# Iron(II) complexes containing thiophenesubstituted "bispicen" ligands — Spin-crossover, ligand rearrangements, and ferromagnetic interactions

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Abstract: The synthesis and characterization of three new tetradentate "bispicen-type" ligands containing a substituted thiophene heterocycle are described [2,5-thienyl substituents = H (7), Ph (8), or 2-thienyl (9)]. Iron(II) bis(thiocyanate) coordination complexes containing 7–9 were prepared, and the electronic and variable-temperature magnetic properties of complexes containing 7 (10) and 9 (12) are described. Complex 10 features a gradual and incomplete spin crossover in the solid state, and 12 remains high-spin over the entire temperature range. Complex 11 is extremely unstable and rearranges to another iron(II) complex (13), which was structurally characterized. The temperature-dependent magnetic properties of 13 are described as a one-dimensional ferromagnetic chain, with interchain antiferromagnetic interactions and (or) zerofield splitting dominant at low temperatures. The magnetic analysis is corroborated by the molecular packing and density functional theory calculations, which suggest intermolecular interactions between coordinated thiocyanate ligands bearing a significant spin density.

Key words: spin crossover, iron(II), thiophene, ferromagnetic interactions.

**Résumé :** On décrit la synthèse et la caractérisation de trois nouveaux ligands tétradentates de type bispicène contenant un hétérocycle thiophène substitué [substituants 2,5-thiényl = H (7), Ph (8) ou 2-thiényl (9)]. On a préparé les complexes de coordination bis(thiocyanate) de fer(II) contenant les ligands 7–9 et on décrit les propriétés magnétiques en fonction de la température des complexes contenant le ligand 7 (10) et le ligand 9 (12). Le complexe 10 par une inversion graduelle et incomplète de spin à l'état solide alors que le complexe 12 garde un spin élevé sur toute la plage de température. Le complexe 11 est extrêmement instable et il se réarrange en un autre complexe du fer(II) (13) dont on a caractérisé la structure. On décrit les propriétés magnétiques du complexe 13 en fonction de la température comme une chaîne ferromagnétique unidimensionnelle avec des interactions antiferromagnétiques interchaînes et (ou) un dédoublement de champ dominant nul à basses températures. L'analyse magnétique est corroborée par des calculs d'empilement moléculaire et par la théorie de la fonctionnelle de la densité, ce qui suggère qu'il existe des interactions intermoléculaires entre les ligands thiocyanates porteurs d'une densité de spin significative.

Mots-clés : inversion de spin, fer(II), thiophène, interactions ferromagnétiques.

# Introduction

Spin-crossover (SCO) in iron(II) coordination complexes provides the best example of molecular bistability.<sup>1</sup> There are many examples of iron(II) complexes exhibiting abrupt spin state transitions and concomitant thermal hysteresis, confering true bistability on these materials.<sup>2</sup> Exploration of new avenues for research with SCO complexes is underway, including coupling SCO with other properties in singlecomponent materials (so-called multifunctional materials).<sup>3</sup> SCO complexes also exhibiting magnetic exchange coupling, liquid crystalline behaviour, porosity, and photochromism have all now been reported. A number of research groups have also reported single-component ioniccoordination complexes containing SCO cations and electrically conducting anions as fascinating SCO conductors.<sup>4</sup> We are also interested in SCO conduting materials and our approach is focused on combining SCO properties with electrical conductivity in novel metallopolymer materials.<sup>5</sup> To date, all reported SCO conductors have contained iron(III), and we thought it would be interesting to produce SCO conductors instead containing iron(II).

As an initial foray into this research, we have designed

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Fig. 1. Structural relationship between known bispicen ligands and

 Table 1. Crystallographic data and structure refinement for 13.

Empirical formula	$C_{58}H_{40}FeN_{10}S_4$
Formula mass	1061.09
Habit	Rod
Color	Orange
Crystal size (mm)	0.37×0.13×0.10
Crystal system	Monoclinic
Space group	C2/c
Ζ	4
a (Å)	17.343(4)
b (Å)	17.136(4)
c (Å)	17.227(4)
$\alpha$ (°)	90
$\beta$ (°)	108.315(5)
γ (°)	90
Collection ranges	–16≤ <i>h</i> ≤21
	-16≤ <i>k</i> ≤21
	-21≤ <i>I</i> ≤20
V (Å <sup>3</sup> )	4860(2)
$D_{\text{calcd.}}$ (Mg m <sup>-3</sup> )	1.450
$\mu \text{ (mm}^{-1})$	0.535
<i>F</i> (000)	2192
$\theta$ range for data collection (°)	1.88-26.00
Observed reflections	26762
Independent reflections	4768 ( $R_{int} = 0.0713$ )
Data/restraints/parameters	4768/3/335
GOF on $F^2$	1.326
Final $R_1$ indices $[I > 2\sigma(I)]$	0.0670, 0.1791
$wR_2$ indices (all data)	0.1162, 0.2037
Largest diff. peak and hole (e $Å^{-3}$ )	0.816 and -0.524

new tetradentate ligands with structural features that could enable electropolymerization of the precursor iron(II) coordination complexes. We also wanted the ligand to coordinate the metal ion close to the polymer backbone to facilitate stronger interactions among the coordinated SCO unit and the conducting polymer. Inspection of the SCO literature led us to the bis(2-pyridylmethyl)-diamine type (bispicen) reported by Toftlund and co-workers in the 1980s (Fig. 1).<sup>6</sup> These tetradentate ligands feature an ethyl or propyl spacer between the 2-pyridylmethylamine substituents, which could easily be replaced with a polymerizable thiophene heterocycle substituted at the 3,4-ring positions (bispicth 7). Also, *cis*-iron(II) complexes containing bispicen (or other derivatives) and two equivalents of thiocyanate have been observed to exhibit SCO, including abrupt transitions with small thermal hysteresis cycles.

Herein, we describe the multistep syntheses of three new bis-(2-pyridylmethyl) ligands containing thienyl substituents and the preparation, electronic, and variable-temperature magnetic properties of mononuclear iron(II) coordination complexes containing these ligands, including the observation of SCO. We also report an unusual ligand-centered structural rearrangment in solutions containing these coordination complexes, which produces new iron complexes. One of these complexes features significant intermolecular ferromagnetic interactions.

# Experimental

#### General procedures

All reagents were commercially available and used as received unless otherwise stated. Deaerated and anhydrous solvents were obtained from a Puresolve PS MD-4 solventpurification system, and all air- and (or) moisture-sensitive reactions were carried out using standard Schlenk techniques, unless otherwise stated. 1H/13C NMR spectra were recorded on a Bruker Advance 300 (or 600) MHz spectrometer (as indicated) with a 7.05 (or 14.1) T Ultrashield magnet using deuterated solvents. FTIR spectra were recorded on a Shimadzu IR/Affinity spectrometer as KBr discs or thin films on KBr plates. EI and FAB mass spectra were obtained using a Kratos Concept 1S High Resolution E/B mass spectrometer, and ESI mass spectra were obtained using a Bruker HCT Plus Proteineer LC-MS. Room temperature vis-NIR spectra were recorded on a Shimadzu 3600 UV-vis-NIR spectrophotometer as solutions in appropriate solvents. Spectra at 77 K were obtained as frozen ethanol glasses in 5 mm NMR tubes immersed in a liquid N<sub>2</sub> Dewar. Elemental analyses were carried out by Guelph Chemical Laboratories LTD, Guelph, ON, Canada.

#### X-ray crystallography

An orange rod was mounted on a MiTeGen mount, and placed in the cold stream at 100 K. Data were collected on a SMART APEX II diffractometer with Mo K $\alpha$  radiation ( $\lambda$ = 0.71073 Å) located at the McMaster Analytical X-ray Diffraction Facility (MAX). Data were collected using omega and phi scans, integrated, and a numerical face-indexed absorption correction was applied with a secondary absorption correction using redundant data (SADABS). The space group chosen was C2/c, based on systematic absences. Data were solved using direct methods (SHELXS-97), and refined using least-squares techniques. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were located and then treated as riding on their constituent atoms and updated after each cycle of refinement. The NCS ligand showed a 73:27 disorder over two positions, which were symmetry-related to each other due to the twofold axis at Fe1. The non-bonded pyridine also showed disorder between N5 and C13/C17, which was similar in magnitude to the NCS disorder, and due to some intermolecular interactions between these moieties, we chose to couple the C/N disorder in the pyridine ring to the NCS disorder.

The possibility of choosing a lower-symmetry space group to solve the structure was investigated, with the expectation that the disorder would be resolved; however, solving the data in Cc (the *c*-glide is obvious in the reciprocal lattice) gave a highly correlated structure, with the same

Scheme 1. Preparation of ligands. Reagents and conditions: (a) concentrated  $H_2SO_4/HNO_3$ . (b) Phenylboronic acid, 6 mol% Pd(PPh<sub>3</sub>)<sub>4</sub>,  $K_2CO_3(aq)$ , dimethoxyethane, 13 h reflux. (c) 2-Thienylboronic acid, 6 mol% Pd(PPh<sub>3</sub>)<sub>4</sub>,  $K_2CO_3(aq)$ , dimethoxyethane, 8 h reflux. (d) Sn, HCl/EtOH. (e) KOH(aq), 2-pyridinecarboxaldehyde, NaBH<sub>4</sub>, MeOH, 1 h reflux.



Scheme 2. Preparation of cis-iron(II) complexes 10 and 12.



R = H (10), 2-thienyl (12)

Scheme 3. Ligand structural rearrangement in solutions of complex 11.



disorder of the NCS ligand. Twin refinement indicated the presence of the twofold rotation axis in the molecule, and in the end, it was decided that C2/c was the correct space group. In the final cycles of refinement,  $R_1 = 6.70\%$ ,  $wR_2 = 20.37\%$  (Table 1).

#### **Electrochemical measurements**

Cyclic voltammetry (CV) experiments were performed with a Bioanalytical Systems Inc. Epsilon electrochemical workstation. Compounds were dissolved in anhydrous solvent (CH<sub>3</sub>CN) and deaerated by sparging with N<sub>2</sub> gas for 20 min. Solution concentrations were approximately  $10^{-3}$  mol/L in analyte containing 0.1 mol/L supporting electrolyte (Bu<sub>4</sub>NPF<sub>6</sub>). A typical three-electrode setup was used including a platinum working electrode, Ag-wire pseudoreference electrode, and a platinum-wire auxiliary electrode. Ferrocene was used in all cases as an internal standard and was oxidized at a potential of +0.51 V in our setup; all potentials quoted are versus the ferrocene redox potential. Scan rates for CV experiments were, generally, 100 mV/s.

Fig. 2. ORTEP view of 13. Thermal ellipsoids are drawn at the 50% probability level.



# Variable-temperature magnetic susceptibility measurements

Variable-temperature magnetic susceptibility measurements were recorded on a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS) with a 5.5 T magnet (temperature range: 1.8 to 400 K) in an external field of 5000 Oe. Samples were carefully weighed into gelatin capsules, with empty gelatin capsules above and below to eliminate background contribu-

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Bond lengths (Å)	
Fe—N(1)	2.203(3)
Fe—N(2)	2.293(3)
Fe—N(4)	2.127(5)
Fe—N(4')	1.983(10)
C(9)—C(18)	1.502(6)
C(10)—C(24)	1.469(6)
C(5)—C(6)	1.474(5)
C(30)—S(2)	1.642(7)
C(30')—S(2')	1.642(8)
N(2)—C(6)	1.338(5)
N(2)—C(8)	1.404(5)
N(3)—C(6)	1.375(5)
N(3)—C(7)	1.388(5)
N(4)—C(30)	1.163(7)
N(4')-C(30')	1.163(8)
Bond angles (°)	
N(1)–Fe– $N(2)$	73.46(11)
N(1)-Fe-N(4)	92.9(4)
N(1)-Fe-N(4')	87.2(12)
N(2)-Fe-N(4)	91.0(3)
N(2)-Fe-N(4')	100.2(10)
Fe-N(1)-C(5)	118.1(2)
Fe-N(2)-C(6)	108.7(2)
Fe-N(2)-C(8)	136.5(3)
Fe-N(4)-C(30)	166.3(6)
Fe-N(4')-C(30')	163(3)
N(4)-C(30)-S(2)	177.4(10)
N(4')-C(30')-S(2')	178(2)

**Table 2.** Selected bond lengths (Å) and<br/>angles (°) for 13.

tions from the gelatin, which were loaded into plastic straws, and attached to the sample transport rod. Diamagnetic corrections were made using Pascal's constants.

#### **Computational details**

All density functional theory (DFT) calculations were performed using the Gaussian 03 package using the B3LYP hybrid functional and the DZVP basis set for all atoms.<sup>7</sup> Tight SCF convergence criteria were used for all calculations. The converged wave functions were tested to confirm that they correspond to the ground-state surface. The evaluation of atomic charges and spin densities was performed using the natural population analysis (NPA).<sup>8</sup> The analysis of molecular orbitals in terms of fragment orbital contributions were carried out using the AOMix program.<sup>9</sup> Time-dependent DFT (TD-DFT) calculations at the B3LYP/DZVP level were performed to calculate the absorption spectra as previously described.<sup>9b</sup>

#### Synthesis

#### 2,5-Dibromo-3,4-dinitrothiophene (1)

 $H_2SO_4$  (18 mol/L, 40 mL) was added to a three-neck round-bottom flask then purged with  $N_2$  for 30 min and cooled in an ice-water bath. Under  $N_2$ , 2,5-dibromothio-phene (10.74 g, 5.00 mL, 44.37 mmol) was added slowly to maintain a temperature below 20 °C. HNO<sub>3</sub> (16 mol/L,

7.00 mL) was then added dropwise, maintaining a temperature under 30 °C. Once the addition was complete, the reaction mixture was allowed to react for an additional 3 h and then poured over ~ 160 g of ice. Upon melting of the ice, the solid residue was recovered by vacuum filtration and washed with water to produce a light yellow powder. Recrystallization from methanol afforded 7.64 g (52%) of pure material. Mp 135–136 °C. The FTIR spectrum of **1** is identical to that previously reported.<sup>1013</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  140.3, 113.4 ppm. MS (EI+): *m/z* 332 (M<sup>+</sup>, 100%).

#### 3,4-Dinitro-2,5-diphenylthiophene (2)

Phenylboronic acid (0.20 g, 1.66 mmol) was added to a Schlenk flask and flushed with N2 gas. Then, 1.8 mL of  $H_2O$  and 5 mL of 1,2-dimethoxyethane were added to the reaction flask, which was sparged with N2 for 30 min. After that, K<sub>2</sub>CO<sub>3</sub> (0.50 g, 3.62 mmol), **1** (0.10 g, 0.60 mmol), 6 mol% Pd(PPh<sub>3</sub>)<sub>4</sub> (0.04 g, 0.04 mmol) were added to the flask, respectively, and the mixture was refluxed at 65 °C under nitrogen for 13 h. The reaction mixture was washed with water and extracted into CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over MgSO<sub>4</sub> and concentrated to dryness. The crude product was chromatographed over silica gel using 1:3 CH<sub>2</sub>Cl<sub>2</sub>:hexane as eluent to yield 0.16 g (80%) of bright yellow crystal. Mp 145-147 °C. FTIR (KBr): 3448 (m, br), 3059 (w), 1963 (w), 1542 (s), 1524 (s), 1448 (m), 1395 (s), 1327 (s), 1261 (m), 1079 (m), 902 (m), 748 (s), 691 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.54 (m, 10H) ppm. <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>): δ 140.8, 136.8, 130.9, 129.3, 129.1, 128.1 ppm. MS (EI+): m/z 326 (M+, 100%). HR-MS (EI+) calculated for  $[C_{16}H_{10}N_2O_4S]^+$ : 326.03613; found: 326.03557.

## 3',4'-Dinitro-2,2':5',2"-terthiophene (3)

Thiophene-2-boronic acid (3.29 g, 25.68 mmol) was added to a Schlenk flask and flushed with N<sub>2</sub>. Then, 1.8 mL of H<sub>2</sub>O and 5 mL of 1,2-dimethoxyethane were added to the reaction flask, which was sparged with N2 for 0.5 h. After that,  $K_2CO_3$  (0.25 g, 1.81 mmol), 1 (3.1 g, 9.34 mmol), 6 mol% Pd(PPh<sub>3</sub>)<sub>4</sub> (0.65 g, 0.56 mmol) were added to the flask, respectively, and the mixture was refluxed at 100 °C for 8 h. The reaction mixture was washed with water and extracted into CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over MgSO4 and concentrated to dryness. The crude product was chromatographed over silica gel using 1:3 CH<sub>2</sub>Cl<sub>2</sub>:hexane as eluent to yield 0.05 g (48%) of yellow solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.20 (m, 2H), 7.57 (m, 2H), 7.62 (m, 2H) ppm. <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>): δ 133.8, 131.3, 131.2, 128.4, 128.1, 96.13 ppm. MS (FAB+): m/z 338 [M+, 100%]. HR-MS (EI+) calculated for  $[C_{12}H_6N_2O_4S_3]^+$ : 337.94897; found: 337.94872.

## 3,4-Diaminothiophene ·2HCl (4)

Concentrated HCl (25 mL) was added to a three-neck round-bottom flask and sparged with  $N_2$  for 0.5 h. Then, **1** (1.28 g, 3.80 mmol) was carefully combined with the HCl, cooled in an ice-water bath. Tin (mossy) metal (3.19 g, 26.89 mmol) was added slowly to maintain a temperature

Fig. 3. Molecular packing of 13 with a view down the *ac* diagonal. Intermolecular  $S2 \cdots S2'$  and  $S2' \cdots S2'$  contacts are indicated by dashed lines.



**Fig. 4.** Left: Visible–NIR spectrum of **10** in ethanol solution at 298 K (grey curve) and as a frozen ethanol glass at 77 K (black curve). Right: Cyclic voltammogram of a  $10^{-3}$  mol/L solution of **12** in CH<sub>3</sub>CN, containing 0.1 mol/L Bu<sub>4</sub>NPF<sub>6</sub>.



Fig. 5. Variable-temperature magnetic properties of 10 ( $\blacksquare$ ), 12 (▲) (left) and 13 ( $\blacklozenge$ ) (right). External magnetic field of 5000 Oe was applied in all experiments. Magnetic data was acquired between 2–350 K for 10 and between 5–325 K for 12 and 13. The best fit to a 1-D Bonner–Fisher chain model is indicated as a solid line.



between 25–30 °C. After stabilizing at 25 °C, the reaction continued until all the tin metal was consumed and then placed in a refrigerator overnight. The solid precipitate was recovered by vacuum filtration and washed with diethyl ether and acetonitrile until the wash was colorless to afford 0.64 g (83%) of white solid. <sup>1</sup>H and <sup>13</sup>C NMR spectra and the FTIR spectrum of **4** are identical to those previously reported.<sup>11</sup> MS (EI+): m/z 114 [(M – 2HCl)<sup>+</sup>, 100%].

#### 3,4-Diamino-2,5-diphenylthiophene 2HCl (5)

To a mixture of **2** (0.33 g, 1.00 mmol) in absolute ethanol (30 mL) and concentrated HCl (60 mL) was added tin (mossy) metal (3.63 g, 30.58 mmol) in small portions. The resulting mixture was stirred at room temperature for 15 h in air. A pale yellow solid was obtained, which was collected by vacuum filtration and washed with H<sub>2</sub>O to afford 0.24 g (71%) of product. Mp 205–207 °C. FTIR (KBr):



Fig. 6. Calculated spin density distribution in 13. NPA-derived atomic spin density is shown for most important contributors. H atoms are not shown for clarity.

3330 (m, d), 3047 (w), 2920 (w), 2848 (w), 1616 (m), 1595 (m), 1523 (m), 1489 (m), 1429 (s), 1313 (w), 970 (m), 754 (s), 703 (m), 621 (w), 573 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  3.67 (br, s, 4H), 7.30 (m, 2H), 7.45 (m, 4H), 7.56 (m, 4H) ppm. <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  134.4, 133.2, 129.1, 127.6, 126.7, 116.5 ppm. MS (FAB+): *m*/*z* 266 [(M – 2HCl)+, 100%]. HR-MS (EI+) calculated for [C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>S]<sup>+</sup>: 266.08777; found: 266.08880.

# 3',4'-Diamino-2,2':5',2"-terthiophene-2HCl (6)

To a mixture of **3** (0.27 g, 0.80 mmol) in absolute ethanol (30 mL) and concentrated HCl (60 mL) was added tin (mossy) metal (2.84 g, 23.96 mmol) in small portions. The resulting mixture was stirred at room temperature for 15 h in air. A deep yellow solid was collected by vacuum filtration and washed with H<sub>2</sub>O to afford 0.28 g (88%) of the product. Melting point and FTIR spectrum (KBr) are identical to those previously report.<sup>11</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  3.76 (br, s, 4H), 7.11 (m, 4H), 7.30 (m, 2H) ppm. <sup>13</sup>C NMR (150.9 MHz, CDCl<sub>3</sub>):  $\delta$  135.9, 133.6, 127.8, 124.0, 123.9, 110.13 ppm. MS (FAB+): *m/z* 278 [(M – 2HCl)<sup>+</sup>, 100%].

#### N,N'-Bis(2-pyridylmethyl)-3,4-diaminothiophene (7)

Compound 4 (0.20 g, 1.07 mmol) was added to an ovendried three-neck round-bottom flask fitted with a reflux condenser. The apparatus was then flushed with N<sub>2</sub> for 5 min. NaOH (0.086 g, 2.15 mmol) was dissolved in methanol (20 mL), the solution was sparged with N<sub>2</sub> for 0.5 h and transferred by syringe into the three-neck flask. The mixture was stirred for 0.5 h, and then 2-pyridinecarboxaldehyde (0.24 g, 0.20 mL, 2.25 mmol) was added. The reaction mixture was refluxed for 1.5 h and protected from light by covering with foil. NaBH<sub>4</sub> (0.21 g, 5.67 mmol) was added in small portions followed by a reflux for 14 h under N<sub>2</sub>. The solvent was removed by rotary evaporation. The residue was extracted into CH<sub>2</sub>Cl<sub>2</sub>, washed with water and dried over MgSO<sub>4</sub>. The solution was filtered by passing through a Celite pad. The filtrate was concentrated by rotary evaporation, and pentane was used to precipitate impurities, which were removed by gravity filtration. The filtrate was then concentrated to dryness and chromatographed over neutral alumina using 2:1 hexane:EtOAc, followed by 1:2 hexane:EtOAc as eluent to yield 0.053 g (17%) of a bright yellow viscous oil. FTIR (KBr): 3447 (s, br), 3105 (m), 2960 (w), 2923 (m), 2851 (w), 1594 (s), 15.7 (m), 1436 (m), 1261 (w), 1097 (w, br), 801 (w), 757 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 4.45 (m, 6H), 6.01 (s, 2H), 7.21 (dd, 2H, J = 5.2, 1.8 Hz), 7.39 (d, 2H, J = 7.8 Hz), 7.67 (td, 2H, J = 7.5, 1.8 Hz), 8.60 (d, 2H, J = 4.5 Hz) ppm. <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>): 8 158.5, 149.3, 139.5, 136.7, 122.2, 121.8, 97.6, 51.4 ppm. MS (FAB+): m/z 297 [(M<sup>+</sup>, 100%)], 93 [(M – (EI+) calculated  $C_{10}H_{10}N_3S)^+$ , 62%]. HR-MS for [C<sub>16</sub>H<sub>16</sub>N<sub>4</sub>S]<sup>+</sup>: 296.10951; found: 296.10957.

## N,N'-Bis(2-pyridylmethyl)-3,4-diamino-2,5diphenylthiophene (8)

Compound 5 (0.12 g, 0.35 mmol) was added to an ovendried three-neck round-bottom flask fitted with a reflux condenser. The apparatus was then flushed with N<sub>2</sub>. Then, KOH (0.04 g, 0.69 mmol) was dissolved in methanol (20 mL) in a round-bottom flask, the solution was sparged with N<sub>2</sub> for 0.5 h, and transferred by syringe into the three-neck roundbottom flask. The mixture was stirred for 0.5 h followed by the addition of 2-pyridinecarboxaldehyde (0.22 g, 0.20 mL, 2.07 mmol). The reaction mixture was refluxed for 1 h while protected from light by covering with foil. The reaction was cooled to RT followed by adding NaBH<sub>4</sub> (0.26 g, 6.90 mmol), and the mixture was again refluxed at 75  $^{\circ}$ C for 1 h. The reaction mixture was diluted into Na<sub>2</sub>CO<sub>3</sub> solution (pH 9.5) and extracted into diethyl ether. The organic extracts were combined and dried over MgSO<sub>4</sub>. Concentration by rotary evaporation and chromatography over neutral alumina using CH<sub>2</sub>Cl<sub>2</sub> as eluent provided 0.12 g of a vibrant orange oil, which is very unstable. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  4.35 (br s, 6H), 7.59–7.13 (m, 16H), 8.49 (dd, 2H) ppm. HR-MS (FAB+) calculated for [C<sub>28</sub>H<sub>25</sub>N<sub>4</sub>S]<sup>+</sup>: 449.17999; found: 449.17897.

### N,N'-Bis(2-pyridylmethyl)-3',4'-diamino-2,2':5',2"terthiophene (9)

Compound 6 (0.10 g, 0.28 mmol) was added to an ovendried three-neck round-bottom flask fitted with a reflux condenser. The apparatus was then flushed with  $N_2$  for 5 min. Then, KOH (0.032 g, 0.57 mmol) was dissolved in methanol (20 mL) and the solution was sparged with  $N_2$  for 0.5 h. The solution was transferred by syringe into the three-neck round-bottom flask. The mixture was stirred for 0.5 h followed by the addition of 2-pyridinecarboxaldehyde (0.18 g, 0.16 mL, 1.71 mmol). The reaction mixture was refluxed for 1 h while protected from light by covering with foil. The reaction was cooled to RT, and NaBH<sub>4</sub> (0.22 g, 5.70 mmol) was carefuly added and the mixture was again refluxed for 1 h under N<sub>2</sub>. The reaction mixture was diluted into NaHCO<sub>3</sub> solution (pH 9.5) and extracted into diethyl ether. The organic extracts were combined and dried over MgSO<sub>4</sub>. Concentration by rotary evaporation provided 0.10 g (76%) of a brown-yellow oil, which required no further purification. FTIR (KBr): 3428 (s), 2922 (s), 2853 (m), 1593 (m), 1466 (m, br), 1431 (m), 1402 (m), 1219 (w, br), 1148 (m), 1045 (m, br), 691 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 4.38 (s, 4H), 4.92 (br, 2H), 7.04 (m, 2H), 7.16 (m, 4H), 7.25 (m, 4H), 7.61 (m, 2H), 8.50 (d, 2H, J = 4.8 Hz) ppm. <sup>13</sup>C NMR (150.9 MHz, CDCl<sub>3</sub>): δ 159.0, 149.1, 138.7, 136.5, 135.7, 127.2, 125.2, 124.9, 122.1, 116.1, 52.6 ppm. MS (FAB+): m/z 461 [(M<sup>+</sup>, 52%)], 369 [(M - C<sub>6</sub>H<sub>6</sub>N)<sup>+</sup>, 100%]. HR-MS (FAB+) calculated for [C<sub>24</sub>H<sub>21</sub>N<sub>4</sub>S<sub>3</sub>]+: 461.09284; found: 461.09655.

# $[Fe^{II}(7)(NCS)_2]$ (10)

A 25 mL Schlenk flask was charged with 7 (0.025 g, 0.08 mmol) and flushed with N<sub>2</sub>. Methanol (8 mL) was then added to the flask, which was sparged with N<sub>2</sub> for 0.5 h. Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.028 g, 0.08 mmol) was added to the solution and the mixture was stirred for 0.5 h under N<sub>2</sub>. KSCN (0.033 g, 0.338 mmol) was dissolved in 10 mL of H<sub>2</sub>O and was added to the mixture noted above. Gradually, a green precipitate was observed, which was isolated by vacuum filtration to afford 0.032 g (80%) of green powder. UV–vis (MeOH):  $\lambda_{max}$  ( $\epsilon$ ) = 640 nm (400 mol/L<sup>-1</sup> cm<sup>-1</sup>). FTIR (KBr): 3448 (s, br), 3159 (m, br), 2920 (m), 2060 (s, br), 1603 (m), 1425 (m), 787 (m), 762 (m) cm<sup>-1</sup>. MS (FAB+): *m*/z 468 [(M<sup>+</sup>, 17%)], 410 [(M – SCN)<sup>+</sup>, 100%], 351 [(M – 2SCN)<sup>+</sup>, 99%]. HR-MS (FAB+) calculated for [C<sub>18</sub>H<sub>16</sub>N<sub>6</sub>S<sub>3</sub>Fe]<sup>+</sup>: 467.98843; found: 467.99476.

# $[Fe^{II}(8)(NCS)_2]$ (11)

A solution of **8** (0.10 g, 0.22 mmol) in 10 mL of MeOH was degassed by sparging with  $N_2$  gas for 0.5 h. Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.08 g, 0.22 mmol) was added to generate a yellow-green solution. A solution of KSCN (0.09 g, 0.89 mmol) in 10 mL of water was added under  $N_2$ , followed by the addition of 10 mL of diethyl ether to instantly produce a green precipitate. The solid residue was isolated by vacuum filtration to afford 0.069 g (50%) of bright green

solid. UV–vis (MeOH):  $\lambda_{max} = 650$  nm. FTIR (KBr): 3424 (m, br), 3194 (w, br), 2921 (m), 2851 (w), 2071 (s), 1602 (w), 1508 (w), 1261 (w), 1102 (m), 1018 (m), 802 (m), 757 (m), 698 (m) cm<sup>-1</sup>. MS (FAB+): *m*/*z* 620 [(M<sup>+</sup>, 3%)], 562 [(M – SCN)<sup>+</sup>, 18%], 503 [(M – 2SCN)<sup>+</sup>, 17%]. Anal. calcd. for C<sub>30</sub>H<sub>24</sub>N<sub>6</sub>S<sub>3</sub>Fe·2C<sub>2</sub>H<sub>6</sub>O (found %): C 59.21 (59.21), H 5.54 (4.97), N 11.21 (11.00)

# $[Fe^{II}(9)(NCS)_2]$ (12)

Compound 9 (0.12 g, 0.25 mmol) was added to a Schlenk flask and flushed with N2. Then, methanol (8 mL) was added to the flask, which was sparged with  $N_2$  for 0.5 h. Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.085 g, 0.25 mmol) was added to the solution, and the mixture was stirred for 0.5 h under N<sub>2</sub>. KSCN (0.10 g, 1.00 mmol) was dissolved in 10 mL of H<sub>2</sub>O, and this solution was added to the reaction. A dark green precipitate was observed, which was isolated by vacuum filtration to afford 0.09 g (57%) of dark green solid. UV-vis (MeOH):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 656 nm (400 mol/L<sup>-1</sup>cm<sup>-1</sup>). FTIR (KBr): 3425 (m, br), 3222 (w), 3107 (w), 3075 (w), 2921 (w), 2851 (w), 2081 (s), 2063 (s), 1602 (m), 1572 (w), 1484 (w), 1440 (w), 1411 (m), 1232 (w), 1101 (w), 899 (w), 760 (w), 697 (m) cm<sup>-1</sup>. MS (FAB+): *m/z* 632 [(M<sup>+</sup>, 20%)], 574 [(M – SCN)<sup>+</sup>, 95%]. Anal calcd. for  $C_{26}H_{20}N_6S_5Fe$  (found %): C 49.38 (49.30), H 3.19 (2.96), N 13.30 (12.86).

# $C_{58}H_{40}N_{10}S_4Fe$ (13)

Complex **11** (20 mg) was recrystallized in 1:1 MeOH:CH<sub>2</sub>Cl<sub>2</sub> (4 mL) to produce orange rod-shaped crystals over a period of two weeks. FTIR (KBr): 2961 (m), 2922 (m), 2855 (m), 2060 (s), 1628 (m), 1597 (w), 1470 (w), 1437 (w), 1261 (m), 1096 (s), 1024 (s), 802 (s), 754 (m), 694 (m) cm<sup>-1</sup>. MS (FAB+): *m/z* 1002 [(M – NCS)<sup>+</sup>, 8%)], 445 [(C<sub>28</sub>H<sub>21</sub>N<sub>4</sub>S)<sup>+</sup>, 100%)], 353 [(C<sub>22</sub>H<sub>15</sub>N<sub>3</sub>S)<sup>+</sup>, 52%)]. Anal. calcd. for C<sub>58</sub>H<sub>40</sub>N<sub>10</sub>S<sub>4</sub>Fe·0.5CH<sub>2</sub>Cl<sub>2</sub> (found %): C 63.86 (63.90), H 3.73 (2.84), N 12.63 (12.13).

# **Results and discussion**

#### Ligand synthesis and coordination chemistry

Ligand preparation is outlined in Scheme 1. 2,5-Dibromo-3,4-dinitrothiophene (1) was prepared by nitration of commecrially available 2,5-dibromothiophene in a modified literature procedure.<sup>10</sup> We chose to use non-fuming concentrated acids and generated 1 in reasonably good yield. To generate the 2,5-disubstituted ligands (where the substituents are phenyl or 2-thienyl), we performed Suzuki-Miyuara cross-coupling reactions between 1 and phenylboronic acid or 2-thienylboronic acid. 3,4-Dinitro-substituted thiophenes (1-3) were reduced with a 30-fold excess of mossy tin and the 3,4-diamino-substituted thiophenes, as dihydrochloride salts, precipitated out in each case.<sup>11</sup> Tetradentate ligands were prepared in one pot by neutralization of the dihydrochloride salts with KOH, followed by condensation reactions in methanol with 2-pyridinecarboxaldehyde to generate the imine intermediates and subsequent imine reduction with NaBH<sub>4</sub>. Ligands 7-9 are very unstable oils (particularly ligand 8, which is so unstable we could not generate a quality <sup>13</sup>C NMR spectrum prior to decomposition) and had to be purified quickly and used directly in coordination reactions. To our knowledge, these instability

issues are not observed with similar reported tetradentate ligands that do not feature thiophene substitution, which could in all cases be purified by short-path vacuum distillation.<sup>6</sup> Our attempts to purify 7-9 in this manner in all cases resulted in decomposition. We speculate that the observed instability likely arises from oligomerization or polymerization of the thiophene heterocycle, and (or) from nucleophilic reaction of the amino N atoms at the 3,4 thiophene ring positions. Unfortunately, our spectral data does not allow us to unambiguously identify the products of the decomposition. We have some mass spectral evidence that would seem to suggest that ligands **8–9**, in solution and over time, undergo a similar rearrangement that is observed in complexes **11** and **12** (vida infra).

Iron(II) complexes were prepared by coordination of 7-9 with iron(II) tetrafluoroborate in deaerated methanol solution, followed by addition of excess aqueous KSCN to generate green precipitates of complexes 10 or 12 (Scheme 2). Complexes 10 and 12 are analytically pure powders, stable to air in the solid state, but very unstable in solution, including deaerated solutions. It is likely that oligomerization or polymerization of the thienyl substituents is at least one destabilizing factor in these materials, but we are not exactly sure what the pathway(s) for decomposition in these complexes is (are). Mass spectral data suggests that decomposition leads to a complex mixture of products. Although X-ray diffraction data could not be obtained from samples of 10 or 12 because of solution instability issues, we could use FTIR spectroscopy ( $v_{C=N}$ ) to identify the stereochemistry about the metal centre. Complexes 10 or 12 feature a strong "doublet" between 2060–2080 cm<sup>-1</sup>, indicating a cis stereochemistry, which has been observed in other similar reported complexes. In fact, the energy of this band has been previously correlated to the electronic ground state of the complex and the energies observed for complexes 10 or 12 suggest a significant population of the high spin (HS)  ${}^{5}T_{2}$ state at room temperature.



Complex 11, which was prepared under identical conditions to 10 or 12, is unstable in the solid state and solution, making characterization difficult; however, based on our spectroscopic data, we are confident in the purported structure. As opposed to 10 or 12, complex 11 features a single sharp strong band at 2070 cm<sup>-1</sup>, which strongly suggests an unusual trans disposition of the thiocyanate ligands (and a HS ground state).

Attempts to recrystallize deaerated solutions of 10-12 consistently resulted in solution color changes, from green to red over a period of days, which we anticipated was the result of iron(II) oxidation. Red solutions of 11 deposited

X-ray quality crystals and, to our surprise, a structurally rearranged material was indicated. Complex **13** contains two coordinated molecules of rearranged **8**. For clarity, the ligand rearrangement is indicated in Scheme 3.

An Oakridge thermal ellipsoid plot (ORTEP) of the molecular structure of 13 is shown in Figure 2. The metal center falls on a twofold axis, rendering each coordinated ligand equivalent. Coordinate bond lengths (Table 2) are consistent with an oxidation state assignment of +2 for the metal ion. Each molecule of rearranged 8 is coordinated through N1 and N2 of a bidentate pyridine–imidazole-type fragment of the molecule. The other imidazole-type ring atom N3 features a covalently bound and uncoordinated 2-pyridylmethylene substituent. Crystallographically equivalent thiocyanate ligands are coordinated cis to the iron center, and are disordered over two positions.

Along the *ac* diagonal, molecules of **13** pack in a one-dimensional chain structure, with intermolecular S···S contacts between coordinated and disordered thiocyanate ligands among adjacent molecules along the chain (Fig. 3). As noted in the Experimental section, the NCS ligand exhibits a 73:27 disorder over two positions. The S···S contacts vary from shorter [3.54(1) Å] than the sum of the van der Waals radii for the interaction between S2'–S2' to longer (3.85 and 4.40 Å) than the sum of the van der Waals radii for the interaction between S2–S2, respectively. This packing structure is possibly implicated in the unusual variable-temperature magnetic properties of **13** because no other close intermolecular contacts were found in the X-ray structure between sites carrying a significant amount of spin density (vida infra).

Red solutions of **12** deposit a dark red powder from which FTIR and mass spectrometric data indicate a similar structural rearrangement occurs. Unforunately, we could not obtain X-ray quality crystals from solutions containing **12**. Solutions of **10** decompose to a mixture of products over time. To our knowledge, similar structural rearrangements have not been reported for other iron(II) bis(thiocyanate) complexes containing tetradentate bis(2-pyridylmethyl)-type ligands, suggesting that the thienyl substituent or the electronic effect of this substituent is possibly involved in the mechanism for this rearrangement.

#### Electrochemistry

The electrochemical properties of complexes 10 and 12 were investigated with cyclic voltammetry, and as an example, the CV of **12** is presented in Fig. 4 (right). Each voltammogram features a number of broad and irreversible processes versus ferrocene. Cathodic scans are unremarkable and each complex exhibits irreversible waves at potentials greater than -1.5 V, which are attributed to pyridine ring reductions. Over anodic potentials, an irreversible oxidation process centered at +0.4 V is observed in the voltammograms of 10 and 12. A similar wave at approximately +0.4 V is observed in the voltammogram of uncoordinated 7 and is likely a ligand-centered oxidation (dehydrogenation of NH bond). Beyond +0.4 V, 10 exhibits a very broad irreversible oxidation at +1.3 V and 12 features irreversible processes at +0.8, +1.0, and +1.3 V, which we attribute to a combination of terthienyl and iron(II) oxidation processes. We attempted to electropolymerize complex 12 by repeated scans over the terthienyl oxidation potential; however, we observed no indication for any successful electropolymerization reactions.

#### Visible–NIR spectroscopy

Ethanol solutions of complexes 11 and 12 exhibit absorption maxima at 650 nm ( $\varepsilon = 400 \text{ mol/L}^{-1} \text{ cm}^{-1}$ ), with absorption intensities that are not temperature-dependent. To help provide the assignments of the absorption bands in 11 and 12, the absorption spectrum of 13 was calculated using TD-DFT at the B3LYP/DZVP level. The calculated spectrum of 13 in the visible region contains a main band at 638 nm with the oscillator strength ( $\phi$ ) of 0.0040 and a weaker band at 629 nm ( $\phi = 0.0011$ ). The 638 nm band originates from the  $\beta$ -spin HOMO  $\rightarrow$  LUMO excitation with the  $\beta$ -spin HOMO being the Fe  $d\pi$  – NCS  $\pi$  orbital (35% Fe and 65%) NCS contributions) and the  $\beta$ -spin LUMO being the Fe d $\sigma$  – pyridine–imidazole  $\pi^*$  orbital (12% Fe and 85% L). As a result, this absorption band has a mixed metal-to-ligand and ligand-to-ligand charge transfer (MLCT/LLCT) character. The 629 nm band originates from a mixture of several electron excitations (the two principal components are the  $\alpha$ -spin HOMO-4  $\rightarrow$  LUMO and  $\beta$ -spin HOMO-4  $\rightarrow$  LUMO excitations). The room-temperature spectrum of 10 in ethanol also features a weak absorption at 640 nm; however, upon cooling to 77 K, a large increase in absorption intensity is observed concomitant with the growth of a shoulder on the low-energy side of the 640 nm absorption. The color of the solution becomes intensely dark green from the pale green/ yellow color observed at room temperature (Fig. 4, left). These observations suggest an electronic change, likely spin-crossover is occurring in solutions containing 10. The new absorption feature centered at 700 nm is likely the band of the low-spin state of 10.

#### Variable-temperature magnetic properties

The variable-temperature magnetic properties of 10, 12, and 13 were probed via SQUID magnetometry and the data are presented as plots of the effective magnetic moment  $(\mu_{eff})$  versus temperature (Fig. 5). The magnetic properties of 12 feature very little temperature dependence and the observed magnetic moment values suggest a high-spin ground state for this complex. The magnetic moment of 12 decreases rapidly below 40 K, which likely results from a combination of zero-field splitting (ZFS) and intermolecular antiferromagnetic interactions.

Data from variable-temperature visible–NIR spectroscopy indicated spin-crossover was operative in solutions of **10**. In the solid state, variable-temperature magnetic susceptibility data indicates a gradual and incomplete spin-crossover without thermal hysteresis in powder samples of **10**. The magnetic moment of **10** at the highest measured temperature (350 K) is 4.95  $\mu$ B and a gradual decrease is observed with decreasing temperature to 2 K, where the observed magnetic moment is 2.4  $\mu$ B, which is higher than anticipated for a complete crossover to the low-spin (LS) state (theoretical value is 0 BM). However, the profile of the data, including the higher than expected moments at very low temperature, is very similar to that observed by Toftlund for structurally similar iron(II) complexes (without thienyl substituents) and points toward an incomplete spin-crossover in these materials.<sup>6</sup>

The variable-temperature magnetic properties of 13 are completely different. At room temperature, the magnetic moment is significantly higher than anticipated for a magnetically isolated mononuclear iron(II) complex (Fig. 5, right). With decreasing temperature, we see a gradual increase in magnetic moment, indicating intermolecular ferromagnetic interactions are operative. The magnetic moment reaches a plateau of 8.1 BM at approximately 8 K, and then slightly decreases. Low-temperature (5 K) magnetization versus field experiments provided no indication of ferromagnetic ordering, with a saturation magnetization of 4.6 NB at 3.5 T, which is a typical value for HS iron(II) (see Supplementary data). In the molecular packing of 13, close intermolecular S...S contacts were observed between coordinated thiocyanate ligands from adjacent molecules, suggesting a possible pathway for magnetic exchange coupling. We used DFT at the B3LYP/DZVP level to calculate the structure and spin density of complex 13, and found significant spin delocalization onto the coordinated thiocyanate ligands (0.16 on each NCS, Fig. 6), suggesting that the magnetic exchange pathway in 13 is possibly that of a 1-D S = 2 ferromagnetic chain. The fit to a Bonner-Fisher 1-D chain model<sup>12</sup> (eq. [1], g = 2.13 and J/k = +7.5 K) containing a correction for interchain magnetic interactions (eq. [2] zJ'/k= -2.2 K) is good between 320 and 30 K, and then deviates at low temperature.

[1] 
$$\chi_{\text{chain}}T = \frac{Ng^2\beta_e^2S(S+1)}{3kT}\left(\frac{1+u}{1-u}\right)$$

$$[2] \qquad \chi_m T = \left(\frac{1}{\chi_{\text{chain}}T} - \frac{zJ'}{kT}\right)$$

where

$$u = \coth \frac{2JS(S+1)}{kT} - \frac{kT}{2JS(S+1)}$$

Since there are no other significant intermolecular magnetic exchange pathways between atoms/fragments with high spin density in the molecular packing of 13, which would suggest that another competing antiferromagnetic interchain coupling is dominant at lower temperatures, it is also reasonable to assume that the deviation from 1-D chain behaviour at lower temperatures is a result of ZFS of the iron(II) S = 2 ground state. The relatively large value of J/kis suprising, especially considering that this exchange pathway is intermolecular. Typically, weak magnetic interactions are mediated in an intramolecular fashion through ambidentate N and S coordinated and bridging thiocyanate between metal ions within bimetallic complexes or coordination polymers.13 We could find no other reported examples of intermolecular ferromagnetic coupling mediated by coordinated thiocyanate ligands.

#### Conclusions

We have described the synthesis of three new thiophenecontaining "Toftlund-like" bispicen ligands (7-9). In apparent contrast to the bispicen family of ligands, 7-9 are unstable oils, which we could isolate and characterize, but must be coordinated quickly, or else suffer decomposition. Coordination of 7 and 9 with iron(II) bis(thiocyanate) resulted in the anticipated cis-pseudo-octahedral complexes (10 and 12), which were characterized and featured incomplete spincrossover (10), or HS iron(II) (12). Coordination of 8 with iron(II) bis(thiocyanate) produced a very unstable complex (11), which in solution undergoes a ligand-centered structural rearrangment to produce a stable complex 13, featuring intriguing variable-temperature magnetic properties. Our analysis indicates that the temperature-dependent magnetic behaviour of 13 is best-described as a one-dimensional ferromagnetic chain with interchain antiferromagnetic interactions and (or) ZFS at low temperatures, which reduces the magnetization. We are currently exploring the synthesis of derivatives of 13, including other iron(II) complexes with different ligand structures as precursors to novel iron(II) containing spin-crossover conductors.

# Supplementary data

Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca). CCDC 758104 contains the X-ray data in CIF format for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/ conts/retrieving.html (or from the Cambridge Crystallo-graphic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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