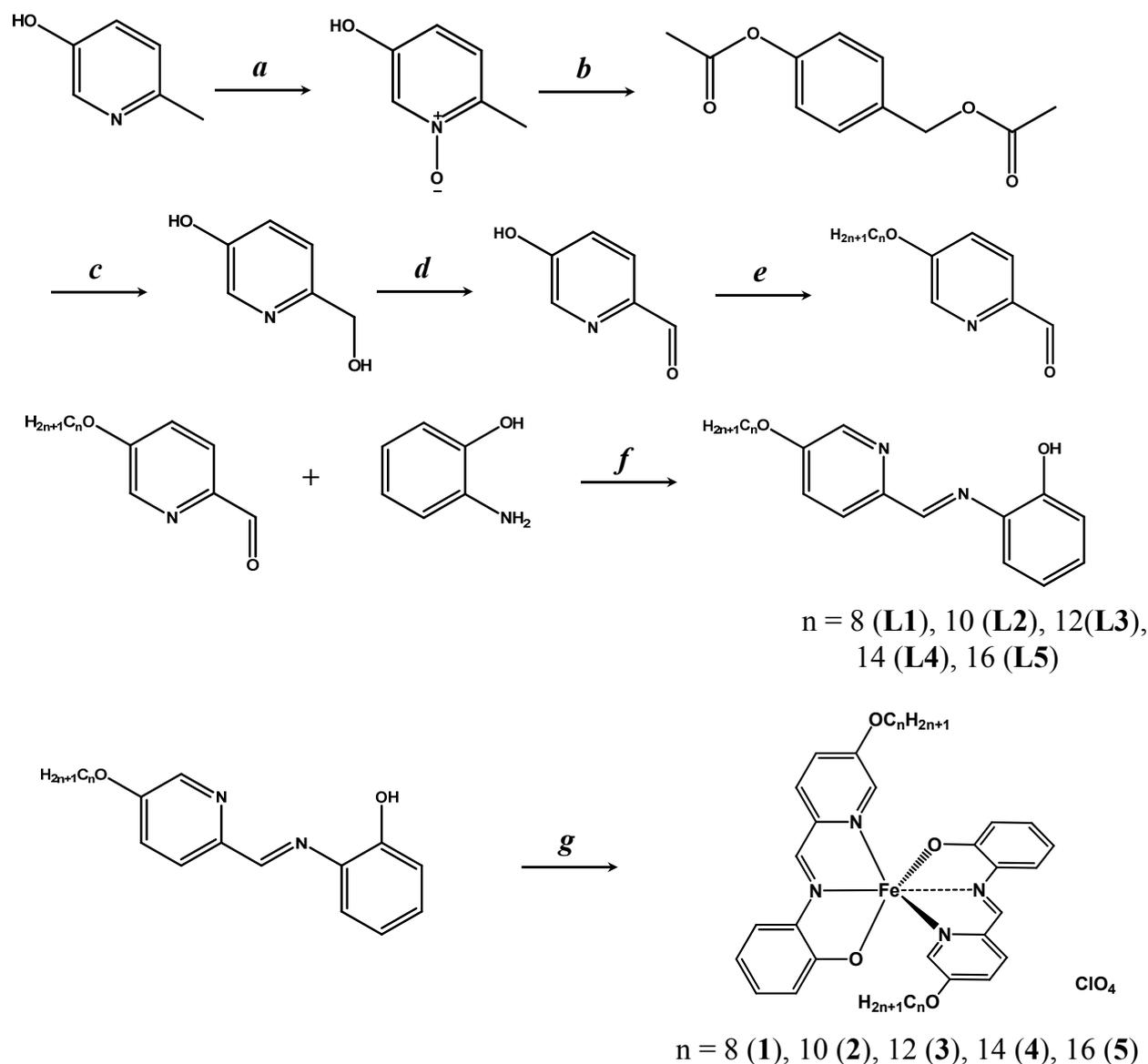


Figure 1. (a) Single crystal structure and (b) a projection of the crystal structure along the *a* axis for **4**.

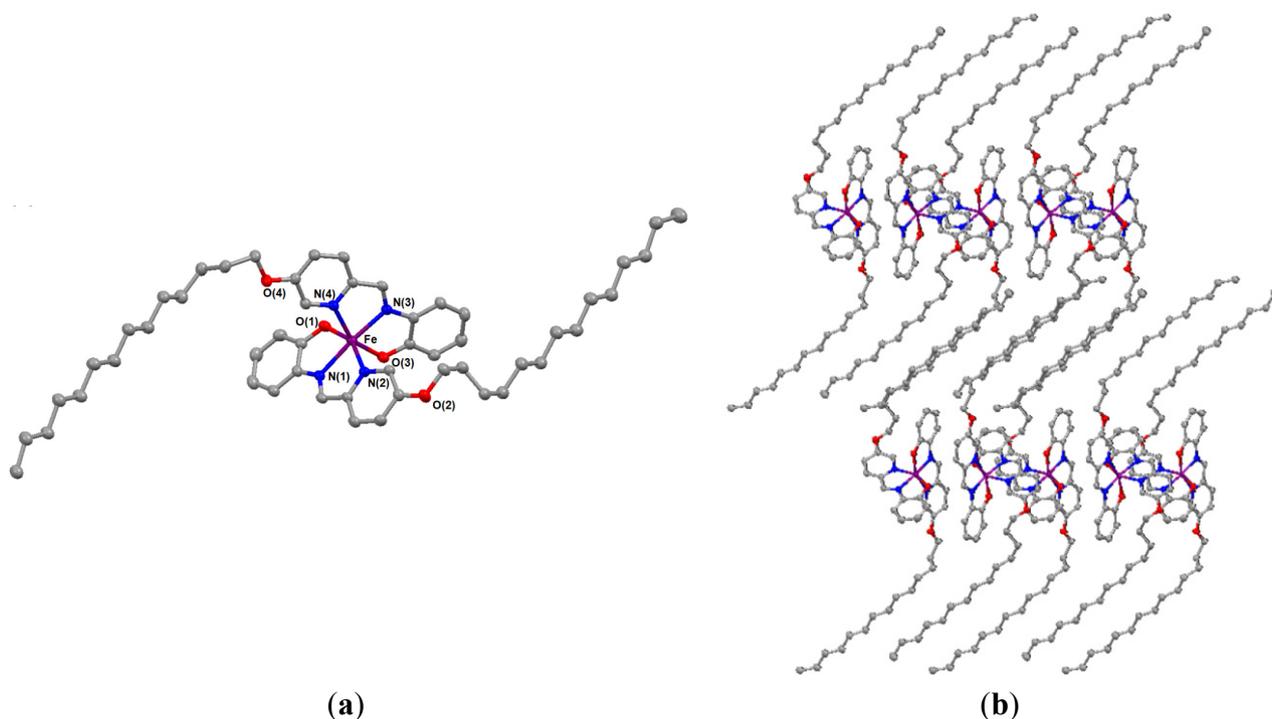
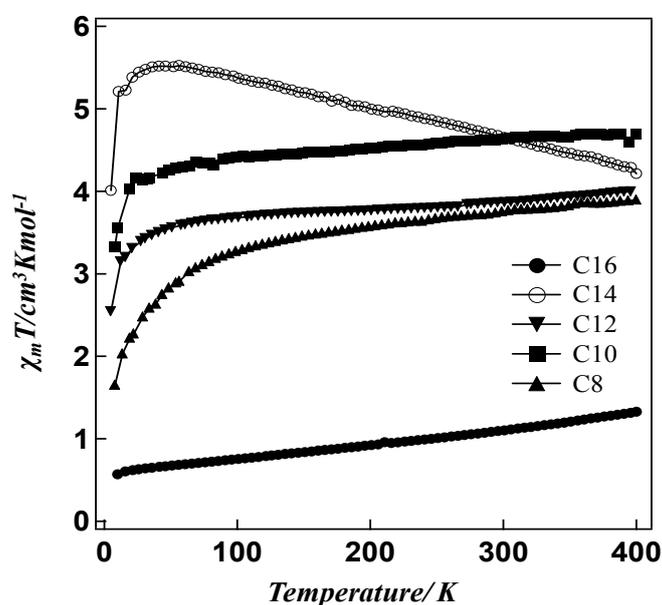


Figure 2. $\chi_m T$ vs. T plots for **1–5** in the temperature range of 5 to 400 K.



The temperature dependences of the magnetic susceptibility for the compounds **1–5** were measured in the form of the $\chi_m T$ versus T curve, where χ_m is the molar magnetic susceptibility and T is the temperature (Figure 2). The compounds **1–4** are in the HS state in the temperature range of 5–400 K. The $\chi_m T$ value for **1** increased abruptly from $1.64 \text{ cm}^3 \cdot \text{Kmol}^{-1}$ at 5 K to $3.00 \text{ cm}^3 \cdot \text{Kmol}^{-1}$ at 65 K and increased gradually to $3.89 \text{ cm}^3 \cdot \text{Kmol}^{-1}$ at 400 K. The value at 400 K is smaller than that in iron(III) HS ($4.38 \text{ cm}^3 \cdot \text{Kmol}^{-1}$), and it is proposed that an LS specie is mixed even at 400 K. The $\chi_m T$ value for **2** increased abruptly from $3.32 \text{ cm}^3 \cdot \text{Kmol}^{-1}$ at 5 K to $4.16 \text{ cm}^3 \cdot \text{Kmol}^{-1}$ at 24 K and increased gradually

to $4.69 \text{ cm}^3 \cdot \text{Kmol}^{-1}$ at 400 K. The $\chi_m T$ value for **3** increased abruptly from $2.54 \text{ cm}^3 \cdot \text{Kmol}^{-1}$ at 5 K to $3.39 \text{ cm}^3 \cdot \text{Kmol}^{-1}$ at 27 K and increased gradually to $4.00 \text{ cm}^3 \cdot \text{Kmol}^{-1}$ at 400 K. The value also indicates the mixture of a small amount of LS specie. The $\chi_m T$ value for **4** increased abruptly from $4.01 \text{ cm}^3 \cdot \text{Kmol}^{-1}$ at 5 K to $5.55 \text{ cm}^3 \cdot \text{Kmol}^{-1}$ at 41 K and decreased gradually to $4.21 \text{ cm}^3 \cdot \text{Kmol}^{-1}$ at 400 K. Compound **4** shows weak ferromagnetic interactions between the complexes, it is proposed that the ferromagnetic interaction results from interchain interactions. Furthermore, the decrease in the $\chi_m T$ value below 50 K is due to zero field splitting. On the other hand, the $\chi_m T$ value for **5** increased gradually from $0.57 \text{ cm}^3 \cdot \text{Kmol}^{-1}$ at 5 K to $1.32 \text{ cm}^3 \cdot \text{Kmol}^{-1}$ at 400 K, in accord with compound **5** being in the LS state at room temperature. This compound has the longest alkyl chain (C16), and hence the strongest interchain interaction can be expected, in accord with it adopting the LS state.

Table 1. Crystal parameter, and bond lengths and angles for compound **4**.

Compound	4	Metal-ligand Ligand-metal-ligand	Bond lengths (Å) and angles (°)
CCDC Number [17]	988486	Fe–N(1)	2.109
Chemical form	$\text{C}_{52}\text{H}_{74}\text{ClFeN}_4\text{O}_8$	Fe–N(2)	2.207
M_r	974.48	Fe–N(3)	2.112
Crystal size/mm ³	$0.200 \times 0.180 \times 0.020$	Fe–N(4)	2.221
Crystal system	triclinic	Fe–O(1)	1.935
Space group	P-1 (#2)	Fe–O(3)	1.936
$a/\text{Å}$	10.6395(10)	–	–
$b/\text{Å}$	12.2937(10)	O(1)–Fe–N(1)	78.75(8)
$c/\text{Å}$	22.129(3)	O(1)–Fe–N(2)	152.76(8)
$\alpha/^\circ\text{C}$	74.026(9)	O(1)–Fe–N(3)	103.78(9)
$\beta/^\circ\text{C}$	84.735(11)	O(1)–Fe–N(4)	90.98(7)
$\gamma/^\circ\text{C}$	65.255(9)	O(1)–Fe–O(3)	99.79(7)
$V/\text{Å}^3$	2526.2(5)	O(3)–Fe–N(1)	113.24(7)
Z	2	O(3)–Fe–N(2)	88.55(8)
$D_x/\text{g} \cdot \text{cm}^{-3}$	1.281	O(3)–Fe–N(3)	78.87(7)
μ/mm^{-1}	0.41	O(3)–Fe–N(4)	152.42(7)
$F(000)/e$	1042	N(1)–Fe–N(2)	74.15(8)
T/K	143	N(1)–Fe–N(3)	167.26(6)
$\theta_{\text{max}}/^\circ$	27.4	N(1)–Fe–N(4)	93.67(7)
h, k, l range	$-13 \leq h \leq 13$	N(2)–Fe–N(3)	103.26(8)
	$-15 \leq k \leq 15$	N(2)–Fe–N(4)	93.37(8)
	$-28 \leq l \leq 28$	N(3)–Fe–N(4)	73.90(7)
Measured reflections	28551	–	–
Independent reflections (R_{int})	11,396 (0.0499)	–	–
Observed reflections [$I \geq 2\sigma(I)$]	9,058	–	–
Restraints/parameters	597	–	–
$R1/wR2$ [$I \geq 2\sigma(I)$]	0.0685/0.1811	–	–
$R1/wR2$ (all data)	0.0847/0.1811	–	–
$\Delta\rho_{\text{max/min}}/e \text{ Å}^{-3}$	0.74/−0.108	–	–

3. Experimental Section

All reagents were obtained commercially (Wako, Kumamoto, Japan) and were used in the form that they were received. The reactions were performed under N₂.

3.1. Synthesis of 5-Hydroxy-2-Methylpyridine N-Oxide

A solution of 5-hydroxy-2-methylpyridine (7.50 g, 0.70 mol, 1 eq.) and hydrogen peroxide 30% (16.5 mL, q.s.) in CH₃COOH (150 mL) was heated at 80 °C for 2.5 h. A solution color change was observed from orange to pale yellow. The solution was further stirred at room temperature for 24 h and concentrated *in vacuo*. Acetone was added to force precipitation. The resulting pale yellow precipitate was collected by vacuum filtration (6.60 g, 77%). ¹H-NMR (CD₃OD): 7.93 (d 1H) 7.32 (d 1H) 7.03 (dd 1H) 2.41 (s 3H).

3.2. Synthesis of 2-Pyridylmethanol Acetate

5-Hydroxy-2-methylpyridine N-oxide (6.60 g, 0.05 mol, 1 eq.) was added slowly to (CH₃CO)₂O (65 mL) at 110 °C. The resultant dark brown reaction mixture was stirred for 2 h at 140 °C. EtOH (150 mL) was added and the solution was concentrated *in vacuo* to yield a brown oil. CHCl₃ (40 mL) was added and the solution was neutralized with saturated NaHCO₃. The organic layer was collected and washed with saturated NaHCO₃ (30 mL × 2), dried (MgSO₄, q.s.) and filtered. The solvent was removed *in vacuo* to yield a brown oil, which was further dried under high vacuum for 2 h. Without purification the product was used for next reaction. ¹H-NMR (CDCl₃): 8.40 (d 1H) 7.49 (d 1H) 7.39 (dd 1H) 5.21 (s 2H) 2.33 (s 3H) 2.15 (s 3H).

3.3. Synthesis of 5-Hydroxy-2-Hydroxymethylpyridine

A solution of 2-pyridylmethanol acetate (q.s.) in conc. HCl (10 mL) was heated under reflux for 1.5 h. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. CHCl₃ (40 mL) was added and the solution neutralized carefully with saturated NaHCO₃. The aqueous layers were collected through washings with saturated NaHCO₃ and concentrated *in vacuo*. The brown solid was triturated with MeOH and filtrates collected through filtration. The solvent was removed *in vacuo* yielding a brown solid (3.20 g). ¹H-NMR (CDCl₃): 7.85 (d 1H) 7.18 (d 1H) 7.01 (dd 1H) 4.51 (s 2H).

3.4. Synthesis of 5-Hydroxypyridine 2-Carbaldehyde

A suspension of 5-hydroxy-2-hydroxymethylpyridine (3.20 g, 0.03 mol) and MnO₂ (oven dried, q.s.) in *iso*-PrOH (100 mL) was heated under reflux for 24 h. The hot mixture was filtered through Celite[®] and washed thoroughly with hot MeOH (q.s.). The solution was allowed to cool to room temperature and concentrated *in vacuo*, yielding a brown solid. The solid was purified by chromatography on a short silica gel column (gradient elution; 0% to 5% methanol in CH₂Cl₂). The solvent was removed *in vacuo* to yield a brown solid (0.96 g, 26%). ¹H-NMR (CD₃OD): 9.60 (s 1H) 7.90 (d 1H) 7.74 (d 1H) 6.84 (dd 1H).

3.5. Synthesis of 5-(*n*-alkoxy)Pyridine 2-Carbaldehyde (*n* = 8, 10, 12, 14, 16)

5-Hydroxypyridine-2-carbaldehyde (3.30 mmol, 1 eq.), K₂CO₃ (3.30 mmol, 1 eq) and *n*-alkylbromide (3.50 mmol, *n* = 8–16) were stirred vigorously in dry DMF at 100 °C for 6 h. After cooling to room temperature, the solvent was removed *in vacuo*. The solid was purified by chromatography on a short silica gel column (hexane:ethyl acetate = 5:1). The solvent was removed *in vacuo* to yield a white solid.

3.6. Synthesis of *Cn*-pap (*n* = 8, 10, 12, 14, 16) (L1)–(L5)

5-(*n*-Alkoxy)pyridine-2-carbaldehyde (1 eq) and 2-aminophenol (1 eq) were stirred in MeOH. A solution color change from yellow to orange was observed. The solution was concentrated *in vacuo* and left in a refrigerator for several hours. The precipitate was collected by vacuum filtration.

¹H-NMR (500 MHz; CDCl₃): **L1**; 8.85 (s, 1H, pyH), 8.20 (s, 1H, pyH), 7.61 (d, 1H, pyH) 7.49 (m, 1H, N–CH₂), 7.14 (m, 2H, ArH), 6.78 (m, 2H, ArH), 4.88 (s, 1H, OH), 3.95 (m, 2H, CH₂ of main chain), 1.73 (m, 2H, CH₂ of main chain), 1.33 (m, 2H, CH₂ of main chain), 1.25 (s, 8H, CH₂ of main chain), 0.95 (s, 3H, CH₃), **L2**; 8.79 (s, 1H, pyH), 8.21 (s, 1H, pyH), 7.59 (d, 1H, pyH) 7.40 (m, 1H, N–CH₂), 7.12 (m, 2H, ArH), 6.75 (m, 2H, ArH), 4.90 (s, 1H, OH), 3.92 (m, 2H, CH₂ of main chain), 1.73 (m, 2H, CH₂ of main chain), 1.30 (m, 2H, CH₂ of main chain), 1.20 (s, 12H, CH₂ of main chain), 0.92 (s, 3H, CH₃), **L3**; 8.81 (s, 1H, pyH), 8.22 (s, 1H, pyH), 7.59 (d, 1H, pyH) 7.47 (m, 1H, N–CH₂), 7.11 (m, 2H, ArH), 6.75 (m, 2H, ArH), 4.85 (s, 1H, OH), 3.99 (m, 2H, CH₂ of main chain), 1.70 (m, 2H, CH₂ of main chain), 1.35 (m, 2H, CH₂ of main chain), 1.25 (s, 16H, CH₂ of main chain), 0.93 (s, 3H, CH₃), **L4**; 8.84 (s, 1H, pyH), 8.19 (s, 1H, pyH), 7.63 (d, 1H, pyH) 7.45 (m, 1H, N–CH₂), 7.14 (m, 2H, ArH), 6.80 (m, 2H, ArH), 5.01 (s, 1H, OH), 3.94 (m, 2H, CH₂ of main chain), 1.75 (m, 2H, CH₂ of main chain), 1.35 (m, 2H, CH₂ of main chain), 1.24 (s, 20H, CH₂ of main chain), 0.96 (s, 3H, CH₃), **L5**; 8.80 (s, 1H, pyH), 8.18 (s, 1H, pyH), 7.58 (d, 1H, pyH) 7.44 (m, 1H, N–CH₂), 7.10 (m, 2H, ArH), 6.88 (m, 2H, ArH), 4.85 (s, 1H, OH), 3.91 (m, 2H, CH₂ of main chain), 1.77 (m, 2H, CH₂ of main chain), 1.36 (m, 2H, CH₂ of main chain), 1.27 (s, 24H, CH₂ of main chain), 0.90 (s, 3H, CH₃).

3.7. Synthesis of [Fe(*Cn*-pap)₂]ClO₄ (*n* = 8, 10, 12, 14, 16) (1)–(5)

Cn-pap (2 eq) was dissolved in CHCl₃ and Fe(ClO₄)₃·*n*H₂O (1.5 eq) in MeOH (10 mL) was added to the solution. The solution was stirred and then concentrated. The microcrystals of product that formed were collected by filtration and recrystallized from MeOH/CHCl₃.

The composition of the bulk materials were confirmed through elemental analyses. [Fe(C8-pap)₂]ClO₄ (**1**), Anal. Calcd. for C₄₀H₅₀O₈N₄Cl₁Fe₁: C, 59.60; H, 6.25; N, 6.95. Found: C, 59.76; H, 6.38; N, 6.85. [Fe(C10-pap)₂]ClO₄ (**2**), Anal. Calcd. for C₄₄H₅₈O₈N₄Cl₁Fe₁: C, 61.29; H, 6.78; N, 6.50. Found: C, 61.13; H, 6.73; N, 6.08. [Fe(C12-pap)₂]ClO₄ (**3**), Anal. Calcd. for C₄₈H₆₆O₈N₄Cl₁Fe₁: C, 62.78; H, 7.24; N, 6.10. Found: C, 62.62; H, 7.53; N, 6.27. [Fe(C14-pap)₂]ClO₄ (**4**), Anal. Calcd. for C₅₂H₇₄O₈N₄Cl₁Fe₁: C, 64.09; H, 7.65; N, 5.75. Found: C, 64.02; H, 7.53; N, 5.87. [Fe(C16-pap)₂]ClO₄ (**5**), Anal. Calcd. for C₅₆H₈₂O₈N₄Cl₁Fe₁: C, 65.26; H, 8.02; N, 5.44. Found: C, 65.62; H, 8.13; N, 5.47.

The magnetic properties were determined by temperature-dependent susceptibility measurement with a Superconducting Quantum Interference Device (SQUID) magnetometer at field strengths of 1 T.

4. Conclusions

[Fe(C_n-pap)₂][ClO₄] (*n* = 8, 10, 12, 14, 16) have been synthesized and characterized. The single crystal X-ray analysis for compound **4** showed that there is fastener effect between long alkyl chains of neighboring molecules. The compounds **1–4** are in the HS states and compound **5** is in the LS state. Furthermore **4** shows weak ferromagnetic interaction between individual complexes in accord with the presence of a cooperative interaction being an important factor for inducing such a magnetic interaction.

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Author Contributions

Manabu Nakaya, Saliu Alao Amolegbe, Masaaki Nakamura, and Shinya Hayami conceived the project. Manabu Nakaya, Saliu Alao Amolegbe, Masaaki Nakamura, Kodai Shimayama, Kohei Takami, Kazuya Hirata and Shinya Hayami designed the experiments. Manabu Nakaya and Kodai Shimayama performed all synthesis and characterisation experiments. Manabu Nakaya, Leonald F. Lindoy and Shinya Hayami analysed the data and co-wrote the manuscript. All authors discussed the results and commented on the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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16. Crystal data for **4** at 143 K: $f_w = 974.48$; colorless prism, crystal dimensions of 0.200 mm \times 0.180 mm \times 0.020 mm, triclinic, space group P-1; $a = 10.6395(10)$ Å, $b = 12.2937(10)$ Å, $c = 22.129(3)$ Å, $\alpha = 74.026(9)^\circ$, $\beta = 84.735(11)^\circ$, $\gamma = 65.255(9)^\circ$, $V = 2526.2(5)$ Å³, $Z = 2$, $D_{\text{calc}} = 1.281$ g·cm⁻³, $R1 = 0.0685$ for $I > 2\sigma(I)$, $R = 0.049$ and $R_w = 0.181$ for all data with a linear absorption coefficient $\mu(\text{Mo K}\alpha) = 4.073$ cm⁻¹.
17. CCDC 988486 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).