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# Fe<sup>II</sup> Spin crossover materials based on dissymmetrical N<sub>4</sub> Schiff bases including 2-pyridyl and 2R-imidazol-4-yl rings: Synthesis, crystal structure and magnetic and Mössbauer properties

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#### Abstract

The synthesis and characterization of new symmetrical  $Fe^{II}$  complexes,  $[FeL^A(NCS)_2](1)$ , and  $[FeL^{Bx}(NCS)_2](2-4)$ , are reported (L<sup>A</sup> is the tetradentate Schiff base N,N'-bis(1-pyridin-2-ylethylidene)-2,2-dimethylpropane-1,3-diamine, and L<sup>Bx</sup> stands for the family of tetradentate Schiff bases N,N'-bis[(2-R-1*H*-imidazol-4-yl)methylene]-2,2-dimethylpropane-1,3-diamine, with: R = H for L<sup>B1</sup> in **2**, R = Me for L<sup>B2</sup> in **3**, and R = Ph for L<sup>B3</sup> in **4**). Single-crystal X-ray structures have been determined for 1 (low-spin state at 293 K), **2** (high-spin (HS) state at 200 K), and **3** (HS state at 180 K). These complexes remain in the same spin-state over the whole temperature range [80–400 K]. The dissymmetrical tetradentate Schiff base ligands L<sup>Cx</sup>, N-[(2-R<sub>2</sub>-1*H*-imidazol-4-yl)methylene]-N'-(1-pyridin-2-ylethylidene)-2,2-R<sub>1</sub>-propane-1,3-diamine (R<sub>1</sub> = H, Me; R<sub>2</sub> = H, Me, Ph), containing both pyridine and imidazole rings were obtained as their [FeL<sup>Cx</sup>(NCS)<sub>2</sub>] complexes, **5**–10, through reaction of the isolated aminal type ligands 2-methyl-2-pyridin-2-ylhexahydropyrimidine (R<sub>1</sub> = H, **5**–7) or 2,5,5-trimethyl-2-pyridin-2-ylhexahydropyrimidine (R<sub>1</sub> = Me, **8**–10) with imidazole-4-carboxaldehyde (R<sub>2</sub> = H: **5**, **8**), 2-methylimidazole-4-carboxaldehyde (R<sub>2</sub> = Me: **6**, **9**), and 2-phenyl-imidazole-4-carboxaldehyde (R<sub>2</sub> = Ph: **7**, **10**) in the presence of iron(II) thiocyanate. Together with the single-crystal X-ray structures of **7** and **9**, variable-temperature magnetic susceptibility and Mössbauer studies of **5**–10 showed that it is possible to tune the spin crossover properties in the [FeL<sup>Cx</sup>(NCS)<sub>2</sub>] series by changing the 2-imidazole and/or C2-propylene substituent of L<sup>Cx</sup>.

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# 1. Introduction

Numerous  $3d^4-3d^7$  octahedral transition-metal complexes exhibit a thermally induced crossover between the low-spin (LS) and high-spin (HS) states [1]. Spin crossover (SC) materials are increasingly investigated due to their potential technological applications in molecular electronics [2], and memory devices [3]. Among them, most interest has been focused on Fe<sup>II</sup> complexes because their bi-stability

(LS, S = 0,  ${}^{1}A_{1} \leftrightarrow HS$ , S = 2,  ${}^{5}T_{2g}$ ) is easily triggered thermally, magnetically, by pressure or by light irradiation [4]. N<sub>6</sub> but also N<sub>4</sub>O<sub>2</sub> [5], N<sub>3</sub>O<sub>2</sub> [6], P<sub>2</sub>N<sub>2</sub>X [7], P<sub>4</sub>X [8] or P<sub>4</sub>X<sub>2</sub> [9] (X = Cl, Br) ligand environments around Fe<sup>II</sup> may yield SC behavior, but there are no defined conditions for designing SC materials. Slight modifications of the ligand(s) can provide conditions favoring SC, depending on the balance between the ligand field and the mean spin-pairing energy.

 $Fe^{II}$  SC complexes characterized by an  $[FeN_6]$  core may be classified into two main families. One family includes the cationic complexes  $[Fe(L)_x]^{2+}$  where x = 1, 2, 3 or 6 when

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L is hexadentate [10], tridentate [11], bidentate [12] or monodentate [13], respectively. These cationic species show a large variety of SC behaviors, depending on the noncoordinated counter anions and solvent of crystallization. The other family includes neutral compounds  $[Fe(L),(A)_2]$ where y = 1 or 2 when L is tetradentate [14] or bidentate [15], respectively. The monodentate ligands A are most often NCS<sup>-</sup> or NCSe<sup>-</sup> anions because halides or pseudohalides like  $N_3^{\,-}$  or  $NCO^-$  yield HS compounds (low ligand-field) while LS complexes can be obtained with CN<sup>-</sup> (strong ligand field). To our knowledge, very few SC complexes have been prepared with tetradentate ligands [14,16] and an unique example of dissymmetrical ligand is depicted for an Fe<sup>II</sup> complex [17]. The synthesis of new SC compounds is of utmost importance in this research area, particularly when the synthesis is performed in a controlled manner with the aim of obtaining compounds exhibiting a predictable SC behavior.

In the present contribution, we report an original synthetic route for the synthesis of new SC materials. We first synthesized new Fe<sup>II</sup> complexes from symmetrical tetradentate Schiff base ligands: [FeL<sup>A</sup>(NCS)<sub>2</sub>] (1) (L<sup>A</sup> stands for *N*,*N'*-bis(1-pyridin-2-ylethylidene)-2,2-dimethylpropane-1,3-diamine), and [FeL<sup>Bx</sup>(NCS)<sub>2</sub>] (2–4) (L<sup>Bx</sup> stands for *N*,*N'*-bis[(2-R-1*H*-imidazol-4-yl)methylene]-2,2-dimethylpropane-1,3-diamine, with: R = H for L<sup>B1</sup> in 2, R = Me for L<sup>B2</sup> in 3, and R = Ph for L<sup>B3</sup> in 4 (Fig. 1)). Complexes 1–4 remaining in the same spin-state over the 80–400 K range, dissymmetrical tetradentate Schiff bases L<sup>Cx</sup> containing both pyridine and imidazole rings (Fig. 1) were then prepared as their [FeL<sup>Cx</sup>(NCS)<sub>2</sub>] complexes, 5–10 (L<sup>Cx</sup> stands for *N*-[(2-R<sub>2</sub>-1*H*-imidazol-4-yl)methylene]-*N'*-(1-pyridin-2-ylethylidene)-2,2-R<sub>1</sub>-propane-1,3-diamine, with:

 $R_1 = H$  in 5–7, and Me in 8–10;  $R_2 = H$  for  $L^{C1}$  in 5 and 8,  $R_2 = Me$  for  $L^{C2}$  in 6 and 9, and  $R_2 = Ph$  for  $L^{C3}$  in 7 and 10). Together with the single-crystal X-ray structures of 7 and 9, variable-temperature magnetic susceptibility and Mössbauer studies of 5–10, showed that it is possible to tune the spin-crossover properties in the [FeL<sup>Cx</sup>(NCS)<sub>2</sub>] series by changing the 2-imidazole and/or C2-propylene substituent of  $L^{Cx}$ .

#### 2. Experimental

#### 2.1. Materials

All reagents and solvents were commercially available (Aldrich, Wako) and were used without further purification.

# 2.2. Syntheses

#### 2.2.1. Ligands

The ligands were characterized by <sup>1</sup>H and in some cases by <sup>13</sup>C NMR in CDCl<sub>3</sub> ( $\delta$ , ppm; s, singlet; d, doublet; t, triplet; dt = doublet of triplets; m, multiplet; b, broad).

2.2.1.1. Symmetrical ligands  $L^{A}$  and  $L^{Bx}$ . 2,2-Dimethyl-1,3diaminopropane (0.102 g,  $10^{-3}$  mol) and 2-acetyl-pyridine (0.242 g,  $2 \times 10^{-3}$  mol) for  $L^{A}$ , imidazole-4-carboxaldehyde (0.192 g,  $2 \times 10^{-3}$  mol) for  $L^{B1}$ , 2-methylimidazole-4carboxaldehyde (0.220 g,  $2 \times 10^{-3}$  mol) for  $L^{B2}$ , 2-phenylimidazole-4-carboxaldehyde (0.344 g,  $2 \times 10^{-3}$  mol) for  $L^{B3}$ , were stirred for 2 h in 20 mL of methanol at room temperature. Slow evaporation of the solvent yielded brown-yellow oils (yield: 0.280 g (90%); 0.210 g (80%); 0.243 g (85%); 0.330 (80%) for  $L^{A}$ ,  $L^{B1}$ ,  $L^{B2}$ , and  $L^{B3}$ ,



Fig. 1. Schematic representation of ligands  $L^A$ ,  $L^{Bx}$ ,  $L^{Cx}$  and of the half units L and L' ( $R_1 = H$ , Me;  $R_2 = H$ , Me, Ph).

respectively).<sup>1</sup>H (250 MHz): L<sup>B1</sup>,  $\delta$  7.91 (s, H5, 2H),  $\delta$  7.67– 7.65 (sb, H1 and H3, 4H),  $\delta$  3.59 (s, H6, 4H),  $\delta$  1.06 (s, H8, 6H); L<sup>B2</sup>,  $\delta$  7.98 (s, H5, 2H),  $\delta$  7.40 (s, H3, 2H),  $\delta$  3.37 (s, H6, 4H),  $\delta$  2.40 (s, H1, 6H),  $\delta$  0.93 (s, H8, 6H); L<sup>B3</sup>,  $\delta$ 7.97 (s, H5, 2H),  $\delta$  7.900–7.30 (m, H1, 10H),  $\delta$  7.69 (s, H3,2H), 3.42 (s, H6, 4H),  $\delta$  1.06 (s, H8, 6H). <sup>1</sup>H NMR spectra of L<sup>A</sup> could not be assigned due to the presence of a mixture including the aminal resulting from single condensation followed by cyclization, and the Schiff base resulting from the usual bis-condensation [18]. Nevertheless, complexation with Fe(NCS)<sub>2</sub> · xsolvent led to quantitative formation of the desired symmetrical complex.

2.2.1.2. Synthesis of the half-units L and L'. 2-Acetyl-pyridine (0.121 g,  $10^{-3}$  mol) was added to a solution of 1,3-diaminopropane (0.074 g,  $10^{-3}$  mol) for L or of 2,2dimethyl-1,3-diaminopropane (0.102 g,  $10^{-3}$  mol) for L' in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>. The resulting pale yellow solution was stirred for 30 min and kept undisturbed at room temperature until complete evaporation of the solvent (yield: 0.17 g, 85% for L; 0.15 g, 83% for L'). Colorless crystals and an oil were obtained for L and L', respectively. Both ligands were characterized by elemental analyses, IR (L), and 2D <sup>1</sup>H-<sup>13</sup>C NMR. Ligand L: Anal. Calc. for  $C_{10}H_{15}N_3$  (177 g mol<sup>-1</sup>): C, 67.76; H, 8.53; N, 23.71. Found: C, 66.63; H, 8.25; N, 23.90%. IR (cm<sup>-1</sup>): 1589, 1558, 1463, 1429, 786. <sup>1</sup>H NMR (400 MHz):  $\delta$  8.59 (d, H1, J = 5.5 Hz, 1H),  $\delta$  7.10 (t, H2, J = 5 Hz, 1H),  $\delta$ 7.73 (t, H3, J = 1.5 Hz, 1H),  $\delta$  7.76 (d, H4, J = 6 Hz, 1H),  $\delta$  1.35 (s, H7, 3H),  $\delta$  2.62 and 2.93 (s, H8, 2H + 2H),  $\delta$  1.63 (m, H9, 2H). <sup>13</sup>C {<sup>1</sup>H}NMR (100.6 MHz): δ 164.3 (C5), δ 158.2 (C1), δ 137.2 (C3), δ 121.3 (C2), *δ* 121.2 (C4), *δ* 71.7 (C6), *δ* 41.8 (C8), *δ* 27.0 (C9). Ligand L'. Anal. Calc. for  $C_{12}H_{19}N_3$  (205 g mol<sup>-1</sup>): C, 70.20; H, 9.33; N, 20.47. Found: C, 69.23; H, 9.26; N, 20.54%. <sup>1</sup>H (400 MHz):  $\delta$  8.61 (d, H1, J = 5.5 Hz, 1H),  $\delta$ 7.77 (d, H4, J = 7 Hz, 1H),  $\delta$  7.71 (td, H3, J = 2 Hz and J = 7 Hz, 1H),  $\delta$  7.19 (td, H2, J = 5.5 Hz and J = 2 Hz, 1H),  $\delta$  1.41 (s, H7, 3H),  $\delta$  2.38 and 2.99 (s, H8, 2H + 2H),  $\delta$  0.69 and 1.14 (s, H10, 6H). <sup>13</sup>C {<sup>1</sup>H} NMR (100.6 MHz):δ 164.1 (C5), δ 149.4 (C1), δ 137.1 (C3), δ 122.2 (C2), δ 122.0 (C4), δ 71.3 (C6), δ 53.7 (C8), δ 28.7 (C9), δ 23.3 and 23.88 (C10).

# 2.2.2. Complexes

All complexation reactions and sample preparations for physical measurements were carried out in a purified nitrogen atmosphere within a glovebox (Vacuum Atmospheres H.E.43.2) equipped with a dry train (Jahan EVAC 7).

2.2.2.1.  $Fe(NCS)_2 \cdot xMeOH$ .  $Fe(ClO_4)_2 \cdot xH_2O$  (10<sup>-3</sup> mol) was reacted with potassium thiocyanate (0.195 g,  $2 \times 10^{-3}$  mol) in 10 mL of MeOH following a procedure adapted from the preparation of  $Fe(py)_4(NCS)_2$  [19]. After removal of potassium perchlorate through filtration, the freshly prepared  $Fe(NCS)_2 \cdot xMeOH$  was used immediately for the preparation of complexes 1–10.

*Caution*: Although no such behavior was observed during the present work, perchlorate salts are potentially explosive and should be handled in small quantities and with much care.

2.2.2.2. General procedure (1-4). To a methanolic solution  $(10^{-3} \text{ mol in } 10 \text{ mL})$  of the ligand was added slowly a methanolic solution  $(10^{-3} \text{ mol in } 10 \text{ mL})$  of  $[\text{Fe}(\text{NCS})_2]$ · *x*MeOH. The solution immediately changed from pale yellow to dark blue (1) or orange-yellow (2-4) and was left under stirring for 30 min.

[FeL<sup>A</sup>(NCS)<sub>2</sub>] (1): Slow crystallization (over 1 month) yielded dark blue crystals suitable for X-ray analysis. Yield: 0.34 g, 68%. *Anal.* Calc. for  $FeC_{21}H_{24}N_6S_2$  (480.4 g mol<sup>-1</sup>): C, 52.50; H, 5.04; N, 17.49; S, 13.35; Fe, 11.62. Found: C, 52.25; H, 5.05; N, 17.27; S, 13.29; Fe, 11.57%. IR (cm<sup>-1</sup>): 2110–2090 (NCS); 1600 (imine).

 $[FeL^{B1}(NCS)_2]$  (2): Orange crystals suitable for X-ray analysis were obtained after addition of Et<sub>2</sub>O to the methanolic solution of **2**. Yield: 0.32 g, 75%. *Anal.* Calc. for  $FeC_{15}H_{18}N_8S_2$  (430.3 g mol<sup>-1</sup>): C, 41.87; H, 4.22; N, 26.04; S, 14.90; Fe, 12.98. Found: C, 41.78; H, 3.91; N, 25.88; S, 14.65; Fe, 12.89%. IR (cm<sup>-1</sup>): 2110–2090 (NCS); 1603 (imine).

 $[FeL^{B2}(NCS)_2]$  (3): Slow crystallization (over one week) yielded orange crystals suitable for X-ray analysis. Yield: 0.32 g, 70%. *Anal.* Calc. for  $FeC_{17}H_{22}N_8S_2$  (458.4 g mol<sup>-1</sup>): C, 44.55; H, 4.84; N, 24.45; S, 14.00; Fe, 12.20. Found: C, 44.47; H, 4.55; N, 24.44; S, 13.93; Fe, 11.61. IR (cm<sup>-1</sup>): 2110–2090 (NCS); 1611 (imine).

 $[FeL^{B3}(NCS)_2]$ (4): Yellow microcrystalline powder. Yield: 0.38 g, 65%. *Anal.* Calc./found for  $FeC_{27}H_{27}N_8S_2$  (583.5 g mol<sup>-1</sup>): C, 55.67; H, 4.50; N, 19.24; S, 11.00; Fe, 9.58. Found: C, 55.60; H, 4.27; N, 19.05; S, 10.29; Fe, 9.20%. IR (cm<sup>-1</sup>): 2110–2090 (NCS); 1603 (imine).

2.2.2.3. General procedure (5-10). To a pale yellow solution  $(10^{-3} \text{ mol}, 10 \text{ mL} \text{ methanol})$  of the aminal L (5-7) or L' (8-10) the freshly prepared Fe(NCS)<sub>2</sub> solution  $(10^{-3} \text{ mol}, 10 \text{ mL} \text{ methanol})$  was slowly added. The color of the reaction mixture immediately turned to dark blue and was stirred for 5 min. The appropriate 2R-imidazole-4-carboxaldehyde  $(10^{-3} \text{ mol}, 10 \text{ mL} \text{ methanol})$  was then added (imidazole-4-carboxaldehyde for 5 and 8, 2-methy-limidazole-4-carboxaldehyde for 7 and 10). No further color change was observed; the solution was stirred for 30 more minutes and then left undisturbed until a microcrystalline powder or crystals quantitatively formed.

[FeL<sup>C1</sup>(NCS)<sub>2</sub>] (**5**): Dark blue powder. Yield: 0.32 g, 75%. *Anal.* Calc. for FeC<sub>16</sub>H<sub>17</sub>N<sub>7</sub>S<sub>2</sub> (427.3 g mol<sup>-1</sup>): C, 44.97; H, 4.01; N, 22.94; S, 15.01; Fe, 13.07. Found: C, 45.15; H, 4.00; N, 22.85; S, 14.67; Fe, 12.72%. IR (cm<sup>-1</sup>): 2112–2060 (NCS); 1620 (imine).

[FeL<sup>C2</sup>(NCS)<sub>2</sub>] (6): Dark blue powder. Yield: 0.32 g, 73%. *Anal.* Calc. for FeC<sub>17</sub>H<sub>19</sub>N<sub>7</sub>S<sub>2</sub> (441.4 g mol<sup>-1</sup>): C, 46.26; H, 4.34; N, 22.22; S, 14.53; Fe, 12.65. Found: C,

46.33; H, 4.49; N, 20.32; S, 14.39; Fe, 12.50%. IR (cm<sup>-1</sup>): 2060 (NCS); 1638 (imine).

[FeL<sup>C3</sup>(NCS)<sub>2</sub>] (7): Dark blue single crystals. Yield: 0.30 g, 60%. *Anal.* Calc. for FeC<sub>22</sub>H<sub>21</sub>N<sub>7</sub>S<sub>2</sub> (503.4 g mol<sup>-1</sup>): C, 52.49; H, 4.21; N, 19.48; S, 12.74; Fe, 11.09. Found: C, 52.19; H, 3.84; N, 19.09; S, 12.70; Fe, 10.90%. IR (cm<sup>-1</sup>): 2068 (NCS); 1641 (imine).

 $[FeL^{C4}(NCS)_2]$  (8): Dark blue powder. Yield: m = 0.32 g, 72%. *Anal.* Calc. for  $FeC_{18}H_{21}N_7S_2$  (455.4 g mol<sup>-1</sup>): C, 47.48; H, 4.65; N, 21.53; S, 14.08; Fe, 12.26. Found: C, 47.82; H, 4.47; N, 20.74; S, 13.81; Fe, 11.80%. IR (cm<sup>-1</sup>): 2108–2058 (NCS); 1618 (imine).

 $[FeL^{C5}(NCS)_2] \cdot H_2O$  (9): Dark blue single crystals. Yield: 0.35 g, 72%. *Anal.* Calc. for  $FeC_{19}H_{23}N_7S_2 \cdot H_2O$  (487.4 g mol<sup>-1</sup>): C, 46.82; H, 5.17; N, 20.12; S, 13.16; Fe, 11.46. Found: C, 47.10; H, 4.52; N, 20.29; S, 12.73; Fe, 11.30%. IR (cm<sup>-1</sup>): 2058 (NCS); 1634 (imine).

[FeL<sup>C6</sup>(NCS)<sub>2</sub>] (**10**): Dark blue microcrystals. Yield: 0.35 g, 66%. *Anal.* Calc. for FeC<sub>24</sub>H<sub>25</sub>N<sub>7</sub>S<sub>2</sub> (531.5 g mol<sup>-1</sup>): C, 54.24; H, 4.74; N, 18.45; S, 12.06; Fe, 10.51. Found: C, 54.04; H, 4.31; N, 18.16; S, 11.64; Fe, 10.51, 10.37%. IR (cm<sup>-1</sup>): 2072 (NCS); 1643 (imine).

#### 2.3. Physical measurements

Elemental analyses were carried out on a Perkin-Elmer 2400 series II device (C, H, N) at the Microanalytical Laboratory of the Laboratoire de Chimie de Coordination in Toulouse, and on a Maxim Thermoelectron device (S, Fe) at the Service Central de Microanalyses du CNRS in Vernaison, France. 1D <sup>1</sup>H and 1D <sup>13</sup>C NMR spectra were performed on an AC 250 FT spectrometer (Bruker) and 2D <sup>1</sup>H<sup>13</sup>C spectra on an AMX 400 spectrometer (Bruker). Chemical shifts are given in ppm versus TMS (<sup>1</sup>H and <sup>13</sup>C) using CDCl<sub>3</sub> as solvent. IR spectra were measured in the  $400-4000 \text{ cm}^{-1}$  range on a 9800 FTIR spectrometer (Perkin-Elmer). Samples were run as KBr pellets. Mössbauer spectra were recorded on a constant-acceleration conventional spectrometer with a 50 mCi source of <sup>57</sup>Co (Rh matrix). The absorber was a powdered sample enclosed in a 20 mm diameter cylindrical plastic sample holder, the size of which has been determined to optimize the absorption. Spectra were obtained in the 80-400 K range using a MD306 Oxford cryostat (4–293 K) or an home-made vacuum oven (300-500 K), the thermal scanning being monitored by an Oxford ITC4 servo control device (±0.1 K accuracy). A least square computer program [20] was used to fit the Mössbauer parameters and to determine their standard deviations of statistical origin (given in parentheses). Isomer shift values ( $\delta$ ) are relative to iron foil at 293 K. Variable temperature magnetic susceptibility data were collected on powdered samples on a MPMS-55 Quantum Design SQUID magnetometer or a Faraday type susceptometer under applied magnetic fields lower than 0.1 T. Diamagnetic corrections were applied by using Pascal's constants.

# 2.4. Crystallographic data collection and structure determination for 1, 2, 3, 7 and 9

The X-ray data for compounds 1, 2, 7 and 9 were collected on a Stoe Imaging Plate Diffractometer System (IPDS) equipped with an Oxford Cryosystems cooler device using a graphite monochromator ( $\lambda = 0.71073$  Å). Data were collected [21] using  $\varphi$  rotation movement with the crystal-to-detector distance equal to 70 mm ( $\phi = 0.0$ -270°,  $\Delta \phi = 1.5^{\circ}$  for **1**,  $\phi = 0.0-200^{\circ}$ ,  $\Delta \phi = 1.5^{\circ}$  for **2** and **9** and  $\varphi = 0.0-250^\circ$ ,  $\Delta \varphi = 1.4^\circ$  for **7**). Diffraction data for 3 were collected using an Oxford-Diffraction XCALIBUR CCD diffractometer equipped with a graphite-monochromated Mo Ka radiation source. The crystal was placed 50 mm from the CCD detector. More than the hemisphere of reciprocal space was covered by combination of four sets of exposures; each set had a different  $\varphi$ -angle (0°, 90°, 180°, 270°) and each exposure of 20 s covered 0.75° in  $\omega$ . Coverage of the unique set is 99.5% complete up to  $2\theta = 63.22^{\circ}$ . The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction [22]. All structures were solved by direct methods using SHELXS-97 [23] and refined by full-matrix least-squares on  $F_{0}^{2}$  with shelxl-97 [24] with anisotropic displacement parameters for non-hydrogen atoms. The hydrogen atoms were placed in calculated positions (C–H 0.96 Å) and they were included in the refinement in the riding-model approximation with  $U_{iso} = 1.1$  U (atom of attachment). Positional parameters of the H(water) atoms in compound 9 were obtained from difference Fourier syntheses and verified by the geometric parameters of the corresponding hydrogen bonds. Scattering factors were taken from the standard compilation [25]. The molecular plots were obtained by using the ZORTEP program [26]. Numerical absorption corrections [27] were applied for 3, while for compounds 1, 2, 7 and 9 the absorption corrections were introduced by semiempirical methods based on equivalent reflections, using the program MULTISCAN [28]. The final full-matrix least-squares refinement, minimizing  $\left[\sum w(|F_o^2| - |F_c^2|)^2\right]^2$ , converged at the values of *R* and *wR* listed in Table 1, together with the main crystallographic parameters. The relatively high *R*-factors for complex 7 are due to the low quality of the crystals: among several sets of diffraction data obtained from different crystals which all diffracted poorly, the best one was used to solve this structure.

### 3. Results

#### 3.1. Syntheses

While the reaction of 2 equiv of 2R-imidazole-4-carboxaldehyde with 1 equiv of 2,2-dimethyl-1,3-diaminopropane yielded pure samples of the corresponding acyclic tetradentate bis-Schiff bases  $L^{Bx}$ , the corresponding condensation reaction carried out with 2-acetyl-pyridine yielded a mixture including the cyclic aminal L' resulting from single

Table 1					
Crystallographic data collectio	n and structure determination	for complexes $1, 2, 3, 7$ and $9$			
Compound	$[FeL^A(NCS)_2]$ (1)	[FeL <sup>B1</sup> (NCS) <sub>2</sub> ] (2)	$[FeL^{B2}(NCS)_2]$ (3)	$[FeL^{C3}(NCS)_2]$ (7)	$[FeL^{C5}(NCS)_2] \cdot H_2O$ (9)
Formula	$\mathrm{C_{21}H_{24}FeN_6S_2}$	$C_{30}H_{36}Fe_2N_{16}S_4$	$\mathrm{C_{17}H_{22}FeN_8S_2}$	$C_{22}H_{21}FeN_7S_2$	$C_{19}H_{25}FeN_7OS_2$
Formula weight	480.43	860.69	458.40	503.43	487.43
Crystal system space group	triclinic $P\overline{l}$ (no. 2)	triclinic $P\overline{l}$ (no. 2)	monoclinic $P2_1/n$ (no. 14)	monoclinic $P2_1/c$ (no. 14)	orthorhombic $Pna2_1$ (no. 33)
a (Å)	8.4584(17)	12.4503(12)	9.3308(5)	12.561(2)	25.719(5)
$b(\mathbf{\hat{A}})$	8.7682(18)	12.7279(13)	13.6987(6)	12.4395(14)	8.0906(16)
$c(\mathbf{A})$	16.110(3)	13.5717(13)	16.7115(7)	15.649(3)	11.638(2)
α (°)	98.33(3)	98.289(12)	06	06	90
β ( <sub>0</sub> )	104.53(3)	95.886(12)	90.755(4)	100.047(19)	90
γ (°) γ	94.39(3)	110.475(11)	90	90	90
$V(\mathbf{\mathring{A}}^3)$	1136.3(4)	1966.4(3)	2135.89(17)	2407.7(6)	2421.7(8)
Z	2	7	4	4	4
$ ho_{ m calcd}~({ m gcm^{-3}})$	1.404	1.454	1.426	1.389	1.337
$\lambda$ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Absolute structure parameter					0.30(6)
$T(\mathbf{K})$	293	200	180	180	293
$\mu(Mo K\alpha) (cm^{-1})$	0.867	0.996	0.921	0.824	0.819
$R[I>2\sigma(I)]^{ m a}$	0.0525	0.0375	0.0265	0.1155	0.0446
$w R^{\mathrm{b}}$	0.0675	0.0741	0.0710	0.2915	0.0780
<sup>a</sup> $R = \sum   F_o  -  F_c   / \sum  F_o $ <sup>b</sup> $wR = \left[ \sum w( F_o^2  -  F_c^2 )^2 / \right]$	$\int w  F_{\alpha}^2 ^2  ^{1/2}$				
1	5				

condensation, and the Schiff base resulting from the usual bis-condensation. This lower reactivity of ketone compared to aldehvde carbonyl function is well documented [29] but has been scarcely exploited to prepare so-called 'half-unit' synthons through 1:1 condensation with the aim to generate dissymmetrical ligands through opening of the aminal ring and condensation of the amine function with a different carbonyl [30]. One of the reasons is the occurrence of redistribution reactions that yield mixtures of the respective symmetrical bis-Schiff bases corresponding to each carbonyl synthon, including or not a small percentage of the targeted dissymmetrical bis-Schiff base. Using a metal ion in order to favor the acyclic Schiff base versus the cyclic aminal intermediate through complexation, and to subsequently favor formation of the tetracoordinated dissymmetric bis-Schiff base has occasionally allowed avoiding redistribution reactions, and has thus allowed preparing dissymmetric bis-Schiff base cleanly and quantitatively in a very few cases [31].

Based on these results, we explored the 1:1 condensation reactions between 2-acetyl-pyridine and 1,3-diaminopropane or 2,2-dimethyl-1,3-diaminopropane. These reactions yielded the isolated aminal type ligands L: 2-(2-methyl-hexahydro-2-pyrimidinyl)pyridine and L': 2-(2-methyl-5-dimethylhexahydro-2-pyrimidinyl)pyridine, respectively (first reaction sketched in Fig. 2).

The NMR spectra clearly showed that, in the case of L and L', in the absence of metal ion the acyclic single condensation intermediate is not stable and the equilibrium is totally shifted toward the cyclic aminal form. Addition of 2R-imidazole-4-carboxaldehyde to L (L') yielded mixtures of the respective symmetrical bis-Schiff bases and possibly a small amount of the targeted dissymmetrical bis-Schiff base, as suggested by the NMR spectra that showed a large number of intricated absorption resonances.

Clean and quantitative syntheses of the dissymmetrical ligands L<sup>Cx</sup> could only be performed in the presence of  $Fe(NCS)_2 \cdot xMeOH$  yielding their  $[FeL^{Cx}(NCS)_2]$  (x = 1-6) complexes (Fig. 2). These results suggest that the metal ion displaces totally the equilibrium from the cyclic aminal toward the acyclic Schiff base intermediate through complexation as sketched in the second reaction of Fig. 2. The presence of the pyridine aromatic ring conjugated with Fe<sup>II</sup> results in a strong MLCT band [32] responsible for the intense blue color of compounds 5–10 which are crystals (7, 9), microcrystals (10), or more or less microcrystalline powders (5, 6, 8). The homogeneity (in color and texture) of all samples has been checked by microscopy. Moreover, Mössbauer spectroscopy has confirmed the presence of both HS and LS spin isomers in temperature dependent ratios for all compounds in this series, except for 6 which is 100% HS (see Mössbauer section and Table SM.2). Compounds 5-10 are oxidized in aerobic solutions. However, in the solid state, they are reasonably stable in aerobic conditions provided the samples are not exposed to moisture and/or heat. The absence of oxidation for all samples of compounds 1-10 in the solid state has been checked by



Fig. 2. Synthetic pathway for the family of complexes  $[FeL^{Cx}(NCS)_2]$  based on the dissymmetrical tetradentate Schiff base ligands  $L^{Cx}$  ( $R_1 = H$ , Me;  $R_2 = H$ , Me, Ph).

EPR spectroscopy. Formation of the intermediate complexes FeL(NCS)<sub>2</sub>(MeOH) and FeL'(NCS)<sub>2</sub>(MeOH) sketched in Fig. 2 as resulting from addition of the ferrous salt to L (L') is assessed on the basis of the color change observed upon addition of Fe(NCS)<sub>2</sub> · *x*MeOH and on the rationale that complexation with the acyclic Schiff base intermediate is more likely due to the entropy gain upon conversion of the bidentate cyclic aminal into the tridentate Schiff base. However, these dark blue intermediate complexes are very soluble and we have not attempted to isolate them.

#### 3.2. Description of the structures

ORTEP plots of complexes 1, 3, and 9 are shown in Figs. 3–5, respectively. Selected inter-atomic distances and angles for complexes 1, 2, 3, 7 and 9 are collated in Table 2.

The overall molecular structure of the five complexes is similar: the distorted octahedral  $[FeN_6]$  coordination environment includes four nitrogen atoms belonging to the tet-



Fig. 3. ORTEP plot of complex 1 at the 40% probability level. H-atoms have been omitted for clarity.

radentate Schiff base ligand (L<sup>A</sup> (1), L<sup>Bx</sup> (2 and 3), and L<sup>Cx</sup> (7 and 9)) in the equatorial positions, while the apical positions are occupied by nitrogen atoms from two NCS<sup>-</sup> ligands. Within the estimated standard deviations, the iron atom is in the mean plane of the four equatorial nitrogen donors. However, the tetradentate Schiff base ligands, as a whole, exhibit more or less significant deviations from planarity. This can be due to the steric constraints imposed by the pyridine and/or imidazole moieties upon coordination to the metal center, and results in tilts of the aromatic rings from the mean plane of the tetradentate ligand. The larger tilt is observed for the py-py dihedral angle of 1 (32.6°), and the smaller one for the py-imidazole dihedral angle of 9 (4.8°). The Fe-N bond distances are characteristic of the spin-state of Fe<sup>II</sup>: the average 1.949 Å value for 1 (293 K) is in good agreement with those observed for similar LS iron(II) complexes, while the average Fe-N bond distances of 2.185 Å (2, 200 K), 2.189 Å (3, 180 K), 2.196 Å (7, 180 K) and 2.150 Å (9, 293 K) indicate that the Fe<sup>II</sup> center is in the HS state at the temperatures of the X-ray data collections for the four remaining compounds that have been structurally characterized [4,18]. In average, in the HS structures the N-Fe-N angles depart more from those expected for a regular octahedron (Table 2). It may thus be concluded that, except for the metric differences resulting from the difference in Fe<sup>II</sup> spin-state, the complexes based on the  $L^A$ ,  $L^{Bx}$  and  $L^{Cx}$ ligands have similar molecular structures.

On the other hand, these compounds provide a diversity of crystal packing modes, with a large variety of network topologies and these peculiarities deserve detailed consideration.

The crystal packing of **1** results from an extended 3D network of C–H···S contacts. A fragment of the crystal structure showing five H-bonded molecules is displayed in Fig. 6. The C···S distances between C–H···S bonded molecules are in the 3.59–3.69 Å range, in keeping with previous reports [18,33]. In addition,  $\pi$ – $\pi$  stacking interactions involving the pyridine rings of molecules related by a crystallographic inversion center participate in the crystal



Fig. 4. ORTEP plot of complex 2 at the 50% probability level. H-atoms have been omitted for clarity.



Fig. 5. ORTEP plot of complex 9 at the 30% probability level. H-atoms have been omitted for clarity.

packing, as evidenced by the short interplanar (3.64 and 3.93 Å) and centroid to centroid (3.88 and 4.47 Å) distances between interacting pyridine rings.

C18D S2 C18D S2 C16C S1E Fe FeB S1E Fe C16C S2F FeC S2F S1 FeB S1E FeA S2F S1 C2A

Fig. 6. Intermolecular interactions responsible for the supramolecular structure of  $[FeL^A(NCS)_2]$  (1).  $\pi$ - $\pi$  stacked pairs of pyridine rings are linked by broken double lines.

The asymmetrical unit of **2** contains two crystallographically independent  $[FeL^{B1}(NCS)_2]$  complex molecules denoted A and B (Fig. 7). Molecules A and B are linked

Table 2 Selected bond lengths  $({\rm \AA})$  and angles (°) for complexes 1, 2, 3, 7 and 9

Selected bold lengths (1) and angles (1) for complexes 1, 2, 3, 7 and 9								
Compound $[FeL^A(NCS)_2](1)$	$[FeL^{B1}(NCS)_2](2)$		$[FeL^{B2}(NCS)_2](3)$	$[FeL^{C3}(NCS)_2]$ (7)	$[FeL^{C5}(NCS)_2] \cdot H_2O$ (9)			
	Molecule A	Molecule B						
1.964(5)	2.216(2)	2.241(2)	2.2838(11)	2.28(2)	2.188(17)			
1.953(6)	2.188(2)	2.191(2)	2.1603(11)	2.11(2)	2.158(15)			
1.939(5)	2.180(2)	2.194(2)	2.2170(10)	2.284(15)	2.184(13)			
1.961(6)	2.216(2)	2.245(2)	2.2178(10)	2.31(2)	2.125(15)			
1.938(6)	2.189(3)	2.115(3)	2.1124(12)	2.109(15)	2.135(10)			
1.939(6)	2.121(3)	2.132(3)	2.1409(12)	2.082(16)	2.112(12)			
81.3(3)	77.35(9)	77.03(9)	76.09(4)	79.2(9)	76.3(8)			
102.1(2)	118.05(9)	120.42(9)	120.10(4)	117.3(8)	119.5(8)			
96.8(2)	87.10(8)	86.05(9)	86.58(4)	90.4(9)	88.5(7)			
80.6(2)	77.46(8)	76.43(8)	77.13(4)	73.2(8)	75.6(6)			
173.3(2)	172.36(10)	168.90(11)	166.04(5)	168.8(6)	164.2(5)			
	[FeL <sup>A</sup> (NCS) <sub>2</sub> ] (1) 1.964(5) 1.953(6) 1.939(5) 1.961(6) 1.938(6) 1.939(6) 81.3(3) 102.1(2) 96.8(2) 80.6(2) 173.3(2)	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $			



Fig. 7. Intermolecular interactions responsible for the supramolecular structure of  $[FeL^{B1}(NCS)_2]$  (2). Metric parameters  $(d, A; \angle, \circ)$ : N7A···S1B', 3.296(3); H···S1B', 2.48;  $\angle$ N7A-H···S1B', 160.1; N8A···S2B, 3.353(3); H···S2B, 2.62;  $\angle$ N8A-H···S2B, 144.4; N8B··· N5A, 2.887(4); H···N5A, 2.03;  $\angle$ N8B-H···N5A, 172.0; N7B···S2A", 3.339(2); H···S2A", 2.70;  $\angle$ N7B-H···S2A", 132.4; symmetry codes: (') x, y - 1, z; (") -x + 1, -y + 1, -z.

into a 3D supramolecular network via NH···S and NH···N hydrogen bonds, responsible for the crystal packing. A view of this supramolecular network showing four H-bonded molecules is displayed in Fig. 7, along with the hydrogen-bonding parameters. The four non-coordinated nitrogen atoms of molecules A and B act as proton donors, thus fulfilling all H-bonds opportunities in the crystal. The complex molecules inside each [A, B] pair are linked through N8B-H···N5A and N8A-H···S2B hydrogen bonds. It is noteworthy, that one of these hydrogen bonds involves as acceptor the nitrogen atom N7A coordinated to FeA, while the other one involves as acceptor the noncoordinated atom S2B. Further association of the complex molecules results from the N7B-H···S2A short contact which leads to the formation of tetra-molecular centrosymmetrical aggregates and finally to a 3D network through the N7A–H···S1B' hydrogen bond (Fig. 7).

The crystal packing of **3** results from an extended 3D network of intermolecular interactions. Each  $[FeL^{B2}-(NCS)_2]$  complex molecule is involved in NH····S hydrogen bonds with its three nearest neighbors. A view of the supramolecular network showing four H-bonded molecules is displayed in Fig. 8, along with the hydrogen-bonding parameters, illustrating how this 3D supramolecular network is generated by two short intermolecular contacts involving the two non-coordinated imidazole nitrogen atoms and both sulfur atoms of the coordinated NCS<sup>-</sup> anions. As for compound **2**, all H-bond opportunities are realized.

The molecular structure and crystal packing of 7 are shown in Fig. 9. The latter consists of alternate two-dimensional layers oriented along an *ac* crystallographic plane. Each layer is built from infinite chains connected through short intermolecular contacts (3.797(6) Å) between the S1 and S2 atoms related by translation along *a*. Two types of interactions are responsible for the association of the neutral [FeL<sup>C3</sup>(NCS)<sub>2</sub>] molecules into a chainlike structure:



Fig. 8. Intermolecular interactions responsible for the supramolecular structure of [FeL<sup>B2</sup>(NCS)<sub>2</sub>] (**3**). Metric parameters (d, Å;  $\angle$ , °): N7···S2', 3.320(1); H···S2', 2.457;  $\angle$ N7–H···S2', 146.7°; N8···S1", 3.340(1); H···S1", 2.569;  $\angle$ N8–H···S1", 166.7°; symmetry codes: (') 1 – x, 1 – y, 2 – z; (") 1.5 – x, 0.5 + y, 1.5 – z.



Fig. 9. Projection of the crystal structure of  $[FeL^{C3}(NCS)_2]$  (7) perpendicularly to an *ac* plane. Centroid to centroid distances between overlapping rings are materialized by broken double lines.

(i) the N7–H···S2' (x, 0.5 – y, -0.5 + z) hydrogen bond (N7···S2', 3.37(2) Å; H···S2', 2.52 Å;  $\angle$ N7–H···S2', 170.3°); (ii) the  $\pi$ -stacking interaction between the pyridine and imidazole rings of adjacent molecules (centroid to centroid distances of 3.87 Å).

A view of the crystal packing of complex **9** is shown in Fig. 10. The supramolecular network is built from aggregates of complex molecules connected via two intermolecular H-bonds through the solvated water molecules. The water molecule acts as proton acceptor towards the non-coordinated imidazole nitrogen atom (N7···O1w, 2.83(2) Å; H···O1w, 1.97 Å;  $\angle$ N7–H···O1w, 173.8°). The water molecule also acts as proton donor towards the sulfur atom S2 of the symmetry related (0.5 – x, y – 0.5, z – 0.5) complex molecule (O1w···S2', 3.59(2) Å; H···S2',



Fig. 10. View of the crystal packing of  $FeL^{CS}(NCS)2] \cdot H_2O(9)$ . Centroid to centroid distances between overlapping rings are materialized by broken double lines.

2.74 Å;  $\angle O1w-H\cdots S2'$ , 152.8°). The chains of H-bonded molecules extend into a 3D network through  $\pi$ -stacking interactions between pyridine and imidazole rings belonging to adjacent chains, as evidenced by their centroid to centroid distances of 3.77 Å (Fig. 10). The dihedral angles between  $\pi$ -stacked rings equals 5.3°.

# 3.3. Magnetic studies

The thermal variation of the magnetic susceptibility  $\chi_{\rm M}$  has been explored for complexes 1–10 and the  $\chi_{\rm M}T$  data for selected temperatures (*T*) are collated in Table SM.1. The complete sets of  $\chi_{\rm M}T$  versus *T* data are shown in Figs. 11 and 12 (1–4) (5–10). The  $\chi_{\rm M}T$  product for 1 remains lower than 0.12 cm<sup>3</sup> mol<sup>-1</sup> K between 110 and 400 K, indicating that the iron(II) center in this material is LS over the whole temperature range. The  $\chi_{\rm M}T$  product for the [FeL<sup>Bx</sup>-(NCS)<sub>2</sub>] complexes 2–4 is comprised between 4.12 and 3.70 cm<sup>3</sup> mol<sup>-1</sup> K in the 80–300 K temperature range, indicating that the iron(II) center in this series of materials is HS over the whole temperature range. These data agree with the structural studies of complexes 1–3 that indicate Fe–N bond lengths characteristic of the LS (1, 293 K)



Fig. 11. Thermal variation of the  $\chi_M T$  product for  $[FeL^A(NCS)_2]$  (1), and the  $[FeL^{Bx}(NCS)_2]$  complexes **2–4**.



Fig. 12. Thermal variation of the  $\chi_M T$  product for the [FeL<sup>Cx</sup>(NCS)<sub>2</sub>] complexes **5–10**.

and HS (2, 200 K; 3, 180 K) states, respectively. However, the  $\chi_M T$  product at room temperature for 2–4, as well as that for 7 and 10 that will be discussed next, is higher than the spin-only value of ~3 cm<sup>3</sup> mol<sup>-1</sup> K expected for S = 2(g = 2), as often observed for HS Fe<sup>II</sup> compounds. The presence of small amounts of HS Fe<sup>III</sup> (possibly resulting from oxidation of the prepared Fe<sup>II</sup> materials) being discarded by their Mössbauer spectra (see following subsection), these high  $\chi_M T$  values are attributed to operation of spin-orbit coupling (SOC). The <sup>5</sup>T<sub>2</sub> ground state is split by SOC yielding levels separated by energies on the order of kT (thermally populated in the high temperature range) which results in slightly temperature dependent  $\chi_M T$  values above ca. 60 K [34].

With the exception of compound 6, and at variance with the two previous series, the  $\chi_M T$  product for the  $[FeL^{Cx}(NCS)_2]$  complexes 5–10 is not constant over the explored temperature range (Fig. 12). The  $\chi_M T$  product for complexes 7 and 10 ( $R_2(imidazole) = Ph$ ) is practically constant from 300 to 160 K and characteristic of a large predominance of HS Fe<sup>II</sup>. Then it decreases between 150 and 50 K: for 7,  $\chi_{\rm M}T$  decreases from 3.03 to 2.25 cm<sup>3</sup>  $mol^{-1}$  K, indicating a partial HS  $\rightarrow$  LS transition centered around 100 K of ca. 20% Fe<sup>II</sup> centers. The transition is much more gradual for 10 (Table SM.1). The thermal variation of the  $\chi_M T$  product for complex 9 (R<sub>1</sub> = Me,  $R_2(\text{imidazole}) = \text{Me}$ ) showing a very gradual and partial SC between 250 and 50 K (ca. 25%) is similar to that described above for 7 and 10 ( $R_2(imidazole) = Ph$ ). All three compounds exhibit a sharp  $\chi_M T$  decrease below 30 K resulting from zero field splitting (ZFS) of HS  $Fe^{II}$ . The  $\chi_M T$  product for complex 6 (R<sub>1</sub> = H, R<sub>2</sub>(imidazole) = Me) is practically constant over the 80–300 K temperature range indicating the absence of SC for Fe<sup>II</sup> in this material above 80 K.

On the other hand, the magnetic behavior of complexes **5** and **8** (R<sub>2</sub>(imidazole) = H) is strikingly different: their  $\chi_M T$  product, practically constant and lower than 0.10 (**5**) and 0.13 (**8**) cm<sup>3</sup> mol<sup>-1</sup> K from 80 to 300 K, is characteristic of LS Fe<sup>II</sup>. Then, above 330 K,  $\chi_M T$  increases up to 1.29 and 1.37 cm<sup>3</sup> mol<sup>-1</sup> K at 400 K for **5** and **8**, respectively, indicating a LS  $\rightarrow$  HS transition centered above

400 K (ca. 30%  $Fe^{II}$  centers are involved between 330 and 400 K).

#### 3.4. Mössbauer spectroscopy

Mössbauer spectra have been recorded at selected temperatures in the 20–400 K range for complexes 1–10. Values of the Mössbauer parameters (isomer shift,  $\delta$ , quadrupole splitting,  $\Delta E_Q$ , and line width,  $\Gamma$ ) resulting from fitting the 80 and 293 K spectra are collated in Table SM.2. The isomer shift values slightly decrease with increasing temperature, indicating operation of second-order Doppler effect [35].

# 3.4.1. $[FeL^{A}(NCS)_{2}]$ and $[FeL^{Bx}(NCS)_{2}]$ complexes

As expected from the structural and magnetic data, the Mössbauer spectrum of 1 at 293 K consists of a unique doublet characteristic of LS  $\text{Fe}^{\text{II}}$  ( $\delta$ , 0.328(2) mm s<sup>-1</sup>;  $\Delta E_{\rm O}$ , 0.865(3) mm s<sup>-1</sup>). In agreement with the structural and magnetic data, Mössbauer spectra of complexes 3 and 4, recorded between 80 and 293 K, show a unique quadrupole split doublet characteristic of HS Fe<sup>II</sup> (Table SM.2). At variance with those of 3 and 4, the Mössbauer spectra of 2 evidence two HS doublets in agreement with the presence of two distinct  $Fe^{II}$  sites,  $Fe^{II}(A)$  and  $Fe^{II}(B)$ , in the crystal structure. These doublets present similar isomer shifts ( $\sim 1.15 \text{ mm s}^{-1}$  at 80 K, Table SM.2) as expected for identical N<sub>6</sub> donor sets around the  $Fe^{II}(A)$  and  $Fe^{II}(B)$ sites and quite different  $\Delta E_Q$  values (~1.51 and ~2.58 mm s<sup>-1</sup> at 80 K for Fe<sup>II</sup>(A) and Fe<sup>II</sup>(B), respectively), in agreement with different low symmetry environments [36]. The differences in Fe-N bond lengths and N-Fe-N angles associated to the different hydrogen contacts lead to significant differences in symmetry of the ligand environment for the Fe<sup>II</sup> centers of molecules A and B, see Section 3.2.

# 3.4.2. $[FeL^{Cx}(NCS)_2]$ complexes

The Mössbauer spectra of complexes **6–10** confirm the spin-states deduced from the magnetic data for these materials; however, due to poor counting statistics, the high temperature spectra (350–400 K) of complexes **5** and **8** could not be fitted. As an example, in the following we describe the behavior of complex **7**,  $[FeL^{C3}(NCS)_2]$ , for which representative Mössbauer spectra recorded in the cooling mode are shown in Fig. 13. These spectra, measured in the 20–293 K range, confirm the partial SC deduced from the magnetic measurements.

The relative area of the HS doublet ( $\delta = 1.113(2)$  and  $\Delta E_Q = 2.563(4) \text{ mm s}^{-1}$  at 80 K) slightly decreases from 80% at 293 K to 60% at 20 K, confirming the gradual and incomplete character of the SC in this material. The Mössbauer parameters of the LS doublet ( $\delta = 0.439(3)$  and  $\Delta E_Q = 0.732(5) \text{ mm s}^{-1}$  at 80 K) are in agreement with previously reported values [4,18,35].

Comparison of Table SM.1 and Figs. 11 and 12 on the one hand to Table SM.2 and Fig. 13 on the other hand



Fig. 13. Selected Mössbauer spectra of [FeL<sup>C3</sup>(NCS)<sub>2</sub>] (7).

illustrates how important it is to use a local probe like Mössbauer spectroscopy in addition to bulk susceptibility measurements in order to assess the presence or absence of SC, and the relative percentages of spin isomers. Among compounds 6–10 for example, 7 shows the second highest  $\chi_M T$  product in the high temperature range, suggesting the absence of LS fraction at high temperature. However, Mössbauer spectroscopy evidences a partial SC with ~20% of residual LS fraction at 293 K, the second highest among materials 6–10. On the other hand, 6 shows the lowest  $\chi_M T$  product at room temperature while Mössbauer spectroscopy evidences the absence of LS fraction at 293 K.

#### 3.5. IR spectroscopy

The IR study has been focussed on the NCS stretching absorptions (2000–2100  $\text{cm}^{-1}$  range) which constitute a good sensor for the cis or trans conformation of coordinated thiocyanate anions. Usually, trans isomers give a single absorption whereas cis isomers are characterized by a splitting of the v<sub>CN</sub> absorption [15b,37]. However, this criterion must be considered with much caution because the splitting of this band is very sensitive to slight deformations of the coordination sphere (in particular the N-M-N angle between the two thiocyanate ligands coordinated to the metal center). The structural study of complex 3 has evidenced a distorted octahedral geometry around Fe<sup>II</sup> with a trans conformation of the thiocyanate ligands. Two well distinct  $v_{CN}$  absorption bands were observed in the IR spectra at 2093 and 2065  $cm^{-1}$  in compliance with the strong deviation from an ideal *trans* conformation evidenced by the 158.8° (C17–N8–Fe) and 137.5° (C16–N7–Fe) angles. The same conclusion can be drawn from the IR spectra of complexes 2 and 4, as well as for complexes 5-10 ([FeL<sup>Cx</sup>(NCS)<sub>2</sub>] series). The larger splitting  $(64 \text{ cm}^{-1})$ 

observed for 4 suggests a larger deformation of the ligand environment symmetry around Fe<sup>II</sup>, in agreement with the large quadrupole splitting evidenced by Mössbauer spectroscopy. The third band (low intensity) observed for 2 can be explained by the presence of two types of NCS ligands, depending on the atom through which they participate into hydrogen bonds (NH···SCN or NH···NCS that leads to two Fe<sup>II</sup> sites distinguishable crystallographically and by Mössbauer spectroscopy, see the corresponding subsections above). In line with our previous report on parent iron(II) compounds with related dissymmetric Schiff bases [32], the  $v_{C=N}$  (imine) absorptions observed for compounds 1–10 do not seem to depend on the spin-state of iron(II). This is possibly because they are no longer pure  $v_{C=N}$ (imine) stretches, but correspond to the simultaneous involvement of  $v_{C=N}(\text{imine})$ ,  $v_{C=N}(\text{py})$  and  $v_{C=N}(\text{imidazole})$ vibrators.

## 4. Discussion

Tetradentate ligands including exclusively nitrogen donors have been scarcely used in association with coordinating pseudohalide anions to prepare Fe<sup>II</sup> SC complexes with a N<sub>6</sub> ligand environment. The first examples were reported by Toftlund et al. [14a]. and included tripodal ligands of the tris-pyridylamine (tpa) type associated with two cis-coordinated pseudohalide anions: varying the tpa substituents or the pseudohalide vielded different SC behaviors or mixtures of spin isomers. A related type of Fe<sup>II</sup> SC material, also including a tripodal N<sub>4</sub> ligand (dppa) and two cis-coordinated NCS<sup>-</sup>, was reported later by Matouzenko et al. [14c]. Finally, Toftlund et al. [14b] also reported a series of Fe<sup>II</sup> compounds including acyclic Schiff bases resulting from condensation of R-pyridinecarboxaldehydes (R = H, Me) or acetylpyridine with ethylenediamine or propylenediamine (bpn ligand type) associated with two pseudohalide anions: again, depending on the ligand substituents and alkyl bridge, they observed different magnetic behaviors. While the ciscoordination mode of NCS anions was imposed by the tpa or the dppa topology, no such constraint was imposed by the bpn ligands; however the NCS anions were also cis-coordinated in the bpn series of Fe<sup>II</sup> compounds [14b]. The diversity of reported SC behaviors in contrast to the scarcity of SC materials built from tetradentate ligands including exclusively nitrogen donors associated with coordinating pseudohalide anions led us to explore the use of such ligand environments with the aim to tune the SC behavior through minute changes in the ligand. An additional incentive to this study was the possibility to benefit from the versatile arrangement of the two pseudohalide ligands: indeed, while the pseudohalide anions are *cis*-coordinated in many SC materials [1,38], a recent work has evidenced that the trans-NCS isomer of a Fe<sup>II</sup> compound including a bidentate triaryltriazole ligand exhibits SC while its cis-NCS counterpart is a HS material [15b].

In this study, the 2:1 condensation of acetylpyridine and 2,2-dimethyl-1,3-diaminopropane followed by reaction with ferrous thiocvanate vielded  $[FeL^{A}(NCS)_{2}]$  (1) where the tetradentate ligand is the symmetrical bis-schiff base including two N(pyridine) and two N(imine) donors. This new ferrous material, although based on a tetradentate ligand closely related to bptn [14b] (bptn results from the 2:1 condensation of pyridine carboxaldehyde with 1,3-diaminopropane), is significantly different from [Fe(bptn)(NCS)<sub>2</sub>]: while the NCS ligands are *cis* in the latter, they are *trans* in compound 1, and while [Fe-(bptn)(NCS)<sub>2</sub>] is a SC material, **1** is LS in the 80–400 K temperature range. The differences between 1 and [Fe(bptn)(NCS)<sub>2</sub>] are the substituents (Me, H, respectively) on the central carbon atom of the alkyl chain, the substituents (Me, H, respectively) on the imine carbon atoms, and the trans versus cis arrangement of the NCS ligands. The possible respective roles of these three factors in the difference of electronic behavior between the two materials cannot be untangled yet: it is one of the aims of [32], this report, and a paper in preparation, [40], to independently assess the role of each of these factors.

Condensation of 2R-imidazole-4-carboxaldehyde with the same diamine in the 2:1 ratio followed by reaction with ferrous thiocyanate was expected to yield ferrous complexes with symmetrical tetradentate ligands similar to that in 1, but better suited to stabilize HS Fe<sup>II</sup> or to yield Fe<sup>II</sup> SC materials, depending on the decrease in ligand field on going from  $L^{A}$  to  $L^{Bx}$ , and on the *cis* or *trans* arrangement of the thiocyanates ligands. Indeed, compounds 2-4 include the expected symmetrical tetradentate ligands L<sup>Bx</sup> and two trans-coordinated thiocyanates. As shown by the results described in the previous section, the ligand field generated by the L<sup>Bx</sup> ligands associated with two *trans*-NCS stabilizes the HS Fe<sup>II</sup> state, regardless of the imidazole substituent  $R_2$  (H, Me, Ph). This is in line with the significant difference between L<sup>A</sup> and L<sup>Bx</sup> that results from the replacement of two pyridyl (strong ligand field N donor) by two imidazolyl rings (weaker ligand field N donor).

Considering that the NCS<sup>-</sup> ligands are *trans*-coordinated in compounds 1–4, regardless of the tetradentate ligand (L<sup>A</sup> or L<sup>Bx</sup>), it was anticipated that combination of pyridyl and imidazolyl rings to yield a dissymmetrical L<sup>Cx</sup> bis-Schiff base chelated to Fe<sup>II</sup> would not affect the *trans*-coordination mode of the NCS<sup>-</sup> anions. Then, the only difference in ligand field would result from the change in the tetradentate ligand. Indeed, the results described in the previous section confirm that the NCS<sup>-</sup> ligands are *trans*-coordinated in compounds 5–10, allowing us to consider the differences between the tetradentate ligands L<sup>A</sup>, L<sup>Bx</sup> and L<sup>Cx</sup> as the sole origin of the different electronic behaviors among all materials reported in this study.

Then, comparison of the electronic behavior of 1-4 on the one hand to that of 5-10 on the other hand evidences that combination of pyridyl and imidazolyl rings to yield a dissymmetrical tetradentate  $L^{Cx}$  ligand has indeed

allowed to bring the ligand field from the high (1) and low-field (2–4) ranges to the intermediate SC ligand field range (5–10).

Within the series, the differences originate from: (i) the substituents on the central carbon atom of the alkyl chain  $(R_1 = H (5-7), Me (8-10))$ , and (ii) the 2-substituent on the imidazolyl ring  $(R_2 = H (5, 8), Me (6, 9), Ph (7, 10))$ . The most important difference in the SC properties within this series is the SC temperature  $T_{1/2}$ : it is higher than 400 K for 5 and 8, while it is around 100 K for the remaining compounds. In other words, substitution of the phenyl or methyl group by an hydrogen atom at the C2 imidazolyl shifts the transition temperature  $T_{1/2}$  by ~300 K towards higher temperatures.

This result evidences that a prominent electronic effect is exerted by  $R_2$  but not  $R_1$ : in other words, the tuning of the ligand field is essentially obtained through modifications of the heterocyclic aromatic rings of the tetradentate ligand. In this report we concentrate on the imidazolyl ring; the effect of pyridyl ring substituents has been described in a previous report [32]. Considering that the ligand fields exerted by  $L^{C1}$  (5) and  $L^{C4}$  (8) ( $R_2 = H$ ) are weaker (higher  $T_{1/2}$ ) than those exerted by the remaining  $L^{Cx}$  ligands ( $R_2 = Me$  or Ph), it may be suggested that the steric effect of the R2 substituent overpasses its inductive (+I, Me) or mesomeric (+M, Ph) effect. As estimated through roughly approximated  $T_{1/2}$  values, the role of  $R_1$ in tuning the ligand field is much more limited. However, although subtle, the trend is the same within the three pairs (5, 8), (6, 9) and (7, 10): the lower  $T_{1/2}$  is associated with  $R_1 = H$  (5–7). This seems to indicate that the inductive effect of  $R_1$  (Me for 8–10) slightly lowers the ligand field with regard to its counterpart (5-7) in each pair. This trend is further substanciated by the results described in [32].

For clarity, only intramolecular effects have been taken into account in the above considerations: this is of course a first approximation because intermolecular effects may also indirectly but significantly contribute to the ligand field onto the Fe<sup>II</sup> center [39].

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### Appendix A. Supplementary material

CCDC 613879, 613880, 613881, 613882 and 613883 contain the supplementary crystallographic data for 1, 2, 3, 7 and 9. These data can be obtained free of charge via htpp://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +(44) 1223-336033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.12.017.

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