

# Spin crossover in mononuclear Fe(II) complexes based on a tetradentate ligand

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Received 14 October 2019, revised 10 December 2019

Accepted for publication 8 January 2020


Published 28 January 2020



## Abstract

Three isostructural complexes with the formula  $[\text{Fe}(\text{L}_{5\text{Me}})(\text{NCE})_2]$ :  $\text{L}_{5\text{Me}} = N,N'$ -bis(5-methyl-2-pyridylmethyl)ethane-1,2-diamine and  $\text{E} = \text{S}$  (**1-S**),  $\text{E} = \text{Se}$  (**1-Se**),  $\text{E} = \text{BH}_3$  (**1-BH<sub>3</sub>**) have been synthesized and characterized by single-crystal x-ray diffraction, magnetic susceptibility and DSC studies. All the three derivatives are spin crossover (SCO) active, showing complete one-step spin conversion. The SCO midpoint temperatures ( $T_{1/2}$ ) are 193 K for **1-S**, 226 K for **1-Se**, and 330 K for **1-BH<sub>3</sub>**, which are among the highest values for the homologous Fe(II)-NCE complexes with comparable tetradentate ligands. The almost linear Fe–N  $\equiv$  C(E) angles are consistent with the strong ligand field (LF) strength imposed by these  $\text{NCE}^-$  co-ligands. Strong hydrogen-like bonding N–H...E was observed to connect the molecules into 2D supramolecular sheets parallel to the *bc* plane. However, such supramolecular interaction is not sufficient enough to transmit strong cooperativity. A discussion on the factors governing the LF strength and the cooperativity has been made, based on the comparison of analogous complexes and also based on UV–vis spectroscopy studies of the Ni(II) complexes.

Keywords: tetradentate ligand, magneto-structural relationship, spin crossover

 Supplementary material for this article is available [online](#)

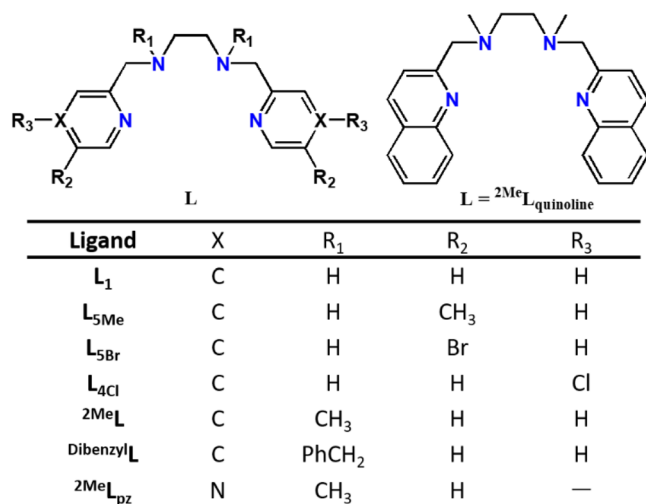
(Some figures may appear in colour only in the online journal)

## 1. Introduction

Switchable materials have drawn continuing attentions for their potential applications as ultra-high-density data storage devices, molecular switches, logic gates, optical/electronic devices, and sensors [1–3]. Spin crossover (SCO) complexes are considered as one of the most attractive molecule-based switchable materials. Their spin states can be reversibly switched between low-spin (LS) and high-spin (HS) in response to external stimuli (such as temperature, pressure, light [4, 5], or pH [6–10]), resulting in the change of magnetic, optical, electrical and structural properties [11–15]. Moreover, coupling of SCO with other properties such as porosity, dielectric [16], fluorescence [17–19] and conductivity [20] provides an optimal platform for developing multifunctional materials [21].

The rational design of SCO materials with desired properties, i.e. large hysteresis and around room temperature

transition, is a goal that is being constantly pursued [14]. Establishment of the intrinsic magneto-structural relationship is a vital step for such an ambition. Great efforts have been made and significant progress has been achieved in the past few years. Halcrow *et al* reported a correlation between the SCO midpoint temperature ( $T_{1/2}$ ) in solution and Hammett parameter for a family of substituted bpp based complexes (bpp = 2,6-di{pyrazol-1-yl}pyridine) [22]. It has been pointed out that the relationship between the electronic nature of the substituent and the spin state of the metal ion is a fine balance between  $\sigma$ - and  $\pi$ -bonding effect [22]. Shatruk *et al* proposed a simple approach for predicting the spin state of homoleptic Fe(II) tris-diimine complexes, based on the distance between chelating N atoms in the free ligand [23]. Brooker *et al* illustrated that the spin state and the  $T_{1/2}$  value in solution for a particular family can be predicted based on the  $^{15}\text{N}$  NMR chemical shift in the free ligand, which can be obtained by experimental spectra or DFT calculations [24]. Nevertheless,



**Scheme 1.** Structures of the tetradentate ligand L.

studies of SCO phenomenon in solution have drawbacks, such as a limited temperature range and low solubility for many complexes, etc. In addition, the bulk magnetic properties usually have strong deviations from their solution behavior, due to the uncertain effects imposed by intermolecular interactions, counter anions, and lattice solvent molecules.

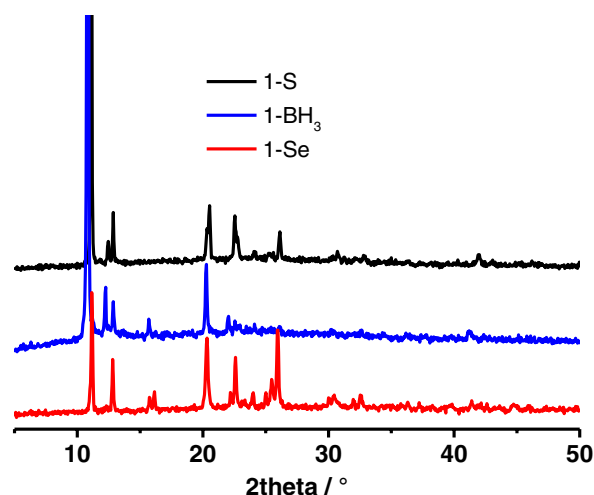
A better understanding of the magneto-structural relationship in the solid state relies on a careful examination of a large library of complexes with similar molecular structures. We have been focusing on the study of SCO properties in a family of Fe(II) mononuclear complexes with the formula [Fe(L)(NCE)<sub>2</sub>] (L is a tetradentate ligand as shown in scheme 1 and E = S, Se, BH<sub>3</sub>) [25–31]. In this study we report the syntheses, crystal structures, and SCO properties of a new series of complexes based on an *m*-methyl substituted ligand, [Fe(L<sub>5Me</sub>)(NCE)<sub>2</sub>], L<sub>5Me</sub> = *N,N'*-bis(5-methyl-2-pyridylmethyl)ethane-1,2-diamine and E = S (**1-S**), E = Se (**1-Se**), E = BH<sub>3</sub> (**1-BH<sub>3</sub>**). Continuous efforts have been made to shed some light on the factors determining the SCO properties in this particular family.

## 2. Results and discussion

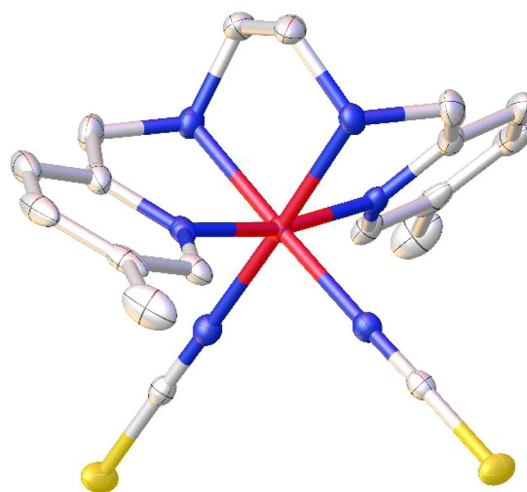
### 2.1. Syntheses

Polycrystalline samples of the three complexes were obtained as precipitate from the reaction of Fe(II) salt, L<sub>5Me</sub>, and MNCE (M = Na, K and E = S, Se, BH<sub>3</sub>) in methanol. The crystalline phase purity was confirmed by powder x-ray diffraction (PXRD) patterns. The yellow color of **1-S** and **1-Se** at room temperature turned dark red at liquid nitrogen temperature, suggesting that they underwent a spin state change from HS to LS. In contrast complex **1-BH<sub>3</sub>** remained a reddish brown color at both temperatures, suggesting that it possibly stayed in an LS state even at room temperature.

Recrystallization of these polycrystalline powders in hot methanol at ambient conditions did not allow the separation of single crystals. The solution turned dark gradually and finally became purple oil in air, suggesting an *in situ* oxidative



**Figure 1.** Experimental PXRD patterns of **1-S**, **1-Se** and **1-BH<sub>3</sub>**.

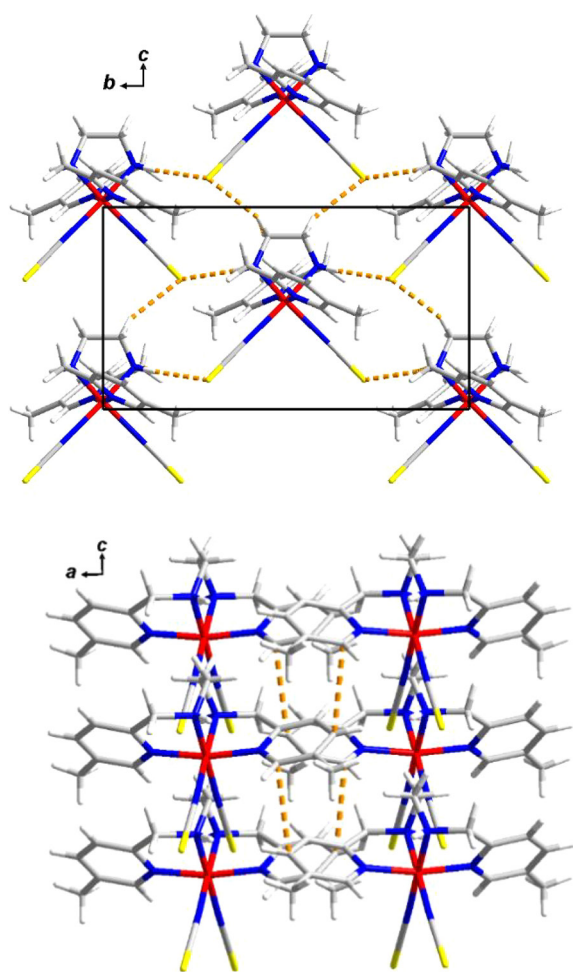


**Figure 2.** View of the molecular structure of **1-S** (120 K) as a representative. Atoms except hydrogens are shown with thermal ellipsoids at 50% probability. Color code: Fe, red; C, gray; N, blue; S, yellow.

dehydrogenation of the L<sub>5Me</sub> ligand, as reported for the non-substituted ligand L<sub>1</sub> [28]. The oxidation could be avoided by doing the syntheses in the glove box or by adding a small amount of ascorbic acid at ambient conditions. Single crystals suitable for x-ray diffraction were obtained in high yield (over 50%) in the case of **1-S** and **1-Se**. Crystals of **1-BH<sub>3</sub>** were not qualified enough for single crystal x-ray diffraction but the structure has been confirmed the same as **1-S** and **1-Se** by PXRD patterns (figure 1).

### 2.2. Crystal structures

The single crystal x-ray structures for **1-S** and **1-Se** were determined at 120 K (LS state) and 298 K (HS state). The refinement parameters are listed in table S1 ([stacks.iop.org/JPhysCM/32/174001/mmedia](https://stacks.iop.org/JPhysCM/32/174001/mmedia)). They crystallize in the orthorhombic space group *Aea*2. As shown in figure 2, the Fe(II) ion adopts a distorted octahedron coordination geometry,



**Figure 3.** The 2D flat layer packed in the *bc* plane (top) and packing between *bc* planes (bottom) for **1-S** at 120 K. Supramolecular interactions are shown in orange dotted lines.

with four N atoms from a tetradentate ligand  $L_{5Me}$  and two N atoms from two  $NCE^-$  anions at *cis* positions. Only half of the molecule is present in the asymmetric unit due to a 2-fold axis passing through the Fe(II) atom.

At 120 K, the average Fe–N bond lengths are  $\sim 1.97$  Å for **1-S** and **1-Se**, consistent with Fe(II) centers in LS state (see the crystallographic data in table S2). The Fe–N  $\equiv$  C(E) angles are almost linear, with values of  $\sim 178^\circ$  in both complexes. The octahedral distortion parameters  $\Sigma$  [32] of  $\sim 38^\circ$  indicate a small deviation of the coordination sphere from a regular octahedron geometry. At 298 K, the average Fe–N bond lengths increase dramatically to 2.17 Å for **1-S** and 2.16 Å for **1-Se**, in agreement with Fe(II) ions in HS state. The Fe–N  $\equiv$  C(E) angles decrease slightly to  $\sim 175^\circ$  for **1-S** and  $\sim 173^\circ$  for **1-Se**. The  $\Sigma$  values increase notably to  $\sim 82^\circ$ , as seen in many SCO complexes that HS Fe(II) has a more distorted coordination sphere.

The crystal packing of **1-S** at 120 K was discussed as a representative. The most significant short contacts between the  $[Fe(L_{5Me})(NCS)_2]$  molecules are found between the S atoms and H atoms attached to  $N_{amine}$ , which are significantly shorter (0.5 Å) than the sum of van der Waals (vdW) radii. Besides, these S atoms also form short contacts with H atoms attached

to ethylene group, with distances  $\sim 0.3$  Å shorter than the sum of vdW radii. These interactions connect the molecules into a 2D supramolecular layer parallel to the *bc* plane (figure 3, top). While between the *bc* layers only quite weak interactions were found (figure 3, bottom), with the distance between the interactional atoms slightly smaller (within 0.1 Å) than the sum of vdW radii. No  $\pi \dots \pi$  stacking was found between the molecules.

According to our systematic studies on the similar  $[Fe(L)(NCE)_2]$  mononuclear complexes, it has been found that they usually show a great structural diversity with different molecular arrangements and crystal packing. Although  $NCS^-$ ,  $NCS^-$  and  $NCBH_3^-$  have similar structural features, a substitution of these ligands, usually results in a change of the solid-state structure. The current research hence provides a second example among this family that all the three  $NCE^-$  derivatives are strictly isostructural. In the other isostructural series  $[Fe(L_{4Cl})(NCE)_2]$  [25], strong N–H...E interactions were also found, highlighting their important role in stabilizing different derivatives in a uniform crystal packing.

### 2.3. Magnetic properties

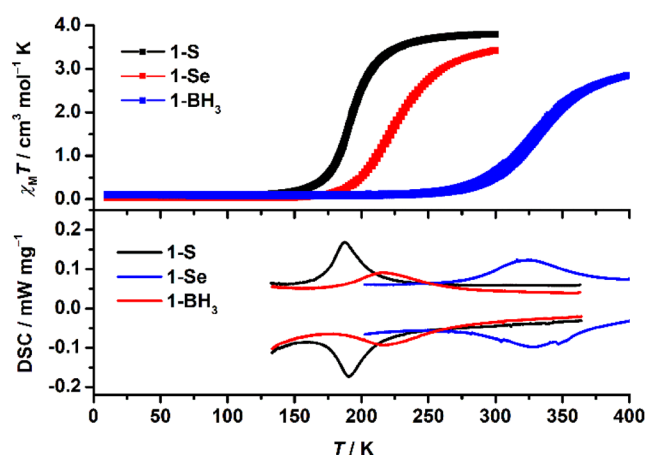
Magnetic susceptibility data were recorded on the crystalline samples between 10 and 300 K for **1-S** and **1-Se**, and between 10 and 400 K for **1-BH<sub>3</sub>**, in both cooling and heating modes at a temperature scan rate of 2 K  $min^{-1}$ . The results are shown in the top of figure 4 in the form of  $\chi_M T$  versus  $T$  plots (where  $\chi_M$  is molar magnetic susceptibility and  $T$  is temperature). All the three complexes undergo a complete one-step SCO, giving the first example among this  $[Fe(L)(NCE)_2]$  family that all the three derivatives, i.e. E = S, Se, and  $BH_3$ , are SCO active.

The  $\chi_M T$  value of **1-S** at 300 K is 3.79  $cm^3 mol^{-1} K$  and decreases gradually to 3.62  $cm^3 mol^{-1} K$  at 240 K, indicating Fe(II) ions are in their HS state. Upon further cooling, the  $\chi_M T$  value drops gradually to 0.15  $cm^3 K mol^{-1}$  at 140 K and reaches 0.08  $cm^3 K mol^{-1}$  at 10 K, corresponding to Fe(II) ions in their LS state. No obvious thermal hysteresis loop was found during cooling and heating cycles. The  $T_{1/2}$  value is 193 K.

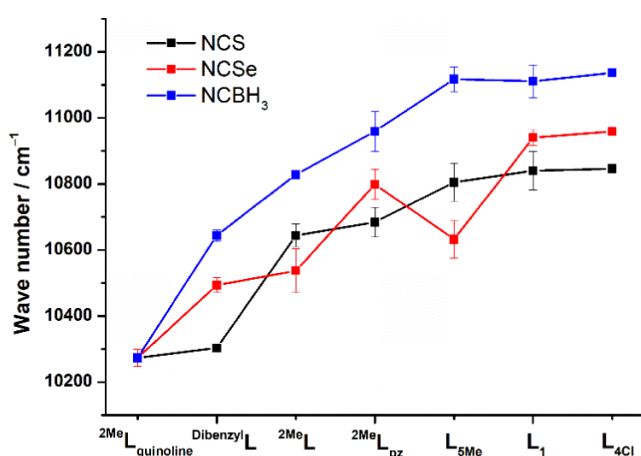
**1-Se** exhibits a similar SCO behaviour with higher  $T_{1/2}$  at 226 K. The  $\chi_M T$  values are 3.42 and 0.02  $cm^3 mol^{-1} K$  in HS and LS states, respectively. The  $\chi_M T$  value of **1-BH<sub>3</sub>** at 400 K is 2.86  $cm^3 mol^{-1} K$ , indicating that most of the Fe(II) ions are in the HS state. Its  $T_{1/2}$  value, 330 K, is the highest among these three complexes.

### 2.4. DSC studies

DSC data were collected for **1-S**, **1-Se** and **1-BH<sub>3</sub>** at a sweep rate of 5 K  $min^{-1}$  (figure 4, bottom). An exothermic peak was observed during the cooling cycle and in the subsequent heating cycle an endothermic peak was observed, corresponding to a reversible SCO process. The  $T_{1/2}$  values determined from DSC for the three complexes (189 K, 216 K, and 322 K, respectively) agree with the magnetic results. The  $\Delta H$  values were estimated to be 14.1, 13.4 and 14.6  $kJ mol^{-1}$  and



**Figure 4.** Top: temperature dependence of the  $\chi_M T$  product for **1-S**, **1-Se** and **1-BH<sub>3</sub>**. Bottom: differential scanning calorimetry (DSC) for **1-S**, **1-Se** and **1-BH<sub>3</sub>**.



**Figure 5.** The LF splitting (10Dq) values obtained from the  ${}^3A_{2g} \rightarrow {}^3T_{2g}$  transition of [Ni(L)(NCE)<sub>2</sub>] complexes in dimethyl formamide solution.

the  $\Delta S$  values were estimated to be 74.9, 62.0 and 45.3 J K<sup>−1</sup> mol<sup>−1</sup> for **1-S**, **1-Se**, and **1-BH<sub>3</sub>**, respectively.

## 2.5. Discussion of the SCO property-structural relationships

Including the current three complexes, 21 structures with a common formula, [Fe(L)(NCE)<sub>2</sub>], have been reported, where L is a tetradentate ligand as shown in scheme 1. In addition, a related complex, [Fe(L<sub>5Br</sub>)(dca)<sub>2</sub>], has also been reported by us that is isolated in three polymorphs (dca is dicyanamide) [26]. Various SCO properties, including gradual spin conversion and first-order spin transition with hysteresis, have been observed. The  $T_{1/2}$  values span a large temperature range from 70 K to 353 K. Some of the structures remain in HS state over all temperatures.

Relatively strong hydrogen-like bonding involving the S/Se/B atoms is present in [Fe(L<sub>5Me</sub>)(NCE)<sub>2</sub>], [Fe(L<sub>1</sub>)(NCBH<sub>3</sub>)<sub>2</sub>] [28] and [Fe(L<sub>4Cl</sub>)(NCE)<sub>2</sub>] [25], however, only gradual SCO curves were observed for these complexes. Such interactions are absent in the three complexes based on 2MeL ligand [27, 30, 31] due to the methyl substitution at the N<sub>amine</sub> site,

while all these complexes show hysteretic SCO. Alternatively,  $\pi \cdots \pi$  interactions were observed for cooperative SCO complexes among this family except for [Fe(L<sub>5Me</sub>)(NCE)<sub>2</sub>], which undergoes a crystallographic phase transition upon spin transition. Strong hydrogen bonds (N–H $\cdots$ N) are present in the two polymorphs of [Fe(L<sub>5Br</sub>)(dca)<sub>2</sub>] showing hysteretic spin transition [26]. These facts indicate that  $\pi \cdots \pi$  interactions and hydrogen bonding play a more important role in transmitting elastic interactions between SCO centers while strong supramolecular interactions involving S/Se/B atoms are not sufficient enough to increase cooperativity.

The current three complexes all undergo SCO at high temperatures ( $T_{1/2} = 193/226/330$  K for **1-S/1-Se/1-BH<sub>3</sub>**) compared with other analogues. We have stated previously that the electronic nature and the coordination arrangement of the NCE<sup>−</sup> co-ligands play a decisive role on the  $T_{1/2}$  values of this [Fe(L)(NCE)<sub>2</sub>] family [29]. Almost linear Fe–N  $\equiv$  C(E) angle in **1-E** corroborates again the relationship between the coordination arrangement of NCE<sup>−</sup> and the transition temperature. A shift of  $T_{1/2}$  to higher temperatures from NCS<sup>−</sup>, NCSe<sup>−</sup> to NCBH<sub>3</sub><sup>−</sup> agrees with the increasing ligand field (LF) strength imposed by the co-ligands. However, a small increase of 33 K between NCS<sup>−</sup> and NCSe<sup>−</sup> derivatives and a large increase of 104 K between NCSe<sup>−</sup> and NCBH<sub>3</sub><sup>−</sup> derivatives are unusual. From the literature survey increases of 50–90 K between NCS<sup>−</sup> and NCSe<sup>−</sup> derivatives and 30–50 K between NCSe<sup>−</sup> and NCBH<sub>3</sub><sup>−</sup> derivatives have been found if they are isostructural [25]. It should be noted that more examples are called for, in order to have a better understanding about to what extent the electronic effect of these NCE<sup>−</sup> ligands could play on the conversion temperatures.

The optical spectra (figure 5) for the [Ni(L)(NCE)<sub>2</sub>] analogous complexes in the range of the  ${}^3A_{2g} \rightarrow {}^3T_{2g}$  transition were examined in order to compare the LF strength. In most of the cases, an increasing tendency of the LF splitting were observed upon NCS<sup>−</sup>, NCSe<sup>−</sup> and NCBH<sub>3</sub><sup>−</sup> substitutions. However, the LF for [Ni(DibenzyL)(NCSe)<sub>2</sub>] is unexpectedly the smallest, among the three NCE<sup>−</sup> derivatives. This may be related to the unusual  $T_{1/2}$  shift observed in the solid state. Concerning the local influence of the tetradentate ligand, substitution at the amine N site results in a decrease of the LF. The significant steric effect in 2MeL<sub>quinoline</sub> should also contribute to its small LF. Slight enhancement in LF was observed from L<sub>5Me</sub>, L<sub>1</sub> to L<sub>4Cl</sub>. A direct comparison of the SCO properties in the solid state between [Fe(L<sub>5Me</sub>)(NCE)<sub>2</sub>] (**1-BH<sub>3</sub>**) and [Fe(L<sub>1</sub>)(NCBH<sub>3</sub>)<sub>2</sub>] [28] confirms a stronger LF for L<sub>1</sub> than L<sub>5Me</sub>. The crystal packing effects can be excluded since these two complexes are isostructural. Electron-donating pyridyl substituents would weaken the LF by enhancing ligand–metal  $\pi$ -donation and stabilize the HS state of the complex [22, 33–35].

## 3. Conclusions

In conclusion, we have synthesized a series of isostructural Fe(II) complexes based on the tetradentate ligand L<sub>5Me</sub> and NCE<sup>−</sup> co-ligands (E = S, Se, BH<sub>3</sub>). Strong N–H $\cdots$ E



interactions between adjacent molecules, with the distances 0.5 Å shorter than the sum of vdW radii, may contribute to stabilize a uniform crystal packing among the three derivatives. However, these supramolecular interactions do not give rise to strong cooperativity. **1-S** displays a gradual SCO curve with  $T_{1/2}$  value of 193 K. The replacement of  $\text{NCS}^-$  by  $\text{NCSe}^-$  and  $\text{NCBH}_3^-$  results in increases of  $T_{1/2}$  by ca. 33 K and 137 K, respectively. The relatively high conversion temperatures are consistent with the large  $\text{Fe-N} \equiv \text{C(E)}$  angles (close to  $180^\circ$ ).

The LF strengths of the tetradentate ligands and the  $\text{NCE}^-$  co-ligands were estimated by the optical spectra of the  $[\text{Ni(L)}(\text{NCE})_2]$  analogues. In most of the cases  $\text{NCS}^-$  imposes the weakest LF strength while  $\text{NCBH}_3^-$  imposes the strongest. However,  $[\text{Ni(L}_{5\text{Me}})(\text{NCSe})_2]$  deviates from this general trend, which still needs further studies for a better understanding. Substitution at the  $\text{N}_{\text{amine}}$  site imposes a larger change of the LF than that at the pyridyl ring, which is reasonable due to a direct modification of the donor atom in the previous case. Electron-donating pyridyl substituent results in a slightly weakening of the LF. The insights into the factors governing the LF and cooperativity for this mononuclear family will aid in the rational design and fine tuning the properties of new switchable materials.

## Acknowledgments

This work was supported by the National Natural Science Foundation of China (21871140 and 21401104).

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