



HAL
open science

A new family of diamagnetic macrocyclic Fe(II) compounds exhibiting the LIESST effect at high temperatures.

Hongfeng Wang, Cédric Desplanches, Philippe Dagault, Jean-François Létard

► **To cite this version:**

Hongfeng Wang, Cédric Desplanches, Philippe Dagault, Jean-François Létard. A new family of diamagnetic macrocyclic Fe(II) compounds exhibiting the LIESST effect at high temperatures.. Dalton Transactions, 2014, 43 (41), pp.15346-15350. 10.1039/c4dt01837k . hal-01074580

HAL Id: hal-01074580

<https://hal.science/hal-01074580>

Submitted on 22 Jun 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

A new family of diamagnetic macrocyclic Fe(II) compounds exhibiting the LIESST effect at high temperatures

Hongfeng Wang,^{a,b,c} Cédric Desplanches,^{*a,b} Philippe Dagault^{a,b} and Jean-François Létard^{a,b}

The photomagnetic properties of a new Fe(II) macrocyclic family $[\text{Fe}(\text{L}_{xyz}\text{N}_5)(\text{CN})_2] \cdot n\text{H}_2\text{O}$ were investigated with respect to the $T(\text{LIESST})$ versus $T_{1/2}$ relationship. These compounds are diamagnetic below 400 K with $T(\text{LIESST})$ values above 100 K, which indicates that this family presents an unconventional LIESST effect that is much higher than the expected $T_0 = 180$ K line for macrocyclic complexes.

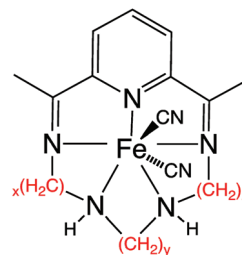
DOI: 10.1039/XXXXXXXXXX

Introduction

Spin crossover (SCO) phenomena continue to be an attractive area of many recent studies.¹ Complexes exhibiting SCO properties can change their spin state by external perturbation such as change of temperature or pressure, light irradiation or guest molecules.² These compounds are especially interesting for their potential application for data storage.³ In 1984, Decurtins *et al.*⁴ have observed a light-induced low-spin (LS) \rightarrow high spin (HS) transition during which the molecules can be quantitatively trapped in the excited HS state at sufficiently low temperatures. This so-called LIESST (light-induced excited spin-state trapping) effect is normally observed at temperatures lower than 80 K,¹ which prevents a direct utilization for data storage. The importance of this phenomenon has led to the introduction of the standard $T(\text{LIESST})$ measurement, which aims to estimate the limiting temperature above which the photoinduced HS metastable state is erased.⁵ Consequently, the increase of $T(\text{LIESST})$ with the ultimate objective of reaching room temperature becomes one of the main topics in the field of LIESST phenomenon. In order to search for key factors to increase the $T(\text{LIESST})$ value, a $T(\text{LIESST})$ versus $T_{1/2}$ database was established by comparing numerous SCO complexes.^{6–8} As a result, an inner coordination sphere has been identified as the effective factor to influence the $T(\text{LIESST})$ value. Following this approach, macrocyclic com-

plexes particularly attracted the attention due to the high coordination degree of the ligand. Tremendous efforts have thus been recently contributed to interpret their fascinating SCO and high $T(\text{LIESST})$ value behaviors.^{9–11} However, since the LIESST effect is the transformation from the LS to the HS state, it means that the target system should exhibit a quite high $T(\text{LIESST})$ value and should be in the LS state at room temperature. Unfortunately, such a kind of system is extremely uncommon with regard to the inverse energy-gap law.¹² Thus the development of LS complexes with the LIESST effect becomes an urgent demand.

The purpose of the present study is to fill this demand. A family of macrocyclic compounds $[\text{Fe}(\text{L}_{xyz}\text{N}_5)(\text{CN})_2]$ with $x,y,z = 2,3,2; 3,2,3$ or $2,2,3$ (Scheme 1) have been prepared and characterized based on previous work,¹¹ where the amine has been modified. Their magnetic properties have been investigated in the temperature range from 4 K to 500 K. The optical and photomagnetic properties are discussed in comparison with the previously reported macrocyclic complex $[\text{Fe}(\text{L}_{222}\text{N}_5)(\text{CN})_2] \cdot \text{H}_2\text{O}$ (compound 1).



Scheme 1 Representation of $[\text{Fe}(\text{L}_{xyz}\text{N}_5)(\text{CN})_2]$ with $x, y, z = 2,2,2; 2,3,2; 2,2,3$ or $3,2,3$ for compounds 1, 2, 3, and 4 respectively.

^aCNRS, ICMCB, UPR 9048, F-33600 Pessac, France.

E-mail: desplanches@icmcb-bordeaux.cnrs.fr

^bUniv. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France

^cWNLO, Huazhong Uni. of Sci. & Tech., Wu Han 430074, China

Results and discussion

Three compounds $[\text{Fe}(\text{L}_{xyz}\text{N}_5)(\text{CN})_2] \cdot n\text{H}_2\text{O}$ with $x,y,z = 2,3,2$ $n = 2.5$ (compound 2); $2,2,3$ $n = 2.5$ (compound 3) or $3,2,3$ $n = 1.5$ (compound 4) were obtained following a procedure described by Nelson *et al.*¹³ The chemical analysis and TGA measurements (see ESI†) confirm the quality of the compound and the presence of one or more water molecules per Fe(II) center. Attempts to obtain single crystals of 2, 3 and 4 using different methods and solvents for solving the structure of the sample were not successful. Magnetic measurements in SQUID show that the three compounds are at low spin ($\chi_{\text{M}}T = 0$) from 300 K down to 4 K. These results are in line with the previously reported magnetic data by Nelson¹³ for compound 2. In order to search for an eventual thermal spin conversion at higher temperature, the magnetic susceptibility has been recorded up to 500 K using a high-temperature susceptometer. The $\chi_{\text{M}}T$ versus T plot is reported in Fig. 1 for compound 3.

Whereas the compound remains diamagnetic below 420 K, a sharp increase is observed above this value for the $\chi_{\text{M}}T$ product, this product reaching the value of $1.25 \text{ cm}^3 \text{ K mol}^{-1}$ at 475 K. If the compound is further cooled, the diamagnetic state is never recovered ($\chi_{\text{M}}T = 0.75 \text{ cm}^3 \text{ K mol}^{-1}$ at 10 K).

For compounds 1, 2 and 4, the magnetic behaviors are similar to compound 3 with the increase of $\chi_{\text{M}}T$ value at 400 K, 420 K and 450 K, respectively (see Fig. S1–S3, ESI†). Moreover, when those complexes are left under an ambient atmosphere for several months after the above experiments, the $\chi_{\text{M}}T$ values for all the four complexes are still around $1 \text{ cm}^3 \text{ K mol}^{-1}$ at room temperature, which further confirms that the increase of $\chi_{\text{M}}T$ values is irreversible. There are two possible reasons for this irreversible increase of $\chi_{\text{M}}T$ value. The first one is that the complexes exhibit an extremely large hysteresis of more than 400 K. Nevertheless, this idea appears unrealistic, with regard to the hysteresis loop up to now encountered for SCO materials that never exceeded 60 K.¹⁴ The second possibility is that a decomposition and/or dehydration process takes place at high temperature, which means that the chemical nature of the complexes has been irreversibly modified.

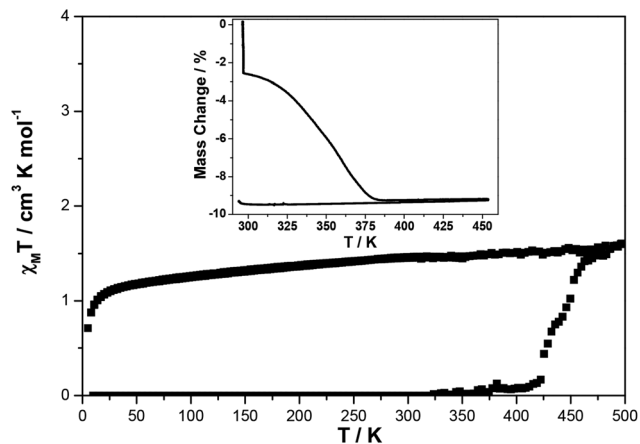


Fig. 1 $\chi_{\text{M}}T$ versus T plot for 3. Inset: TGA for 3.

In order to identify the process that occurs at high temperature, TGA measurements have been carried out. For compound 3 (Fig. 2, insert), a mass loss of 2.5% is observed under nitrogen flux at 300 K. An increase of the temperature up to 380 K leads to a further mass loss of 7.0%, the mass of the sample being stable above 380 K. The total loss observed in TGA (9.5%) is in reasonable agreement with the 2.5 water molecules proposed in the chemical formula (calculated mass loss: 10.2%). Thus the mass loss of compound 3 can be divided into two origins: (1) the loss at room temperature can be attributed to the desorption of water molecules at the surface; (2) the loss during the increase of temperature can be attributed to the water loss in the crystal lattice. Similar origins can be attributed in compounds 1, 2 and 4 with different percentages of mass loss (see Fig. S1–S3 insets, ESI†).

A first correlation between TGA and magnetism has been discussed in the previous paper describing compound 1.¹¹ The mass loss occurs for the different compounds at a temperature below 400 K. On the other hand, the increases in $\chi_{\text{M}}T$ for the different compounds occur above 400 K. It thus seems that the process that takes place at high temperature and that is responsible for the modification of the magnetic properties of the compound is not simply a solvent loss, but is possibly a partial decomposition of the iron complex. It is also very likely that dehydration and some decomposition of the product occur in the same temperature range.

Since the SCO phenomenon, especially the LIESST effect can be probed by the optical properties of the material,^{15,16} the total reflectivity as a function of the temperature has thus been recorded for all the four compounds (Fig. 2). For 1 (Fig. 2a) upon cooling, the total reflectivity shows a sharp increase at around 100 K. The maximum is found to be at *ca.* 60 K for the cooling branch. On further cooling, the total reflectivity signal remains stable until 10 K. Upon warming a sharp decrease of the intensity can be found at *ca.* 100 K. At 175 K the intensity of the warming branch reaches a similar level as compared to the cooling branch. This type of behavior

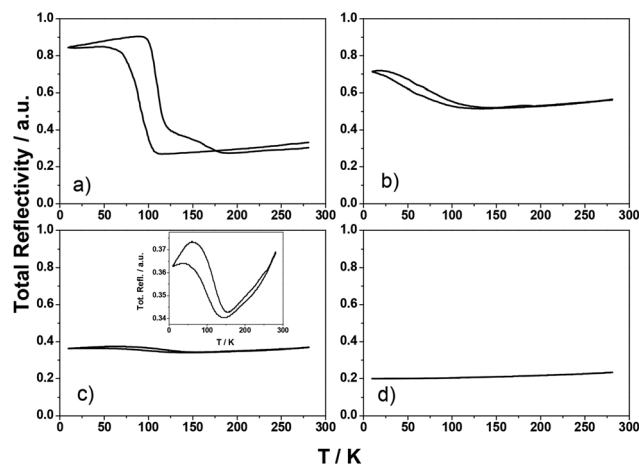


Fig. 2 Total reflectivity of 1 (a), 2 (b), 3 (c) and 4 (d). Inset: enlarged plot for total reflectivity of 3.

corresponds to light induced thermal hysteresis (LITH) introduced in 1998 for the $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$ complex.¹⁷ In this case the width of the LITH loop is 30 K. For **2** (Fig. 2b), the intensity of total reflectivity increases gradually starting at *ca.* 100 K upon cooling. On warming, the intensity decreases gradually from 10 K, merging with the cooling branch at *ca.* 120 K. In comparison with **1**, the size of the thermal hysteresis is smaller and the magnitude of the change in reflectivity at low temperature is about 4.5 times smaller. Moreover, the shape of the LITH loop is really gradual. For **3** (Fig. 2c), under irradiation the change of reflectivity signal is very small, giving a tiny LITH loop at around 100 K (Fig. 2c inset). The intensity of the LITH loop is about 10 times smaller than the one for **2**. Finally for **4** (Fig. 2d) no change of reflectivity is observed.

From previous investigations on **1**, the LITH loop and the LIESST effect are strongly correlated in these diamagnetic complexes. Thus the observation of LITH in **2** and **3** can be attributed to the presence of the LIESST effect, which can also be confirmed by the changes in the absorption spectra as a function of wavelength at different temperatures (see Fig. S4–S5, ESI†). Moreover, from the warming branch of the LITH loop, it may anticipate a relatively long lifetime of the photo-induced HS state for **2** and **3** as the change of reflectivity occurs at around 100 K. Nevertheless, the change of intensity in reflectivity is strongly dependent on the nature of the ligands. Compound **1** shows the highest level of change. When the chain length of the ligands increases, from **2** to **4**, a decrease in the intensity is observed and a decrease of the size of the LITH loop is also observed.

Fig. 3 presents the photomagnetic experiments performed on **1**, **2** and **3**. These measurements have been carried out following the standard procedure.^{5–8} The maximum $\chi_{\text{M}}T$ value reached after irradiation depends on the nature of the compounds: $3.5 \text{ cm}^3 \text{ K mol}^{-1}$ for **1**, $2.5 \text{ cm}^3 \text{ K mol}^{-1}$ for **2** and $1.5 \text{ cm}^3 \text{ K mol}^{-1}$ for **3**. The photoconversion of the compounds

requires a long time of photo-irradiation and quite large power of irradiation: 2 hours (5 mW cm^{-2}) for **1**, 3 hours (20 mW cm^{-2}) for **2** and 10 hours (20 mW cm^{-2}) for **3**. As far as **4** is concerned, the irradiation during several hours (20 mW cm^{-2}) did not lead to any increase of magnetic susceptibility, and thus its $T(\text{LIESST})$ value cannot be measured.

$T(\text{LIESST})$ measurements are therefore performed for the compounds **1**, **2** and **3**. After reaching the photosaturation at 10 K under irradiation, the laser was switched off and the temperature increased at a defined rate of 0.3 K min^{-1} . For complex **1**, the shape and the $T(\text{LIESST})$ value (Fig. 3a and inset 1) are in agreement with the previous work.¹¹ For complex **2**, the shape of the $T(\text{LIESST})$ curve displays two steps at 85 K and 103 K respectively (Fig. 3b and inset 2). For **3**, the $T(\text{LIESST})$ value is estimated at 108 K (Fig. 3c and inset 3). The two $T(\text{LIESST})$ values are related to the domains of sample with different levels of photoconversion saturation (see Fig. S6, ESI†).

Concerning the stability of the photoinduced state, the three evaluated complexes **1**, **2** and **3** display a similar $T(\text{LIESST})$ value of about 100 K. Thus the nature of the ligand in this macrocyclic family affects the photoexcitation (illustrated by the various levels of photosaturation reached), but not the stability of the lifetime. The three complexes display exceptional long lived lifetime for Fe(II) materials in the LS state at room temperature. In fact, if we consider the inverse energy-gap law approach,¹² it is not expected that an Fe(II) material with a LS state at room temperature presents a photo-induced HS state with a long lifetime.

One of the reasons for such atypical stability of the photo-induced HS state may be linked to the role of coordination degree of macrocyclic ligands. It has been previously demonstrated that the $T(\text{LIESST})$ versus $T_{1/2}$ relationship depends on the nature of the ligand surrounding the metal ion (through the denticity, rigidity of the ligand^{7,8} and/or distortion¹⁸). $T(\text{LIESST})$ exhibits, as a first approximation, a linear relationship with the thermal spin transition $T_{1/2}$: $T(\text{LIESST}) = T_0 - 0.3T_{1/2}$.⁷ T_0 is an empirical temperature parameter that is related to the denticity of the ligands surrounding the Fe(II). For monodentate ligands $T_0 = 100 \text{ K}$, for bidentate ligands $T_0 = 120 \text{ K}$, and for tridentate ligands $T_0 = 150 \text{ K}$. An analogous relationship has been observed in Prussian Blue analogues, with $T_0 = 200 \text{ K}$. For macrocyclic ligands, one point has been added on a virtual line with $T_0 = 180 \text{ K}$, *i.e.* $[\text{Fe}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2] \cdot \text{H}_2\text{O}$ ($\text{L}_{222}\text{N}_3\text{O}_2 = 2,13\text{-dimethyl-6,9-dioxa-3,12,18-triazabicyclo [12.3.1]octadeca-1(18),2,12,14,16-pentaene}$). This compound is closely related to **1**, with the two central NH moieties of the amine being replaced by oxygen atoms.⁹ This compound presents a high $T(\text{LIESST})$ of 130 K, the highest to date reported for a mononuclear Fe(II) complex. Therefore one explanation of the long-lived photoinduced HS state for these diamagnetic complexes can be traced to the high denticity of the macrocyclic ligand. A $T_{1/2}$ cannot be defined for **1**, **2** and **3**. Indeed, the thermal dehydration and/or decomposition of the compounds above 400 K prevents the observation of a genuine thermal spin conversion for the hydrated compound. If such a

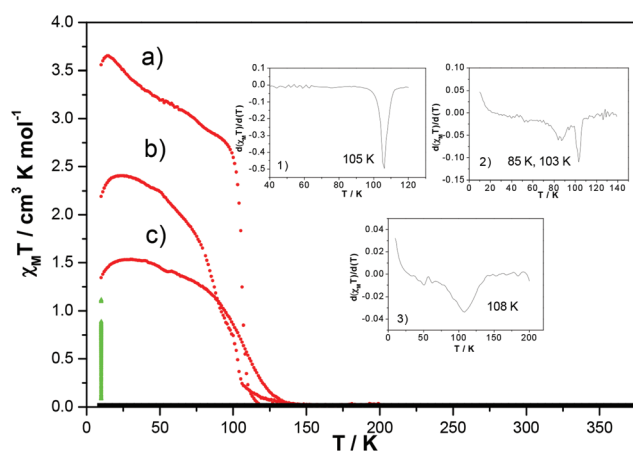


Fig. 3 $T(\text{LIESST})$ measurements of **1**, **2** and **3** plotted in (a), (b), and (c) respectively. Black points = data recorded in the dark without irradiation (along line $\chi_{\text{M}}T = 0$); green points = data recorded under irradiation; red points = data registered by increasing the temperature after irradiation. Inset: plot of $d\chi_{\text{M}}T/dT$ vs. T indicating $T(\text{LIESST})$ values of **1**, **2** and **3** in (1), (2), and (3), respectively.

hypothetical spin conversion was existing for hydrated compounds, the $T_{1/2}$ value would then be higher than 400 K. Following the relationship $T(\text{LIESST}) = T_0 - 0.3T_{1/2}$ with $T_0 = 180$ K for macrocyclic ligands, a $T(\text{LIESST})$ value lower than 60 K should be expected. It is interesting to note that the $T(\text{LIESST})$ values observed are notably higher.

A second reason for the high $T(\text{LIESST})$ may be linked to a possible change in coordination of the Fe(II) metal ion. Indeed, in most of the Fe(II) spin crossover compounds, the metal center remains six coordinated, whatever the spin state. Only the mean Fe–N distance changes from around 2.0 Å in the LS state to 2.2 Å in the HS state. However, one exception has been found in the previously studied oxygen-containing macrocyclic compound $[\text{Fe}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2] \cdot \text{H}_2\text{O}$. It has been determined from the crystal structure that the iron is seven coordinated in the HS state and that it is six coordinated in the LS state.^{9e} For the presented diamagnetic complexes, the crystal structure of **1** in the LS state has been obtained,¹⁹ of which the iron is six coordinated. Since the direct observation of light-induced HS structures involves the complexity of photo-irradiation in single crystal X-ray diffractometer at liquid helium temperature, the attempts for **1** thus still need to be carried on. Nevertheless, a seven coordinated structure of **1** in the HS state has been observed in a molecular magnet using **1** as a building block.¹⁹ These observations indicate the possibility of light-induced structural transition with a change of coordination in **1**, **2** and **3**. Definitely, in this aspect, the structures of the complexes in both LS and photoinduced HS states need to be systematically investigated. Unfortunately, up to now such information is unavailable and our efforts to obtain single crystals failed. Thus our hypothesis on the 6/7 coordination change remains to be confirmed.

Conclusion

To conclude, we have synthesized and characterized a new Fe(II) macrocyclic family with nitrogen coordination atoms on the macrocyclic unit. In this family, the length of chains between the nitrogen atoms was increased and the consequence on the properties of the individual complex was investigated. From thermal analysis, it was illustrated that all the four studied complexes contained two different types of water molecules, *i.e.* the water of surface adsorption and the water in the crystal lattice. From magnetic studies, it was demonstrated that all the four complexes were in the LS state below 420 K and presented an irreversible increase of the $\chi_M T$ product at around 420 K, which indicated that the magnetic properties of the family are independent of the chain length. We then reported the reflectivity properties of the complexes, which demonstrated that three out of the four complexes could be photoexcited to the metastable HS state. The photomagnetic studies further confirmed the observation from reflectivity, and in addition, the three complexes which presented the LIESST effect and the metastable LIESST state of this family can be observed up to 100 K. However, depending on the

nature of the ligands, the level of photoexcitation is different. It can be expected, following the structures already obtained for compound **1**, that the compounds of this series are probably six coordinated in the LS state and seven coordinated in the metastable photoinduced HS state. In order to check this, single crystals should be obtained and studied at low temperature after irradiation. This work is in progress.

Acknowledgements

The authors acknowledge the ANR and the Aquitaine region.

Notes and references

- 1 For a recent general reference see: *Spin-Crossover Materials: Properties and Applications*, ed. M. Halcrow, John Wiley & Sons, Ltd, 1st edn, 2013.
- 2 (a) O. Kahn and C. Jay Martinez, *Science*, 1998, **279**, 44; (b) P. Gütllich, Y. Garcia and T. Woike, *Coord. Chem. Rev.*, 2001, **219–221**, 839; (c) M. A. Halcrow, *Coord. Chem. Rev.*, 2009, **253**, 2493; (d) A. Bousseksou, G. Molnar, L. Salmon and W. Nicolazzi, *Chem. Soc. Rev.*, 2011, **40**, 3313.
- 3 J.-F. Létard, P. Guionneau and L. Goux-Capes, *Top. Curr. Chem.*, 2004, **235**, 221.
- 4 S. Decurtins, P. Gütllich, C. P. Köhler, H. Spiering and A. Hauser, *Chem. Phys. Lett.*, 1984, **105**, 1.
- 5 J.-F. Létard, P. Guionneau, L. Rabardel, J. A. K. Howard, A. E. Goeta, D. Chasseau and O. Kahn, *Inorg. Chem.*, 1998, **37**, 4432.
- 6 (a) J.-F. Létard, L. Capes, G. Chastanet, N. Moliner, S. Létard and J. A. Real, *Chem. Phys. Lett.*, 1999, **313**, 115; (b) S. Marcén, L. Lecren, L. Capes, H. A. Goodwin and J.-F. Létard, *Chem. Phys. Lett.*, 2002, **358**, 87; (c) N. Shimamoto, S.-i. Ohkoshi, O. Sato and K. Hashimoto, *Inorg. Chem.*, 2002, **41**, 678.
- 7 J.-F. Létard, P. Guionneau, O. Nguyen, J. S. Costa, S. Marcén, G. Chastanet, M. Marchivie and L. Capes, *Chem. – Eur. J.*, 2005, **11**, 4582.
- 8 J.-F. Létard, *J. Mater. Chem.*, 2006, **16**, 2550.
- 9 (a) S. Hayami, Z. Z. Gu, Y. Einaga, Y. Kobayashi, Y. Ishikawa, Y. Yamada, A. Fujishima and O. Sato, *Inorg. Chem.*, 2001, **40**, 3240; (b) H. Liu, A. Fujishima and O. Sato, *Appl. Phys. Lett.*, 2004, **85**, 2295; (c) P. Guionneau, J. S. Costa and J.-F. Létard, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2004, **60**, m587; (d) J. S. Costa, P. Guionneau and J.-F. Létard, *J. Phys.: Conf. Ser.*, 2005, **21**, 67; (e) P. Guionneau, F. Le Gac, A. Kaiba, J. S. Costa, D. Chasseau and J.-F. Létard, *Chem. Commun.*, 2007, 3723.
- 10 (a) J. S. Costa, Ph.D. Thesis, Université Bordeaux I, 2005; (b) H. Wang, Ph.D. Thesis, Université Bordeaux I, 2012.
- 11 J. S. Costa, C. Baldé, C. Carbonera, D. Denux, A. Wattiaux, C. Desplanches, J.-P. Ader and P. Gütllich, *Inorg. Chem.*, 2007, **46**, 4114.

- 12 (a) A. Hauser, *Coord. Chem. Rev.*, 1991, **111**, 275;
(b) A. Hauser, *Comments Inorg. Chem.*, 1995, **17**, 17;
(c) A. Hauser, C. Enaschescu, M. L. Daku, A. Vargas and N. Amstutz, *Coord. Chem. Rev.*, 2006, **250**, 1642.
- 13 S. Nelson, P. McIlroy, C. Stevenson, E. König, G. Ritter and J. Waigal, *J. Chem. Soc., Dalton Trans.*, 1986, 991.
- 14 Spin Crossover in Transition Metal Compounds, in *Topics in Current Chemistry*, ed. P. Gülich and H. A. Goodwin, Springer-Verlag, Berlin-Heidelberg-New York, 2004, vol. I, II and III.
- 15 J.-F. Létard, C. Carbonera, E. Courcot and J. S. Costa, *Bull. Mater. Sci.*, 2006, **29**, 567.
- 16 (a) O. Kahn and E. Codjovi, *Philos. Trans. R. Soc. London, A*, 1996, **354**, 359; (b) E. Codjovi, L. Sommier, O. Kahn and C. Jay, *New J. Chem.*, 1996, **20**, 503; (c) W. Morscheidt, J. Jeftic, E. Codjovi, J. Linares, A. Bousseksou, H. Constant-Machado and F. Varret, *Meas. Sci. Technol.*, 1998, **9**, 1311.
- 17 J.-F. Létard, P. Guionneau, L. Rabardel, J. A. K. Howard, A. E. Goeta, D. Chasseau and O. Kahn, *Inorg. Chem.*, 1998, **37**, 4432.
- 18 (a) P. Guionneau, M. Marchivie, G. Bravic, J.-F. Létard and D. Chasseau, *Top. Curr. Chem.*, 2004, **234**, 97; (b) M. Marchivie, P. Guionneau, J.-F. Létard and D. Chasseau, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2005, **61**, 25; (c) M. Marchivie, P. Guionneau, J.-F. Létard, D. Chasseau and J. A. K. Howard, *J. Phys. Chem. Solids*, 2004, **65**, 17.
- 19 R. Ababei, C. Pichon, O. Roubeau, Y. Li, M. Kalisz, N. Bréfuel, L. Buisson, P. Guionneau, C. Mathonière and R. Clérac, *J. Am. Chem. Soc.*, 2013, **135**, 14840.