

DOI:10.1002/ejic.201201085

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# Subtlety of the Spin-Crossover Phenomenon Observed with Dipyridylamino-Substituted Triazine Ligands



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Keywords: Iron / LIESST effect / Calorimetry / Supramolecular interactions / Spin crossover

Reactions of the new, closely related ligands 4,6-dichloro-*N*,*N*-di(pyridine-2-yl)-1,3,5-triazine-amine (Cldpat) and 6chloro-*N'*-phenyl-*N*,*N*-di(pyridin-2-yl)-1,3,5-triazine-2,4-diamine (Cladpat) with iron(II) thiocyanate produced coordination compounds with drastically distinct magnetic properties. The compound *trans*-[Fe(Cldpat)<sub>2</sub>(NCS)<sub>2</sub>](H<sub>2</sub>O) (**1**) is a highspin complex from room temperature down to 5 K whereas the analogous compound *trans*-[Fe(Cldpat)<sub>2</sub>(NCS)<sub>2</sub>] (**2**) exhibits spin-crossover (SCO) properties with  $T_{1/2} = 178$  K. Compounds **1** and **2** (both in its low-spin and high-spin

# Introduction

The phenomenon of spin crossover (SCO) is a particular and very interesting illustration of the ligand-field theory.<sup>[1,2]</sup> For octahedral coordination complexes of transition-metal ions, the d orbitals split into two sets, i.e. the t<sub>2g</sub> and e<sub>g</sub> sets, whose energy difference is given by the crystalfield splitting parameter  $\Delta_{oct}$ .<sup>[3]</sup> The size of  $\Delta_{oct}$  determines the electronic structure of the d<sup>4</sup>–d<sup>7</sup> metal ions. Thus, for iron(II) complexes, a small  $\Delta_{oct}$  will favour the high-spin state (HS, e<sub>g</sub><sup>2</sup>t<sub>2g</sub><sup>4</sup>, S = 2) while a large  $\Delta_{oct}$  will produce a low-spin (LS, t<sub>2g</sub><sup>6</sup>, S = 0) compound. With an appropriate ligand-field strength (namely for an intermediate  $\Delta_{oct}$ value), the transition-metal compound may exhibit LS  $\leftrightarrow$ HS bistability through the application of an external stimulus, like temperature, pressure or light.<sup>[4–7]</sup> Hence, such SCO

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- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201201085.

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states) have been structurally characterized by X-ray diffraction studies, which revealed identical metal coordination spheres. The SCO properties of **2** have been thoroughly investigated by temperature-dependent magnetic susceptibility measurements and differential scanning calorimetry (DSC), and a LIESST process with rapid relaxation of the trapped HS species has been observed. The equivalent coordination compound with selenocyanate anions, namely [Fe(Cladpat)<sub>2</sub>(NCSe)<sub>2</sub>] (**3**) also displays SCO properties, although more gradual and with a lower  $T_{1/2}$  value of 166 K.

materials may find potential applications in molecular switches, data storage devices and optical displays, especially in the case of Fe<sup>II</sup> ions, for which the LS state is diamagnetic.<sup>[8–11]</sup> Therefore, SCO species have received a great deal of attention from the scientific community for the past decade.<sup>[12,13]</sup> A great number of SCO Fe<sup>II</sup> complexes have been synthesized that were principally obtained from ligands based on nitrogen-containing aromatic donor groups (such as pyridine and azole rings).<sup>[14–19]</sup>

For the past seven years, we have been involved in the design and preparation of SCO iron(II) compounds with polypyridine ligands.<sup>[20–22]</sup> In particular, the use of a ligand derived from the *s*-triazine ring and 2,2'-dipyridylamine units, namely 2,4,6-tris(dipyridin-2-ylamino)-1,3,5-triazine (dpyatriz),<sup>[23]</sup> has led to remarkable SCO systems.<sup>[22,24,25]</sup> Subsequently, Murray and coworkers have developed a variety of dipyridylamino-substituted-triazine ligands,<sup>[26–30]</sup> which were easily prepared from the highly versatile building block 2,4,6-trichloro-1,3,5-triazine.<sup>[31–33]</sup> The utilization of these ligands has allowed the preparation of SCO coordination compounds, hence corroborating the great potential of (2,2'dipyridylamine/triazine)-based ligands to generate molecular switches.

In the present study, we have taken advantage of the straightforward and highly selective substitution of the chloride atoms of 2,4,6-trichloro-1,3,5-triazine to synthesize two related dipyridylamino-substituted-triazine ligands, namely 4,6-dichloro-N,N-di(pyridine-2-yl)-1,3,5-triazine-amine (Cldpat) and 6-chloro-N'-phenyl-N,N-di(pyridin-2-yl)-1,3,5-triazine-2,4-diamine (Cladpat) (Scheme 1), whose sole difference lies in the replacement of one of the two



chloride atoms of Cldpat by an aniline unit, producing Cladpat. Actually, the use of these similar ligands to bind iron(II) ions leads to the formation of mononuclear coordination compounds with similar molecular structures, but dissimilar magnetic behaviours, thus revealing the drastic effect of tiny structural changes on the physical properties of related molecules.



Scheme 1. Triazine-based ligands 4,6-dichloro-*N*,*N*-di(pyridine-2-yl)-1,3,5-triazine-amine (Cldpat) and 6-chloro-*N*'-phenyl-*N*,*N*-di-(pyridin-2-yl)-1,3,5-triazine-2,4-diamine (Cladpat).

# **Results and Discussion**

### Synthesis

As evidenced by earlier studies by Murray<sup>[26–29]</sup> and some of us,<sup>[22,24,25]</sup> *s*-triazine-based ligands containing at least one 2,2'-dipyridylamine unit allow the preparation of SCO iron(II) compounds. Herein, it was decided to investigate the potential ability of the simplest member of this family of dipyridylamino-substituted-triazine ligands, namely 4,6-dichloro-*N*,*N*-di(pyridine-2-yl)-1,3,5-triazineamine (Cldpat; Scheme 1), to generate SCO properties upon coordination to an iron(II) ion in the presence of thiocyanates or selenocyanates. Hence, Cldpat was prepared in THF by the reaction of 2,2'-dipyridylamine with 1 equiv. of 2,4,6-trichloro-1,3,5-triazine, in the presence of *N*,*N*-diisopropylethylamine (DIPEA).

Next, one of the chloride atoms of Cldpat was replaced by an aniline group with the aim of examining the influence of this slight modification of the ligand on the magnetic properties of the ensuing iron(II) complex. Thus, the ligand 6-chloro-N'-phenyl-N,N-di(pyridin-2-yl)-1,3,5-triazine-2,4-diamine (Cladpat; Scheme 1) was synthesized from Cldpat through substitution of one of its chloride atoms by aniline, using sodium carbonate as a base in acetone/water. The molecular structure of Cladpat could be determined by single-crystal X-ray diffraction (Figure S1). The solid-state structure of Cladpat shows that the molecules are strongly associated by strong hydrogen-bonding interactions  $[N_{aniline} - H \cdot \cdot \cdot N_{triazine} = 2.972(3) \text{ Å}; \angle N_{aniline} - H - N_{triazine} =$ 176(3)°; Figure S1], giving rise to a 1D supramolecular chain along the crystallographic c axis. Such anticipated H bonds, for which the ligand Cladpat was actually designed, may be crucial to favour the occurrence of cooperative SCO, if maintained in complexes of Cladpat.

The coordination compounds 1–3 were synthesized by the direct addition of a freshly prepared methanolic solution of  $Fe(NCX)_2$  (X = S or Se) to a methanolic solution containing 2 equiv. of the dipyridylamino-substituted-triazine ligand (Cldpat or Cladpat). The solution of Fe-(NCS)<sub>2</sub> was obtained from iron(II) sulfate and potassium thiocyanate while  $Fe(NCSe)_2$  was made from iron(II) perchlorate and potassium selenocyanate.

# Description of the Crystal Structure of *trans*-[Fe(Cldpat)<sub>2</sub>-(NCS)<sub>2</sub>](H<sub>2</sub>O) (1)

Reaction of 1 equiv. of iron(II) thiocyanate with 2 equiv. of Cldpat generates compound 1 with a yield of 73%. Structural information on 1 has been obtained from X-ray diffraction studies at 100 K. The high *R* value found (see Table S2) is most likely due to unresolved crystal twinning. Nevertheless, the data collected are satisfactory for a reasonably accurate determination of the molecular structure of 1. Actually, the iron(II) centre in 1 exhibits the anticipated octahedral coordination environment [typically observed for iron(II) thiocyanate complexes with this family of ligands<sup>[25,34]</sup>], which is formed by two Cldpat ligands in the equatorial plane and two *trans* thiocyanate anions (Fig-



Figure 1. Representation of the molecular structure of compound 1 with partial atom numbering scheme. The thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms and the lattice water molecule are not shown for clarity. Symmetry operation: a, 1 - x, 1 - y, -z.

Table 1. Coordination bond lengths [Å] and angles [°], and supramolecular interactions for compound 1.

Distances			
Fe1–N1	2.090(13)	Fe1–N3	2.264(15)
Fe1-N2	2.214(13)	Fe1····Fe1 <sub>inter</sub> <sup>[a]</sup>	8.396(16)
Angles			
N2-Fe1-N3	81.7(5)	N3a-Fe1-N2 <sup>[b]</sup>	98.3(5)
N2a-Fe1-N3	98.3(5)	N2a-Fe1-N3a	81.7(5)
N1-Fe1-N1a <sup>[b]</sup>	180		
∑Fe1° <sup>[c]</sup>	43	$\Phi^{o[d]}$	74
Hydrogen bond			
C13O2So	2.739(5)		
Lone pair- <i>m</i> inter	ractions		
Cg10····S2s <sup>[e]</sup>	3.242(7)	Cg10S2	3.337(8)

[a] Closest inter-monomer Fe<sup>...</sup>Fe distance. [b] Symmetry operation: a 1 - x, 1 - y, -z. [c]  $\Sigma^{\circ}$  = the sum of  $|90 - \theta|$  for the 12 N– Fe–N angles in the octahedron.<sup>[12,35,36]</sup> [d]  $\Phi^{\circ}$  = sum of  $|60 - \theta|$  for the 24 N–Fe–N angles describing the trigonal twist angle as described by Marchivie and coworkers.<sup>[12,37]</sup> [e] Symmetry operation: o - x, 1 - y, 1 - z; s - x, 1/2 + y, 1/2 - z.



ure 1). Selected bond lengths and angles are listed in Table 1. Surprisingly, The Fe–N<sub>Py</sub> bond lengths in the range 2.214(13)–2.264(15) Å and the Fe–N<sub>NCS</sub> distances of 2.090(13) Å characterize a high-spin iron(II) compound. This fact is confirmed by temperature-dependent magnetic-susceptibility measurements revealing that the FeN<sub>6</sub> species in **1**, rather unexpectedly, does not present a SCO process (see below).

The solid-state structure of **1** shows the occurrence of intramolecular lone pair… $\pi$  interactions [Cg10…S2 = 3.337(8) Å; Table 1]. In addition, the molecules are associated by means of intermolecular lone pair… $\pi$  interactions [Cg10…S2s = 3.242(7) Å; Table 1], which generate a supramolecular 1D chain. The chains interact with each other through S<sub>lonepair</sub>…triazine<sub> $\pi$ </sub> contacts, producing a 2D layer in the crystallographic *bc* plane (Figures 2 and S2). These 2D layers are further connected through hydrogen bonds between lattice water molecules and the chloride atoms of the triazine rings that give rise to a 3D network (Figure S3).



Figure 2. View of the crystal packing of 1 showing the formation of a supramolecular 2D network in the *bc* plane by means of lone pair… $\pi$  interactions (black dotted lines) between the triazine rings and neighbouring thiocyanate anions [Cg10…S2 = 3.337(8) Å and Cg10…S2s = 3.242(7) Å]. Symmetry operation: s - x, 1/2 + y, 1/2 - z.

# Description of the Crystal Structure of *trans*-[Fe(Cladpat)<sub>2</sub>-(NCS)<sub>2</sub>] (2)

Reaction of 1 equiv. of iron(II) thiocyanate with 2 equiv. of Cladpat produces compound **2** with a yield of 89%. Compound **2**, which shows SCO properties (see magnetic studies), crystallizes in the monoclinic space group  $P2_1/c$ , both at 100 K and at 270 K (Table S2). The molecular structure of low-spin **2** is depicted in Figure 3, and selected bond lengths and angles are listed in Table 2. Compound **2** consists of an octahedral iron(II) ion coordinated by four pyridine units from two Cladpat ligands and two *trans* Nbonded thiocyanate anions.

Such a FeN<sub>6</sub> coordination environment is known to potentially produce SCO iron(II) species.<sup>[35]</sup> The Fe–N<sub>Py</sub> distances ranging from 1.965(3) to 2.000(4) Å are typical of a LS iron(II) entity, as is the case for the Fe–N<sub>NCS</sub> distances of 1.945(4) and 1.948(4) Å (Table 2). These bond lengths increase by ca. 0.20 Å for Fe–N<sub>Py</sub> and ca. 0.15 Å for Fe– N<sub>NCS</sub> when the temperature is raised to 270 K (Table 2),



Figure 3. Representation of the molecular structure of compound 2 (LS state, determined at 100 K) with partial atom numbering scheme. The thermal ellipsoids are drawn at the 50% probability level, and only the hydrogen atoms involved in hydrogen-bonding interactions are shown for clarity.

Table 2. Coordination bond lengths [Å] and angles [°], and supramolecular interactions for compound **2** (low-spin and high-spin states).

2	LS <sup>[a]</sup>	HS <sup>[b]</sup>		
	Distances			
Fe1–N1	1.948(4)	2.090(6)		
Fe1–N2	1.945(4)	2.087(6)		
Fe1–N3	1.984(3)	2.190(5)		
Fe1–N4	1.994(4)	2.201(6)		
Fe1-N10	1.965(3)	2.178(5)		
Fe1-N11	2.000(4)	2.214(6)		
Fe1····Fe1 <sub>inter</sub> <sup>[c]</sup>	8.424(4)	8.584(6)		
	Angles			
N3–Fe1–N4	86.27(15)	82.7(2)		
N4–Fe1–N10	93.68(15)	97.7(2)		
N10-Fe1-N11	86.86(15)	82.3(2)		
N11-Fe1-N3	93.19(15)	97.4(2)		
N1-Fe1-N2	176.6(2)	176.6(2)		
ΣFe1 <sup>o[d]</sup>	32	47		
$\Phi^{\circ[e]}$	43	70		
	Hydrogen bonds[f]			
N9–H9····N15a	3.010(5)	3.035(8)		
∠ N9–H9–N15a	177(6)	165(6)		
N16–H16…N8b	2.995(5)	3.023(8)		
∠ N16–H16–N8b	157(5)	157(6)		
	Lone pair– $\pi$ interactions			
Cg5S2	3.459(2)	3.589(4)		
Cg8…S1	3.504(2)	3.564(3)		
	$\pi$ - $\pi$ interactions			
Cg9····Cg10	3.976(3)	4.236(5)		
[a] At 100 K [b] At 27	0 K [c] Closest inter	monomer FemFe d		

[a] At 100 K. [b] At 270 K. [c] Closest inter-monomer Fe<sup>...</sup>Fe distance. [d]  $\Sigma^{\circ}$  = the sum of  $|90 - \theta|$  for the 12 N–Fe–N angles in the octahedron.<sup>[12,35,36]</sup> [e]  $\Phi^{\circ}$  = sum of  $|60 - \theta|$  for the 24 N–Fe–N angles describing the trigonal twist angle as described by Marchivie and coworkers.<sup>[12,37]</sup> [f] Symmetry operations: a 1 – x, –1/2 + y, 1/2 – z; b 1 + x, 1/2 – y, 1/2 + z.

which is indicative of a full spin transition, as also observed during magnetic studies on **2** (see below).



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The distortion parameters  $\Sigma^{\circ}$  and  $\Phi^{\circ}$  reflect the deviation from an ideal octahedral geometry.<sup>[38]</sup>  $\Sigma^{\circ}$  directly measures the distortion from a perfect octahedron while  $\Phi^\circ$  defines the deformation of the octahedral coordination geometry towards a trigonal-prismatic environment.<sup>[12]</sup> For a perfect octahedron,  $\Sigma^{\circ} = \Phi^{\circ} = 0$ . For LS 2,  $\Sigma^{\circ} = 32$  and  $\Phi^{\circ} =$ 43, whereas the respective values for HS 2 are 43 and 70 (Table 2). The lower  $\Sigma^{\circ}$  and  $\Phi^{\circ}$  values for the LS compound are typical since LS complexes are less deformed than HS ones.<sup>[35,37]</sup> Hence,  $\Delta \Sigma^{\circ} (\Sigma^{\circ}_{HS} - \Sigma^{\circ}L_{HS})$  and  $\Delta \Phi^{\circ} (\Phi^{\circ}_{HS} - \Sigma^{\circ}L_{HS})$  $\Phi^{\circ}_{LS}$ ) quantify the magnitude of the structural changes occurring during the SCO. For **2**,  $\Delta \Sigma^{\circ} = 15$  and  $\Delta \Phi^{\circ} = 27$ ; the high  $\Delta \Phi^{\circ}$  value observed for 2 is indicative of a significant alteration of the octahedral geometry upon the  $LS \rightarrow HS$ transition. Such a large structural variation may be associated with cooperativity between the iron(II) centres, possibly through intermolecular interactions (actually, the magnetic measurements show a relatively cooperative SCO; see below). In fact, the crystal packing reveals that the iron(II) molecules are connected through double Naniline-H…N<sub>triazine</sub> bonds (Table 2), which generate a 1D supramolecular chain (Figure 4). These hydrogen bonds are affected by the spin transition (a variation of about 0.025 Å is observed); in particular, the N9-H9...N15a bond experiences a bending of ca. 7%, the angle varying from 177(6)° to  $165(6)^{\circ}$  during the LS  $\rightarrow$  HS transition (Table 2). In addition, the molecules of 2 exhibit intramolecular lone pair··· $\pi$  interactions<sup>[39,40]</sup> (Cg5···S2 and Cg8···S1 contacts; Figure 4), which are also altered by the SCO (Table 2). A closer look at the solid-state structure of 2 reveals that the 1D supramolecular chains are linked into a 2D layer by parallel-displaced  $\pi - \pi$  interactions,<sup>[41,42]</sup> involving neighbouring aniline rings [centroid-to-centroid distance  $Cg9\cdots Cg10 = 3.976(3)$  Å in LS 2; Figure S4]. The shortest arene–arene contact distances are C17···C39i = 3.257(7) Å and C18····C40i = 3.335(7) Å (Figure S4B), and rise to 3.283(12) Å and 3.397(11) Å, respectively, upon LS  $\rightarrow$  HS transition [corresponding to an increase of the centroid-tocentroid distance of ca. 7%, from 3.976(3) to 4.236(5) Å; Table 2]. All these supramolecular bonding interactions

# H9 N9 Cg5 N15a) N8 9 Cg5 N16a) H16a S2 Cg8 N16 N16 H16

Figure 4. View of the crystal packing of LS **2** showing N<sub>aniline</sub>– H···N<sub>triazine</sub> bonds [N9–H9···N15a = 3.010(5) Å and N16a– H16a···N8 = 2.995(5) Å; blue dotted lines] connecting the iron(II) molecules to generate a 1D supramolecular chain. Intramolecular lone pair··· $\pi$  interactions (black dotted lines) take place between the thiocyanate sulfur atoms and the triazine rings [Cg5···S2 = 3.459(2) Å and Cg8···S1 = 3.504(2) Å]. Symmetry operations: a 1 - x, -1/2 + y, 1/2 - z.

may favour cooperativity between the transiting iron(II) ions.

It has to be noted that the  $\Sigma^{\circ}$  and  $\Phi^{\circ}$  values for HS 2 are comparable to those of 1 (see Table 1), therefore suggesting analogous octahedral distortions for the two high-spin molecules, and corroborating the metal coordination environment in 1.

Reaction of the ligand Cladpat with iron(II) selenocyanate [instead of iron(II) thiocyanate] yields the analogous compound [Fe(Cladpat)<sub>2</sub>(NCSe)<sub>2</sub>] (**3**), as indicated by elemental analyses, which also exhibits SCO properties (see the section Magnetic Studies). Although the molecular structure of **3** could not be determined by X-ray diffraction studies, it is expected that the coordination environment of the iron(II) centres in **3** is equivalent to those of **1** and **2**, with two *trans* N-bonded selenocyanate ions. Actually, the IR absorption band observed at 2061 cm<sup>-1</sup> for compound **3** is identical to that reported by Murray and coworkers for an iron(II) SCO complex from a dipyridylamino-substituted-triazine ligand with *trans*-coordinated NCSe ions.<sup>[30]</sup>

#### **Magnetic Studies**

The effect of the substituent (ligands Cldpat and Cladpat) and the replacement of thiocyanate by selenocyanate anions have been investigated by magnetic measurements. Hence, the temperature dependence of the  $\chi T$  product of compounds 1–3,  $\chi$  being the molar paramagnetic susceptibility, were derived from magnetization measurements on bulk samples in an applied field of 0.5 T for 1 and 3, and 1 T for 2 (see Experimental Section), and in the temperature range 2–300 K. The data for compounds 1 and 2, shown in Figure 5, corroborate the structural observations, evidencing the occurrence of a complete thermal SCO for compound 2, and the – surprising – absence of such a process in the case of compound 1. Indeed, the  $\chi T$  product of 1 remains practically constant at 3.11–3.09 cm<sup>3</sup>mol<sup>-1</sup> K from 300 K down to 50 K, the temperature below which a de-



Figure 5.  $\chi T$  vs. T plot for 1 (squares) and 2, showing the process of SCO (full circles), the partial LS to HS photo-induced trapping at 10 K (LIESST effect) and the relaxation back to the LS ground state and normal behaviour upon warming (empty circles).



crease of  $\chi T$  is observed down to 2.18 cm<sup>3</sup> mol<sup>-1</sup> K. The magnetic properties of 1 are thus in agreement with an S =2 HS ground state for the  $Fe^{II}$  ion, with g close to 2, throughout the whole temperature range considered, the decrease at low temperatures being due to zero-field-splitting effects of the S = 2 spins. Magnetization vs. field measurements at 2 K indeed show saturation at ca. 4.05  $N_{\rm A}\mu_{\rm B}$  at 5 T (see Figure S5), in agreement with an S = 2 spin ground state and a g value slightly above 2. On the other hand, the  $\chi T$  product of **2** decreases upon cooling, from similar values to those of 1, i.e. 3.13 cm<sup>3</sup> mol<sup>-1</sup> K at 280 K, reaching a plateau at 0.11 cm<sup>3</sup>mol<sup>-1</sup> K below 100 K, and down to  $0.08 \text{ cm}^3 \text{mol}^{-1} \text{ K}$  at 5 K. Compound 2 thus undergoes a complete SCO centred at ca. 178 K and with a limited cooperative character, as indicated by a  $\Delta T_{80}$  of 50 K (80% of the transition occurs within about 50 K). In agreement with the structural observations, the process of SCO is virtually completed at 100 K. These observations are perfectly reproducible upon warming, thus with no detectable hysteresis, and over various cycles.

The possibility of trapping the HS metastable state at low temperature through irradiation, the so-called LIESST effect,<sup>[43]</sup> was examined on a thin sample of **2**. At 10 K, a fast increase of  $\chi T$  is indeed observed when irradiating with green light, clearly demonstrating the efficiency of the LIESST effect in this compound (Figures 5 and 6 top). Nevertheless, the rate of increase rapidly drops and virtually stable values are reached after ca. 1 h (Figure 6 top). After turning the irradiation OFF and thermalization, the resulting  $\chi T$  value of 1.42 cm<sup>3</sup>mol<sup>-1</sup> K corresponds to ca. 50% of trapped HS centres, based on the  $\chi T$  value of 1 at the same temperature. An incomplete LIESST effect in thin samples with an apparent steady state similar to that observed herein may be due to an overlap of the <sup>5</sup>T<sub>2</sub> $\rightarrow$ <sup>5</sup>E (HS)



Figure 6. Top:  $\chi T$  vs. time evolution for **2** at 10 K showing the increase due to LIESST during irradiation with a green light. Bottom:  $\chi T$  vs. time evolution for **2** at 10 K in obscurity after the irradiation with a green light, showing an exponential-like behaviour. The full red line is a fit to a stretched exponential with  $\beta = 0.67$  and critical time of 765 s.

and  ${}^{1}A_{1} \rightarrow {}^{3}T_{1}$  (LS) bands, resulting in competitive LIESST and reverse-LIESST processes.<sup>[44]</sup> Another cause of such an incomplete light-induced trapping, even in thin samples, is the competition of the light-induced LS→HS trapping with the relaxation of the trapped HS species back to the LS ground state, at the origin of light-induced bistability in cooperative SCO systems.<sup>[45,46]</sup> Measurements vs. time at 10 K after 1 h of irradiation for 2 indeed show that  $\chi T$  rapidly drops in an exponential manner, already reaching values of ca.  $0.40 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  after only 1 h. It is therefore clear that the HS $\rightarrow$ LS relaxation is fast, even at 10 K (Figure 6 bottom). An estimation of the characteristic relaxation time at 10 K of 765 s is obtained by adjusting the experimental data to a stretched exponential with  $\beta = 0.67$  (red line in Figure 6 bottom). Confirmation of the relative instability of the trapped HS state is obtained from the measurements upon warming after irradiation (Figure 5).  $\chi T$  rapidly decreases to reach values similar to those of a normal LS state at temperatures as low as 55 K, as could be expected from the thermal activation of a relaxation process that is already fast at 10 K.

Magnetic properties of compound 3 are shown in Figure 7 as a  $\chi T$  vs. T plot. Similar to 2, a decrease of  $\chi T$  is observed, from 3.43 cm<sup>3</sup> mol<sup>-1</sup> K at 280 K, down to a plateau at ca. 0.15-0.11 cm<sup>3</sup>mol<sup>-1</sup>K below 90 K and down to 0.11 cm<sup>3</sup>mol<sup>-1</sup>K at 5 K, thus confirming a likely comparable molecular structure to that of 2. Compound 3 thus also presents a complete SCO, although centred at a lower temperature, e.g. 166 K, and more gradual than that of 2, with a  $\Delta T_{80}$  of ca. 80 K. Such a low cooperativity in a selenocyanate compound with respect to its thiocyanate analogue is documented, and is possibly related to the participation of the more diffuse Se atom in intermolecular interactions.<sup>[47,48]</sup> This is likely the case here since the S atoms in the structure of 2 do participate in the network of intermolecular interactions (see above). The lower SCO temperature in 3 with respect to 2 is more surprising since the replacement of S by Se in NCX--based SCO compounds usually results in an increase in the SCO temperature.<sup>[47-51]</sup>



Figure 7.  $\chi T$  vs. T plot for 3 (rhombus), showing a complete SCO centred at around 166 K. The data of compound 2 is recalled as light circles for comparison.



### **Thermal Properties**

The molar heat capacity at constant pressure,  $C_{\rm p}$ , of 2 was derived from differential scanning calorimetry (DSC) measurements over the temperature range 110-290 K (see DSC traces in Figure S6). A strong heat capacity anomaly is detected between 135 and 245 K, culminating at ca. 180 K, which can be associated with the SCO phenomenon in 2. Indeed, both the temperature range and maxima are in excellent agreement with the magnetic data. A lattice heat capacity was estimated from data below 135 K and above 245 K (dashed line in Figure 8), allowing the determination of the excess heat capacity associated with the SCO phenomenon in 2 (inset in Figure 8). The related excess enthalpy and entropy were derived by integration of the excess heat capacity and amount to 8.08 kJmol-1 and 44.6 Jmol<sup>-1</sup> K<sup>-1</sup>, respectively (see Figures S7 and S8). Both figures are relatively large, which is usually taken as a consequence of a cooperative character of the SCO. In particular, the excess entropy is well above the purely electronic component, RLn5, thus containing a significant content arising from the coupling of the electronic transition with lattice phonons. The so-called domain model (developed by Sorai and widely used in SCO studies when calorimetric data are available<sup>[52]</sup>) allows such a cooperative character to be quantified through the number n of like-spin SCO centres within an interacting domain; the larger the domains are, the more cooperative the transition is. Values of n close to 1 are typical of solution-like gradual SCO,<sup>[53-55]</sup> while values of ca. 10 to 95<sup>[47,56,57]</sup> have been derived for cooperative to very cooperative systems. Here, the excess heat capacity of **2** is very nicely reproduced by this model with n = 3.33(red line in the inset of Figure 8), indicative of a relatively weakly cooperative SCO, and in agreement with the magnetic studies.



Figure 8. Molar heat capacities of **2** showing a broad hump associated with the SCO. The dashed line is the estimated lattice component. Inset: excess heat capacities associated with the SCO in **2**. The full line is a fit to the domain model of Sorai (see text and SI) with n = 3.3.

## Conclusions

The present study has shown that an apparent minor modification of a ligand, namely the substitution of one of the chloride atoms of Cldpat by an aniline group (ligand Cladpat) gives rise to a drastic change of the magnetic properties of the corresponding iron(II) complexes. Indeed, the coordination compounds 1 and 2, which exhibit identical coordination spheres for their metal centre, display distinct magnetic behaviours; 1 is a high-spin species whereas 2 is a SCO complex with a (weakly cooperative) transition. These opposite comportments are obviously due to the different ligands. Since the coordination bond lengths and angles are comparable for 1 and HS 2, the distinct magnetic properties observed are most likely caused by different ligand-field strengths (i.e. Cldpat has a smaller  $\Delta_{oct}$  value). Theoretical studies and the preparation of dipyridylamino-substituted triazine ligands bearing electron-withdrawing and/or electron-donating substituents may help to understand these disparities. Therefore, these investigations will be carried out and the results will be reported in a future paper.

# **Experimental Section**

**General:** All reagents and solvents were used as received from commercial sources. The reactions were typically carried out in air. IR spectra (as KBr pellets) were recorded with a Nicolet 5700 FTIR spectrometer. Elemental analyses were performed by the Servei de Microanalisi, Consejo Superior de Investigaciones Cientificas (CSIC) of Barcelona. MS spectra were recorded with a MALDI-TOF Voyager DE-RP mass spectrometer equipped with a nitrogen laser (337 nm, 3 ns pulse) and an accelerating voltage of 20–25 kV or an LC/MSD-TOF ESI-mass spectrometer from Agilent Technologies, at the Serveis Cientificotècnics of the University of Barcelona. <sup>1</sup>H NMR spectra were recorded at room temperature with a Varian Unity 300 MHz spectrometer; chemical shifts are reported in ppm relative to the residual solvent signal of CDCl<sub>3</sub> ( $\delta$  = 7.26 ppm). TLC was performed on Alugram<sup>®</sup> SIL G/UV/254 silicagel precoated sheets (Macherey–Nagel, Germany).

Single-Crystal X-ray Diffraction Studies: Data for Cladpat, 1 and 2 (LS and HS states) were collected using Mo- $K_a$  radiation ( $\lambda =$ 0.7107 Å) with a Bruker APEX II QUAZAR diffractometer equipped with a microfocus multilayer monochromator at T =100(2) K and at T = 270(2) K for HS 2. The structures were solved by direct methods and refined on F<sup>2</sup> using the SHELX-TL suite.<sup>[58]</sup> In the case of 1, although the data collected appeared to be of good quality and the processing took place normally, the refinement could only converge to high final R values, and required displacement parameter restraints for most of the organic ligands. This situation is likely due to the presence of twinning; unfortunately, we were not able to settle it. Therefore, even though the molecular structure and the intermolecular interactions are likely accurate, the X-ray structure described herein for 1 should be considered as a preliminary report. Crystal data and refinement parameters are given in Tables S1 (Cladpat) and S2 (1, LS 2 and HS 2). CCDC-901348 (Cladpat), -901349 (1), -901350 (2, 100 K) and -901351 (2, 270 K) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif.

**Magnetic Measurements:** Variable-temperature magnetic-susceptibility data for compound 1–3 were obtained on microcrystalline samples with a Quantum Design MPMS-XL SQUID magnetometer housed at the SAI Physical Measurements of the University of



Zaragoza. Variable-temperature measurements were performed in a 0.5 T applied field, still in the linear range of M vs. H. Pascal's constants were used to estimate diamagnetic corrections to the molar paramagnetic susceptibility, and a correction was applied for the sample holder. Warming and cooling rates were of the order of 0.3 K min<sup>-1</sup>. Irradiation experiments were performed using the Quantum Design fibre optics setup (FOSH). Using this setup, measurements at low fields were noisy, and the applied field was 1 T throughout the whole study. This field was found to be the best compromise to remain close to the linear range of M vs. H curves and obtain good quality data. The light source was a Xenon arc lamp equipped with sets of short-pass and long-pass filters (SPF or LPF). Specifically for the present study, a SPF 650 nm and a LPF at 500 nm were used. Data were corrected for the empty FOSH signal, determined beforehand.

**Differential Scanning Calorimetry Measurements:** DSC experiments were performed with a differential scanning calorimeter Q1000 with the LNCS accessory from TA Instruments. The temperature and enthalpy scales were calibrated with a standard sample of indium, using its melting transition (156.6 °C, 3296 J mol<sup>-1</sup>). Measurements were carried out using aluminium pans with a mechanical crimp, with an empty pan as reference. The zero-heat flow procedure described by TA Instruments was followed to derive heat capacities, using synthetic sapphire as the reference compound. An overall accuracy of ca. 0.2 K in temperature and up to 5 to 10% in the heat capacity was estimated over the whole temperature range, by comparison with the synthetic sapphire.

4,6-Dichloro-*N*,*N*-di(pyridine-2-yl)-1,3,5-triazin-2-amine (Cldpat): 2,4,6-Trichloro-1,3,5-triazine (cyanuric chloride) (2.7 g, 14.6 mmol) was dissolved in THF. N,N-Diisopropylethylamine (DIPEA) (2.55 mL, 1.89 g; 14.6 mmol) was added whilst stirring. The resulting yellow solution was cooled down to 0 °C using an ice bath. Subsequently, a solution of 2,2'-dipyridylamine (5.10 g, 14.6 mmol) in THF (50 mL) was added dropwise, and the reaction mixture was stirred at this temperature for 1 h. The yellow precipitate obtained (i.e. hydrochloride salt of DIPEA) was separated by filtration, and the filtrate was concentrated under reduced pressure using a rotary evaporator at 35 °C. The resulting crude product was purified by column chromatography on silica gel with ethyl acetate as the eluent ( $R_{\rm f} = 0.54$ ) to give pure Cldpat as a white powder (4.44 g, 13.9 mmol, 95%). C<sub>13</sub>H<sub>8</sub>Cl<sub>2</sub>N<sub>6</sub> (319.15): calcd. C 48.92, H 2.53, N 26.33; found C 48.90, H 2.48, N 26.21. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, room temp.):  $\delta$  = 7.24–7.33 (m, 2 H), 7.54 (dt, J = 8.1, J = 0.9 Hz, 2 H), 7.80–7.89 (m, 2 H), 8.50 (ddd, J = 4.9, J = 1.9, J = 0.8 Hz, 2 H) ppm. MS (ESI<sup>+</sup>): m/z = 320.17 [M + H]<sup>+</sup>. IR (KBr):  $\tilde{v} = 1585$  (s), 1548 (br.), 1491 (s), 1461 (s), 1430 (s), 1324 (m), 1220 (s), 1182 (s), 842 (s), 796 (m), 778 (m), 746 (m), 667 (m) cm<sup>-1</sup>.

6-Chloro-N'-phenyl-N,N-di(pyridin-2-yl)-1,3,5-triazine-2,4-diamine (Cladpat): Aniline (0.57 mL, (0.58 g, 6.27 mmol) was added to a solution of Cldpat (2.00 g, 6.27 mmol) in acetone (35 mL). Subsequently, a solution of Na<sub>2</sub>CO<sub>3</sub> (0.30 g, 3.14 mmol) in water (10 mL) was added dropwise, giving rise to a white precipitate. After a reaction time of 6 h, the content was poured into crushed ice and the resulting mixture was stirred until all of the ice had melted. The white precipitate of pure Cladpat was isolated by filtration, washed with water and dried overnight under vacuum (2.33 g, 6.21 mmol, 99%). C<sub>19</sub>H<sub>14</sub>ClN<sub>7</sub> (375.82): calcd. C 60.72, H 3.75, N 26.09; found C 60.64, H 3.67, N 25.96. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, room temp.):  $\delta$  = 6.97–7.33 (m, 8 H), 7.60 (t, J = 16.9, J = 1.8 Hz, 2 H), 7.82 (td, J = 7.9, J = 1.8 Hz, 2 H), 8.49 (d, J = 3.8 Hz, 2 H) ppm. MS (ESI<sup>+</sup>):  $m/z = 376 [M + H]^+$ . IR (KBr):  $\tilde{v} = 3239$ (w), 3079 (w), 1608 (m), 1550 (s), 1464 (s), 1382 (s), 1226 (m), 988 (m), 804 (w), 767 (w), 662 (w)  $cm^{-1}$ .

*trans*-[Fe(Cldpat)<sub>2</sub>(NCS)<sub>2</sub>](H<sub>2</sub>O) (1): A methanolic solution (5 mL) of KNCS (0.019 g; 0.2 mmol) was added to an aqueous solution (2 mL) of FeSO<sub>4</sub>·7H<sub>2</sub>O (0.028 g; 0.1 mmol). After 15 min of stirring, the precipitate of K<sub>2</sub>SO<sub>4</sub> was removed by filtration. Ascorbic acid (in a small quantity) was added to the filtrate to prevent oxidation to iron(III). Subsequently, this iron(II) solution was added to a solution of Cldpat (0.064 g; 0.2 mmol) in dichloromethane (15 mL). The resulting yellow reaction mixture was filtered and the filtrate was left unperturbed for the slow evaporation of the solvent. After two days, small yellow crystals of **1** were obtained (0.605 g, 0.730 mmol, 73%). C<sub>28</sub>H<sub>16</sub>Cl<sub>4</sub>FeN<sub>14</sub>S<sub>2</sub> (**1**-H<sub>2</sub>O): calcd. C 41.50, H 1.99, N 24.20; found C 40.94, H 1.78, N 24.23. IR (KBr):  $\tilde{v} = 3239$  (w), 3079 (w), 1608 (m), 1550 (s), 1464 (s), 1382 (s), 1226 (m), 988 (m), 804 (w), 767 (w), 662 (w) cm<sup>-1</sup>.

*trans*-[Fe(Cladpat)<sub>2</sub>(NCS)<sub>2</sub>] (2): A methanolic solution (5 mL) of KNCS (0.019 g; 0.2 mmol) was added to an aqueous solution (2 mL) of FeSO<sub>4</sub>·7H<sub>2</sub>O (0.028 g; 0.1 mmol). After 15 min of stirring, the precipitate of K<sub>2</sub>SO<sub>4</sub> was removed by filtration. Ascorbic acid (in a small quantity) was added to the filtrate to prevent oxidation to iron(III). Next, a solution of Cldpat (0.075 g, 0.2 mmol) in dichloromethane (5 mL) was added to the iron(II) solution. The resulting yellow reaction mixture was filtered and the filtrate was left unperturbed for the slow evaporation of the solvent. After 2 d, small yellowish-green single crystals of **2**, suitable for X-ray diffraction studies, were obtained (0.082 g; 0.089 mmol, 89%; based on iron). C<sub>40</sub>H<sub>28</sub>Cl<sub>2</sub>FeN<sub>16</sub>S<sub>2</sub> (923.64): calcd. C 52.01, H 3.06, N 24.26; found C 52.11, H 3.02, N 24.34. IR (KBr):  $\tilde{v} = 3433$  (br.), 3244 (w), 2061 (s), 1603 (m), 1558 (s), 1462 (s), 1417 (s), 1383 (m), 1226 (m), 996 (w), 800 (w) cm<sup>-1</sup>.

**[Fe(Cladpat)<sub>2</sub>(NCSe)<sub>2</sub>] (3):** A small quantity of ascorbic acid was added to a methanolic solution (2 mL) of Fe(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.064 g, 0.25 mmol). A methanolic solution (10 mL) of Cldpat (0.188 g, 0.5 mmol) was subsequently added. Finally, a solution of KNCSe (0.072 g, 0.5 mmol) in methanol (10 mL) was added and the resulting reaction mixture was filtered. The filtrate was left unperturbed for the slow evaporation of the solvent. After 2 d, small yellow single crystals of **3** were obtained (0.207 g, 0.203 mmol, 81%). C<sub>40</sub>H<sub>28</sub>Cl<sub>2</sub>FeN<sub>16</sub>Se<sub>2</sub> (1017.44): calcd. C 47.22, H 2.77, N 22.03; found C 47.19, H 2.51, N 21.83. IR (KBr):  $\tilde{v} = 3447$  (br.), 3245 (w), 2061 (s), 1605 (s), 1560 (s), 1461 (m), 1416 (s), 1383 (m), 1225 (m), 996 (w), 799 (w) cm<sup>-1</sup>.

Supporting Information (see footnote on the first page of this article): Crystallographic data for the ligand Cladpat (Table S1), compounds 1, LS 2 and HS 2 (Table S2); representation of the molecular structure of Cladpat (Figure S1); views of the crystal packing of 1 (Figures S2 and S3); view of the crystal packing of 2 (Figure S4); representation of the magnetization vs. applied field at 2 K for compound 1 (Figure S5); DSC traces of compound 2 for warming and cooling modes (Figure S6); Excess enthalpy and entropy involved in the SCO process in compound 2 (Figure S7); Details of modellization of  $\Delta C_p$  data with the so-called domain model.

### Acknowledgments

P. G. acknowledges ICREA (Institució Catalana de Recerca i Estudis Avançats) and the Ministerio de Economía y Competitividad of Spain (Project CTQ2011-27929-C02-01). The Royal Golden Jubilee Ph. D Program (PHD/0234/2550), the Thailand Research Fund and Khon Kaen University, the Higher Education Research Promotion and National Research University Project of Thailand and the Center of Excellence for Innovation in Chemistry (PERCH-CIC), Office of the Higher Education Commission, Min-





istry of Education are also acknowledged. O. R. acknowledges funding from the Ministerio de Economía y Competitividad of Spain (Project MAT2011-24284).

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  - Published Online: November 27, 2012