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Review

Guidelines to design new spin crossover materials

Chahlae Atmani[a], Fatima El Hajj[a], Samia Benmansour[a,b], Mathieu Marchivie[a], Smail Triki[a,*], Françoise Conan[a], Véronique Patinec[a], Henri Handel[a], Gaelle Dupouy[a], Carlos J. Gómez-García[b]

[a] *UMR CNRS 6521, Université de Bretagne Occidentale, BP 809, 29285 Brest Cedex, France*
[b] *Instituto de Ciencia Molecular (ICMol), Parque Científico, Universidad de Valencia, 46980 Paterna (Valencia), Spain*

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ABSTRACT

This review focuses on new families of spin crossover (SCO) complexes based on polynitrile anions as new anionic ligands or on polyazamacrocycles as neutral macrocyclic ligands. We have shown that the structural and electronic characteristics (original coordination modes and high electronic delocalization) of the polynitrile anions can be tuned by slight chemical modifications such as substitution of functional groups or variation of the negative charge to design new discrete or polymeric SCO systems.

In our ongoing work on the design of new molecular systems based on new ligands that can be fine-tuned *via* chemical modifications, another promising way which has been recently developed in our group concerns the use of new neutral polydentate ligands which are able to tune the ligand field energy around the metal centre. Here we report some recent original Fe(II) SCO complexes based on such polydentate ligands.

1. Introduction

The spin crossover (SCO) phenomenon is a very interesting transition that, due to its molecular character in many compounds, may be used to store information reversibly at a molecular level [1,2] by changing the temperature, applying pressure or irradiating with light [3,4]. It presents much higher transition temperatures than other postulated systems for memory recording at a molecular level, as the single molecule magnets (SMM) [5].

The design of new molecular compounds exhibiting the SCO is thus one of the most relevant and challenging questions in the field of magnetic molecular materials [2,3,6–8]. In such electronic switching materials, when the ligand field energy approaches the thermal energy, the magnetic state can be tuned from the high-spin (HS) to a low-spin (LS) configuration through external stimuli such as temperature, pressure, magnetic field or light irradiation [2,3,6,7,9–11]. This magnetic transition can occur in d^4–d^7 transition metals but the most studied examples to date are those based on the Fe(II) ion (d^6 configuration) for which a paramagnetic–diamagnetic transition from the HS ($S = 2$) to the LS ($S = 0$) state is observed. Among these Fe(II) complexes, those presenting a FeN_6 coordination environment are the most studied ones because the ligand field created by six N atoms around a Fe(II) atom is close to the thermal energy. In the past few years, it has been described in the literature several studies related to the correlations between strong intermolecular interactions (π-stacking,

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* Corresponding author. Tel.: +33 298 016 146.
E-mail address: Smail.Triki@univ-brest.fr (S. Triki).

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hydrogen bonding, Van der Waals interactions and nature of covalent link between the metal active centres) and SCO characteristics such as cooperativity, $T_{1/2}$ and T_{LIESST} (LIESST = *light-induced excited spin-state trapping*) [9–12]. However, studies based on synthetic strategies to design new appropriate ligands for the design of new SCO systems are scarcely reported. Nevertheless, the presence or not of such magnetic transitions in the metal complexes is closely related to the ligand field energy of the complex and then to the nature of the ligands around the metal ion. In this contribution, we present some recent examples of new SCO systems based on the polynitrile anionic ligands or on neutral polyazamacrocycle molecules. We will show how the use of different polynitrile ligands allows the tuning of the SCO transition temperature to values above room temperature in a series of neutral SCO complexes formulated as $[Fe(abpt)_2(X)_2]$, where abpt = 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole and X is a series of polynitrile anionic ligands. We will also show how the change in the anionic charge of the polynitrile ligand in the preceding series has led to the synthesis of the first cyanocarbanion-containing chain compound showing a SCO transition. Finally, we will show how is it possible to prepare SCO compounds from neutral polyazamacrocycle ligands, a novel strategy that opens the door to the synthesis of many more series of compounds by simply chemically modifying the functional groups of the polymacrocycle ligand.

2. Spin crossover (SCO) system based on polynitrile anions

2.1. Introduction

If we look more precisely at the structure of these FeN_6 complexes, most of them fall within one of the two most common types: (a) cationic complexes of formula $[FeL_x]^{2+}$, where L is a neutral N-donating ligand that can be mono-, bi- or tridentate (x would accordingly vary from 6 to 3 and 2) and (b) neutral complexes formulated as $[FeL_xX_2]$, where L is again a neutral ligand that can be mono-, bi- or tetra-dentate (x would accordingly vary from 4 to 2 and 1) and X is monoanionic N-donating ligand such as NCS^-, $NCSe^-$, dca⁻ (dicyanamide anion) and tcnq⁻ (tetracyanoquinodimethane radical anion).

Our contribution in this field concerns the use of polynitrile anionic ligands (Scheme 1) as a source of new N-donating anionic ligands to prepare novel SCO complexes of type (b). Since the polynitrile ligands can be easily tuned by chemical substitution or electrochemical reduction/oxidation, it is worth to study the influence of these characteristics on the SCO transition [13–15].

2.2. Discrete systems

Previous works have shown how the polynitrile ligands are good building blocks to construct 0D, 1D, 2D and 3D magnetic architectures [13]. In this section we will show how these ligands can also be used to modulate the ligand field in spin crossover (SCO) complexes [12]. Given the π-acceptor character of the –CN group, the polynitrile ligands (and in general all the –CN-donating ligands) increase the ligand field and, therefore, are expected to increase the thermal energy needed for the SCO transition (i.e., its transition temperature). Here we will illustrate this fact by using different polynitrile anions as axial ligands in neutral complexes of type (b) with the bi-dentate abpt as the neutral L ligand (abpt = 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole). The so-obtained complexes, formulated as $[Fe(abpt)_2X_2]$ constitute a unique family of SCO complexes where the ligand field and, therefore, the temperature of the SCO transition can be modulated in a large temperature range (from ca. 80 K to above 380 K) by simply changing the axially coordinated ligands, X (which may be NCS^- [16,17], $NCSe^-$ [16,17], dca⁻ [18], tcnq⁻ [19,20], tcm⁻ [12], tcnome⁻ [12], tcnoet⁻ [12], tcnopr⁻ [12], tcnoetOH⁻ [21], tcnopr2OH⁻ [21], tcnopr3OH⁻ [21] and tcnsme⁻ [21], Table 1).

The simplest anions used in the $[Fe(abpt)_2X_2]$ system are the NCS^- (compounds **1**, **2** and **3** in Table 1) and $NCSe^-$ (**4** and **5**). In both cases, two different polymorphs (A and B) are obtained [16,17]. In these polymorphs the molecular entities $[Fe(abpt)_2X_2]$ are identical but they differ in the way they pack in the solid state (see below). The molecular structure in all the compounds displayed in Table 1 is similar: the structure consists of isolated $[Fe(abpt)_2X_2]$ molecules with the Fe(II) ion located in an elongated octahedron where the equatorial plane is formed by two bi-dentate abpt molecules and the two X ligands are located in the axial positions coordinated to the Fe(II) ions through one of the terminal –CN groups (Fig. 1).

Besides the simple NCS^- and $NCSe^-$ anions, other simple anions involving more than one –CN group such as dca⁻ (**6** and **7**) and tcnq⁻ (**8**) have been used [18–20], giving in both cases similar structures to that described for the NCS^- and $NCSe^-$ derivatives. The SCO transition temperatures for all these complexes vary between 86 K for the incomplete transition in the dca⁻ derivative to 280 K for the gradual one in the tcnq⁻ derivative. The NCS^- and $NCSe^-$ derivatives present transition temperatures of 180 and 224 K, respectively for the polymorph A [16], whereas polymorph B of both ligands remains in the high-spin state in the whole temperature range and does not present any SCO transition [17].

More recently, it has been shown that the dicyanamide derivative consists also in two polymorphs denoted A (**6**) and B (**7**), which present distinct magnetic behaviours: polymorph A remains HS where polymorph B undergoes a two-step incomplete spin transition [23,24]. Additionally, a third polymorph of the thiocyanate derivative (**3**) has been identified and presents an incomplete spin transition with 50% of the iron centres remaining in the HS state at low temperature [22].

The introduction in this system of more sophisticated polynitrile anions involving various –CN groups and highly conjugated systems is expected to change the ligand field and, therefore, the SCO transition temperature. Accordingly, we have used polynitrile ligands with three or four –CN groups, to obtain the neutral complexes $[Fe(abpt)_2X_2]$ with X = tcm⁻ (**9**), tcnome⁻ (**10**), tcnoet⁻ (**11** and **12**), tcnopr⁻ (**13**), tcnoetOH⁻ (**14**), tcnopr3OH⁻ (**15**), tcnopr2OH⁻ (**16**) and tcnsme⁻ (**17**) (Table 1). All these complexes, except the

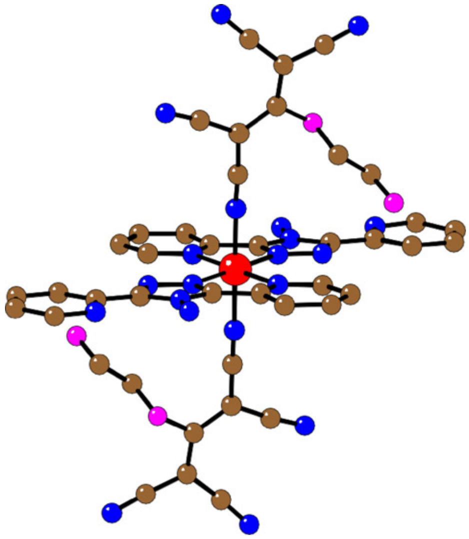
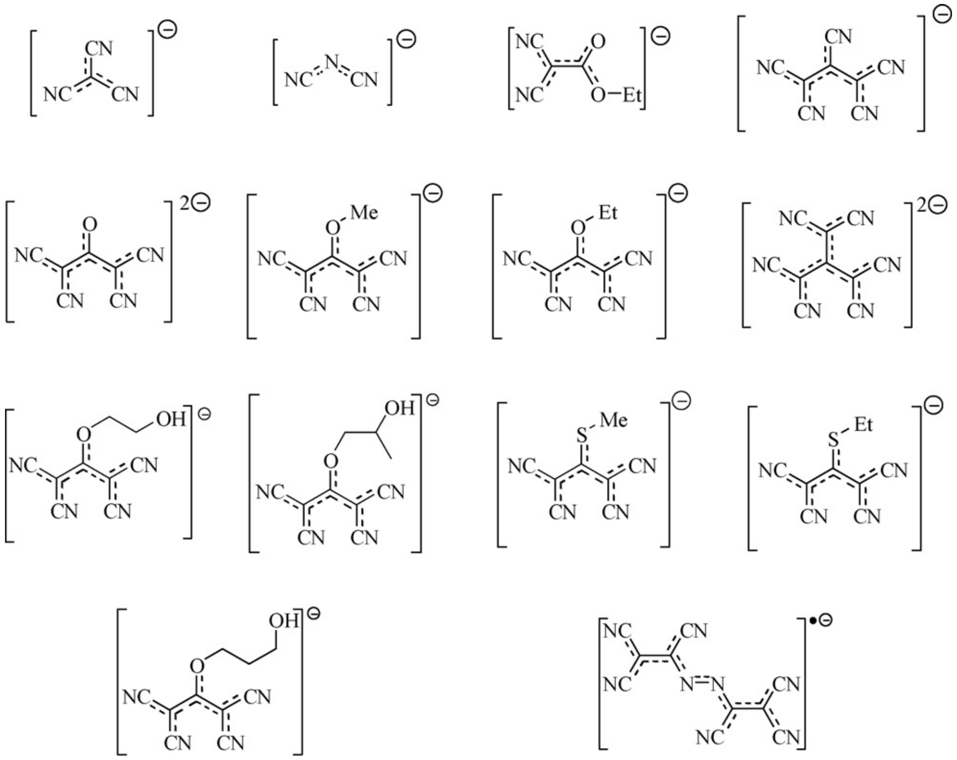


Fig. 1. Typical molecular structure of the neutral complexes $[Fe(abpt)_2X_2]$ (X = tcnoetOH⁻ in this case). Colour code: Fe = red, C = brown, N = blue and O = pink. H atoms have been omitted for clarity.



Scheme 1. Some examples of polynitrile anions.

tcnome$^-$ derivative (**10**), present gradual SCO transitions with $T_{1/2}$ in the range 336–400 K, as indicated by the magnetic measurements (Fig. 2) that show gradual SCO transitions with temperatures so high that in some cases the transition is not complete at 400 K. However for the tcm$^-$ derivative the transition is almost complete at 400 K as also confirmed by the single crystal structural data at 400 K [12].

The molecular structure of all these polynitrile complexes is similar to that described above for the NCS$^-$ and NCSe$^-$ derivatives: discrete [Fe(abpt)$_2$X$_2$] complexes where two equivalent chelating abpt ligands stand in the equatorial plane and two equivalent terminal polynitrile anions (X), acting as terminal ligands, complete the coordination sphere in a *trans*-position (Fig. 1). Each Fe(II) ion is in a distorted [FeN$_6$] octahedral environment.

Careful examination of the intermolecular interactions in these complexes reveals that the main contacts are due to π-stacking interactions between two abpt ligands and two polynitrile anions. The shortest intermolecular contacts for complexes **9**–**12** of the [Fe(abpt)$_2$X$_2$] series (Table 2) are very similar for each abpt overlapping mode (see below). These intermolecular interactions lead to two types of crystal packing: a first one where the abpt ligand of one molecule stacks parallel to those of the neighbouring molecules in the chain (as found in compounds **10** and **11**, Fig. 3b and c, respectively) and a second one where the abpt ligand of one molecule

Table 1
Neutral SCO complexes with the general formula [Fe(abpt)$_2$X$_2$]: overlap mode and SCO parameters (type, $T_{1/2}$ and $\Delta T_{1/2}$).

#	Compound	Phase	X	Overlap mode	Number of π–π close contacts	SCO type	$T_{1/2}$ (K)	Ref.
1	[Fe(abpt)$_2$(NCS)$_2$]	A	NCS$^-$	Frontal	>5	Gradual	180	[16]
2	[Fe(abpt)$_2$(NCS)$_2$]	B	NCS$^-$	Sideways	<3	None (HS)	–	[17]
3	[Fe(abpt)$_2$(NCS)$_2$]	C (Fe1) C (Fe2)	NCS$^-$	Frontal Sideways	>5 <3	Incomplete	>100	[22] [22]
4	[Fe(abpt)$_2$(NCSe)$_2$]	A	NCSe$^-$	Frontal	>5	Gradual	224	[16]
5	[Fe(abpt)$_2$(NCSe)$_2$]	B	NCSe$^-$	Sideways	<3	None (HS)	–	[17]
6	[Fe(abpt)$_2$(dca)$_2$]	A	N(CN)$_2$$^-$	Frontal	>5	None (HS)	–	[18]
7	[Fe(abpt)$_2$(dca)$_2$]	B (Fe1) B (Fe2)	N(CN)$_2$$^-$	Frontal Sideways	>5 <3	Incomplete	86	[23,24]
8	[Fe(abpt)$_2$(tcnq)$_2$]	A	tcnq$^-$	Frontal	>5	Gradual	280	[19,20]
9	[Fe(abpt)$_2$(tcm)$_2$]	A	C(CN)$_3$$^-$	Frontal	>5	Gradual	336	[12]
10	[Fe(abpt)$_2$(tcnome)$_2$]	A	tcnome$^-$	Sideways	<3	None (HS)	–	[12]
11	[Fe(abpt)$_2$(tcnoet)$_2$]	A	tcnoet$^-$	Frontal	>5	Gradual	378	[12]
12	[Fe(abpt)$_2$(tcnoet)$_2$]	B	tcnoet$^-$	Frontal	>5	Gradual	383	[12]
13	[Fe(abpt)$_2$(tcnopr)$_2$]	A	tcnopr$^-$	Frontal	>5	Incomplete	>400	[21]
14	[Fe(abpt)$_2$(tcnoetOH)$_2$]	A	tcnoetOH$^-$	Frontal	>5	Incomplete	>400	[21]
15	[Fe(abpt)$_2$(tcnopr3OH)$_2$]	A	tcnopr3OH$^-$	Frontal	>5	Gradual	360	[21]
16	[Fe(abpt)$_2$(tcnopr2OH)$_2$]	A	tcnopr2OH$^-$	Frontal	>5	Gradual	345	[21]
17	[Fe(abpt)$_2$(tcnsme)$_2$]	A	tcnsme$^-$	Frontal	>5	Gradual	336	[21]

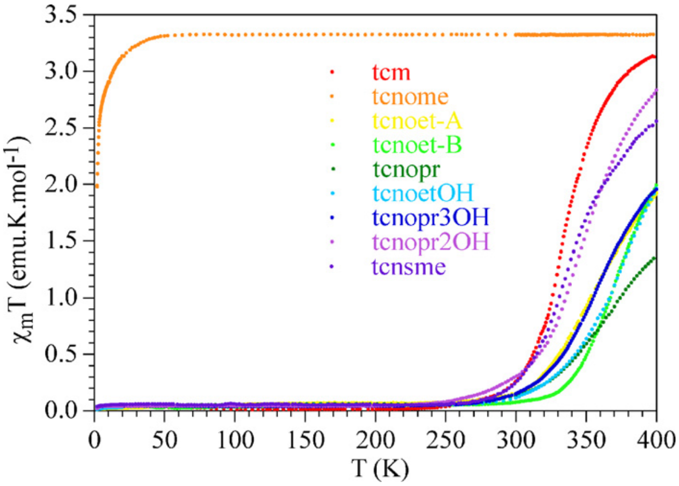


Fig. 2. Thermal variation in the temperature range 2–400 K of the $\chi_m T$ product of the [Fe(abpt)$_2$X$_2$] series (X = tcm$^-$, tcnome$^-$, tcnoet$^-$ (A and B polymorphs), tcnopr$^-$, tcnoetOH$^-$, tcnopr3OH$^-$, tcnopr2OH$^-$ and tcnsme$^-$) showing the SCO transition above room temperature for all complexes except for the tcnome$^-$ derivative.

stack almost perpendicular to those of the neighbouring molecules along the zigzag chain (as found in compounds **9** and **12**, Fig. 3a and d, respectively). As expected, the main difference between the two polymorphs of [Fe(abpt)$_2$(tcnoet)$_2$] (compounds **11** and **12**) lies in these intermolecular arrangements since the packing is parallel in **11** and perpendicular in **12** as clearly shown in Fig. 3c and d, respectively.

In addition to these two different packing modes of the molecules along the chain (parallel and perpendicular), there are also two different overlap modes of the abpt ligands of [Fe(abpt)$_2$X$_2$] complexes belonging to neighbouring chains. These two different overlapping modes are denoted here as "*frontal*" and "*sideways*" π-stacking (Fig. 4).

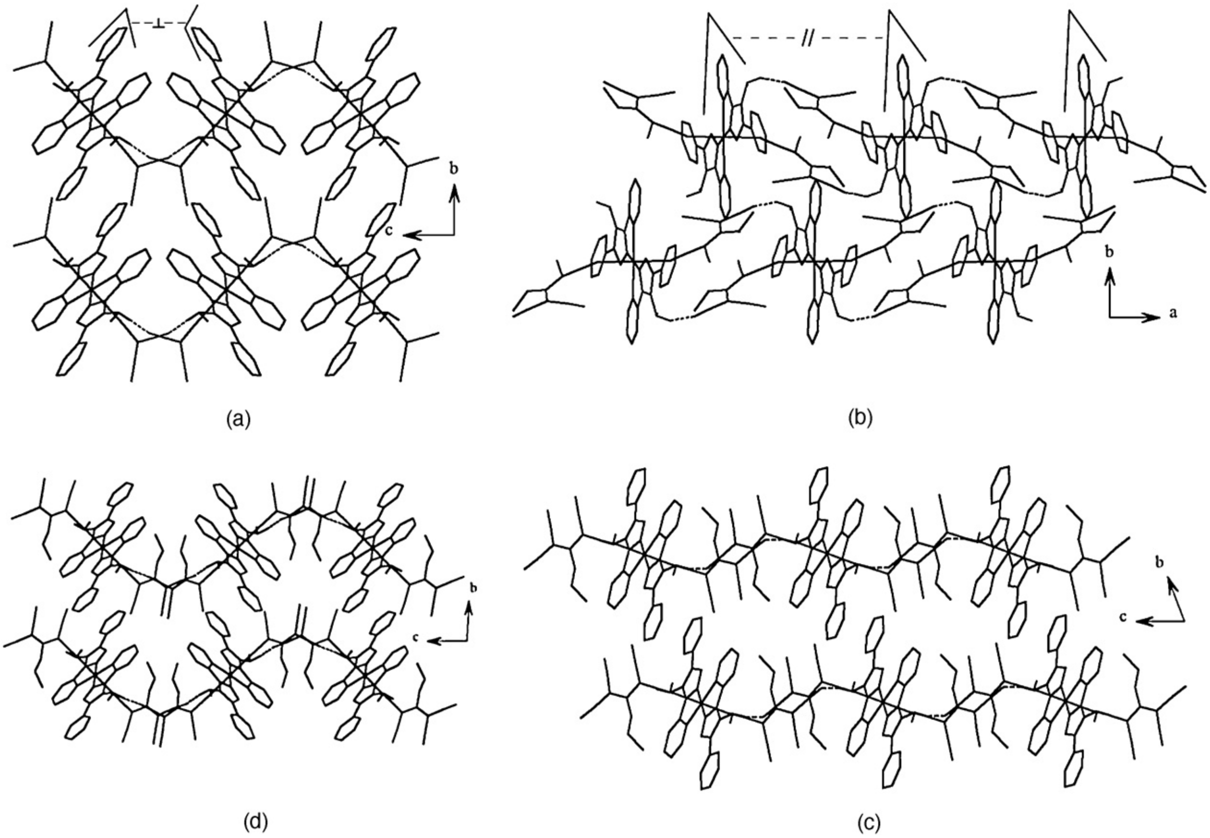
Table 2
Main intermolecular abpt–abpt π-stacking contacts[a] (Å) in compounds **9–12**.

	9	10	11	12	
				Mol. 1	Mol. 2
C···C	3.32(1) 3.36(1) 3.57(1) 3.57(1)		3.37(1) 3.39(1) 3.43(1) 3.52(1) 3.53(1) 3.59(1)	3.32(1) 3.39(1) 3.46(1) 3.48(1) 3.53(1) 3.60(1)	3.38(1) 3.41(1) 3.46(1) 3.60(1)
C···N	3.42(1)	3.36(1) 3.41(1)			3.34(1) 3.38(1) 3.43(1)

[a] Contacts are considered short for C–C (or C–N) <3.60 Å.

It has been shown that complexes **9**, **11** and **12** adopt the frontal π-stacking, whereas complex **10** presents the sideways one [12]. As a consequence, the abpt molecules stack more efficiently in compounds **9**, **11** and **12** than in compound **10**. Indeed, according to Table 2, at least five short C···C or C···N contacts ranging from 3.32 Å to 3.60 Å are observed in the case of frontal π-stacking, while the sideways conformation leads to only two short C···N contacts. Thus, the abpt molecules overlap almost completely for compounds **9**, **11** and **12**, whereas the π-stacking is less efficient in compound **10** and leads to much weaker π–π interactions in this compound.

One of the two abpt overlapping modes are found in all the other complexes and are closely related to the efficiency of the π-stacking as shown in Table 1. One of the most interesting features of this extended series is that among the 17 compounds known to date



(a)

(b)

(d)

(c)

Fig. 3. Crystal packing of the complexes **9** (a), **10** (b), **11** (c) and **12** (d).

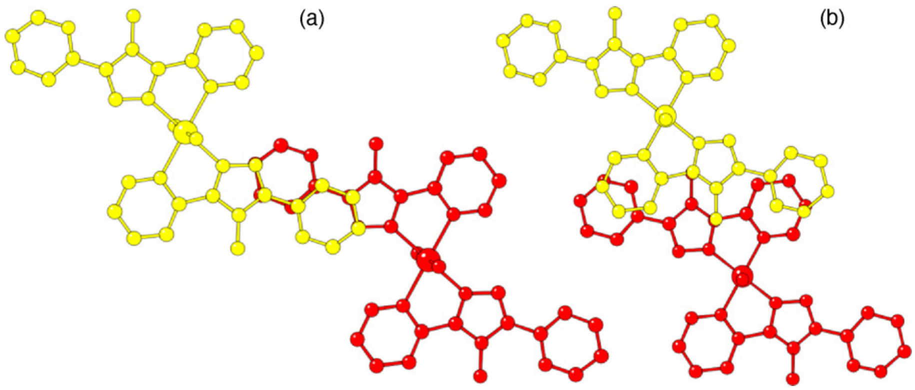


Fig. 4. Sideways (a) and frontal (b) overlap modes of the abpt ligands in the neighbour [Fe(abpt)$_2$X$_2$] molecules (in red and yellow). The polynitrile ligands have been omitted for clarity.

in this series (Table 1), there are only four complexes that do not present SCO transition (the B polymorphs of the NCS$^-$ and NCSe$^-$ derivatives, the tcnome$^-$ derivative and the polymorph A of the dca$^-$ derivative). The key question is why these four derivatives do not present SCO transition whereas the remaining 13 do undergo the SCO transition? The molecular structure is almost identical for the 17 complexes and there are no special features in the molecular structure of the four compounds that do not transit. Therefore, the difference should be due to the intermolecular interactions rather than to the molecular structure itself. A close look at the intermolecular interactions shows that the molecules of the 13 complexes that present SCO phenomenon show a frontal intermolecular interaction, where the three rings of the abpt molecules overlap with the three rings of the neighbouring molecule (frontal overlap, Fig. 4b). In contrast, the complexes that do not display the SCO transition show an overlap mode of the abpt ligands with the neighbouring molecules where only one of the three rings of the abpt ligand overlap (sideways overlap, Fig. 4a); the only exception being the polymorph A of the dca$^-$ derivative. It is very clear, thus, that the π-stacking interaction plays a crucial role in the presence or not of the spin crossover and it can be concluded that efficient π-stacking between neighbouring molecules is an essential condition for the presence of the SCO transition in this family of materials.

A very interesting point concerns the structural properties of the two new polymorphs B-[Fe(abpt)$_2$(dca)$_2$] and C–[Fe(abpt)$_2$(NCS)$_2$] for which the magnetic studies show two-step SCO transitions. In both cases, the crystal structure consists in two independent molecules (Fe1 and Fe2), where the Fe1 molecule presents the frontal abpt overlap mode and Fe2 adopts the sideways mode. According to the iron environment, Pillet et al. [24] have clearly shown that the two-step character of the spin transition of B–[Fe(abpt)$_2$(dca)$_2$] can be explained by the fact that the second molecule (Fe2, sideways mode) does not undergo the SCO transition above 90 K. In the same manner, careful examination of the overlap modes and of the iron environment of C–[Fe(abpt)$_2$(NCS)$_2$] shows that the incomplete spin transition is in agreement with the presence of only one active iron centre (Fe1, frontal mode), while the second one (Fe2, sideways mode) remains clearly in the HS state. Theses observations confirm definitively the crucial role of π–π interactions on the presence of the SCO transition.

2.3. Extended systems

All the SCO complexes of the previous section are discrete molecules and, although they present very high SCO transition temperatures, the lack of large hysteresis precludes their use in many potential applications. As mentioned above, the presence of intermolecular interactions (π-stacking, hydrogen bonding and Van der Waals interactions) is crucial to transmit the SCO transition. Unfortunately, these intermolecular interactions are difficult to control. Even if it is possible to include H-donors and H-acceptor groups in the ligands, the control of the final interactions formed is not so straightforward. And, even worse, the same ligand may present different types of interactions and stacking modes, as described in the previous section with the abpt ligand. In order to try to control the intermolecular interactions, some authors proposed in the 90s a clever strategy consisting in covalently linking the metal atoms by using appropriate bridging ligands [7]. Kahn et al. [7,25], and others [9,26], introduced such an interesting alternative approach based on the use of neutral suitable bridging ligands to covalently connect the metal centres. This resulted in the synthesis of several Fe(II) SCO coordination polymers exhibiting rich and fascinating structural features coupled to their magnetic behaviours. However, these studies concern a limited number of neutral ligands and deal essentially with 4-substituted-1,2,4-triazole and poly-N-donating heterocyclic ligands [7,9,25,26].

Our strategy in this context consists in taking advantage of the bridging ability shown by the polynitrile anionic ligands in order to prepare polymeric materials exhibiting SCO phenomenon. We have detailed in the previous section the first SCO series based on polynitrile anions. In this series, the single charge on the anion induces a terminal coordination mode for the polynitrile unit, resulting in neutral discrete SCO complexes (since a Fe(II) ion is linked to two monoanionic polynitrile ligands). A further step in this direction has been the preparation of original extended SCO networks bearing the Fe(II)-abpt entity by using more potentially bridging anionic polynitrile ligands holding higher anionic charges and more coordination sites.

The first success of this strategy has been very recently obtained by using the potentially hexa-coordinating polynitrile dianionic ligand tcpd^{2-} with abpt and Fe(II). Thus, this ternary system afforded a novel chain compound formulated as [Fe(abpt)$_2$(tcpd)]$_n$ (**18**) which is the first chain containing a cyanocarbanion and presenting a SCO transition [10]. The structure of this compound consists of a linear chain where the Fe(II) ions are bridged by μ$_2$-tcpd^{2-} ligands in the axial positions and contain two abpt ligands in the equatorial plane (Fig. 5).

This compound is very similar to the molecular complexes described in the previous section. The only difference is the presence of two bridging tcpd^{2-} ligands instead of two terminal polynitrile ligands in the axial positions. Since the tcpd^{2-} are shared by two Fe(II) ions, there is only one tcpd^{2-} anion per Fe(II) ion, leading to the neutral chain [Fe(abpt)$_2$(tcpd)]$_n$. The tcpd^{2-} ligand presents a positional disorder with two different possible orientations. The structural data indicate that at room temperature the compound is 100% in high-spin configuration (the average Fe–N

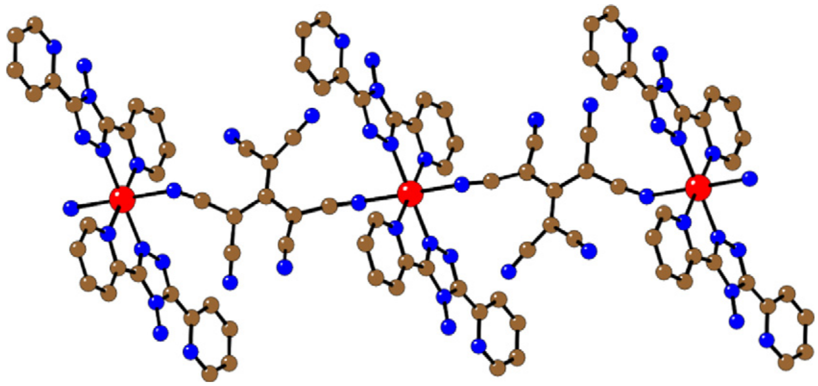


Fig. 5. Chain structure of $[Fe(abpt)_2(tcpd)]_n$. Each $tcpd^{2-}$ ligand is placed on one of the two statistically possible orientations (see Ref. [10]). Colour code: Fe = red, C = brown and N = blue.

bond distance is 2.159(2) Å, in the normal range observed for HS FeN_6 complexes) [27]. On lowering the temperature the average Fe–N bond distances decrease to 2.083(2) Å at 100 K and 2.065(3) Å at 10 K when the crystal is flash cooled, corresponding to ca. 50% low-spin configuration. Upon irradiation at 10 K the average Fe–N bond distance recovers the room temperature value (2.156(3) Å), indicative of a light-induced SCO transition (LIESST effect). After relaxation, the average Fe–N bond distance decreases to 2.018(3) Å, indicating that ca. 25% of the iron centres remain HS at low temperature. All these structural modifications produced by the thermal variation and upon irradiation can also be followed by the variations in the unit cell volume (Fig. 6) and suggests a T_{LIESST} value of ca. 35 K.

The magnetic measurements confirm the structural data and show a gradual SCO transition taking place between 170 and 50 K with two inflexion points at 105 and 60 K. Below 50 K, the $\chi_m T$ product remains quasi constant with a value of ca. 1.0 emu K mol^{-1} indicating that ca. 25% of the iron centres remain in the HS state. When the sample is irradiated at 10 K, it shows a gradual increase of the magnetic moment that vanishes as the temperature is increased with an inflexion point at ca. 35 K (T_{LIESST}) (Fig. 7). Therefore, the structural and magnetic data confirm the presence of a SCO and LIESST effect in the chain compound $[Fe(abpt)_2(tcpd)]$.

The two inflexion points at 105 and 60 K have been explained by the monodimensional character of this compound: as the iron centres are bridged by the polynitrile anion, when a spin transition occurs on a metallic centre, it influences the magnetic behaviour of the neighbouring iron centres. Indeed, such atypical feature may be explained by the contraction, just below 170 K, of the Fe^{II} coordination sphere due to HS–LS transition leading to an increase of the energy gap between HS and LS levels of one or two neighbouring Fe^{II} ions along the chain. Such phenomenon is nearly similar to that observed for some Fe^{II} dinuclear complexes and for the 1D chain $[Fe(NCSe)_2(bdpp)]$, for which their SCO transitions are of the two-step character [28].

From the structural point of view, the principal intermolecular interactions consist here again in π–π interactions between abpt ligands. In this case, the abpt entities stack according to the sideways overlap mode. Nevertheless, the number of abpt/abpt short contacts is more that 5, indicating an efficient π–π interaction between them. This observation is in good agreement with the crucial role of the π-stacking on the presence of the spin crossover. In addition, the extended character of the crystal structure seems to improve the interactions between active centres since an efficient π-stacking is observed despite the sideways overlapping of the abpt entities.

2.4. *Concluding remarks*

As detailed in another contribution in this volume, the polynitrile anions have demonstrated to be a very useful tool for the

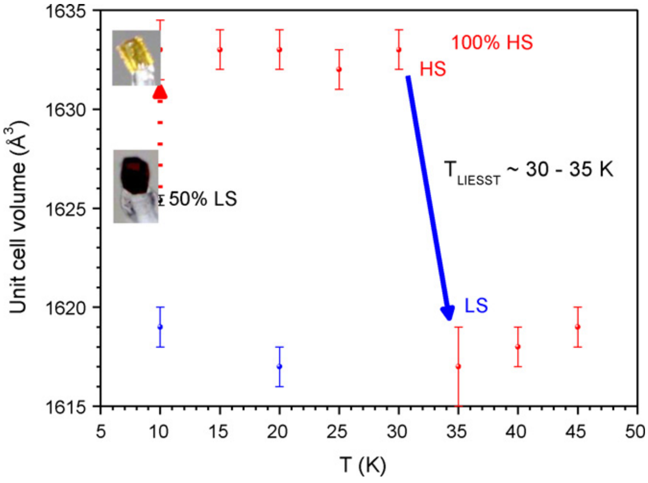


Fig. 6. Evolution of the unit cell volume of $[Fe(abpt)_2(tcpd)]_n$ under irradiation at 534 nm (red points) and after relaxation (irradiation off, blue points).

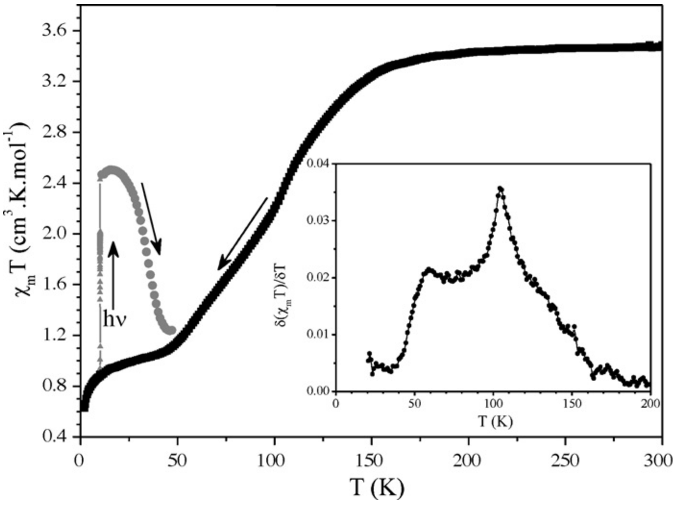


Fig. 7. Thermal variation of the $\chi_m T$ product of $[Fe(abpt)_2(tcpd)]_n$ measured without (black squares) with (grey triangles) and without (grey points) irradiation showing the gradual spin transition and the LIESST effect. Inset shows the thermal variation of the derivative of the $\chi_m T$ product. product showing two inflexion points at 105 and 60 K.

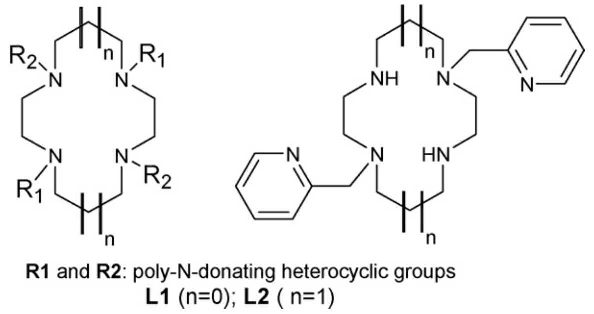
design and synthesis of diverse magnetic materials with discrete, mono-, bi- and tri-dimensional structures. In most compounds reported previously and in those described above, they have shown their ability to act as multi-bridging ligands between two or more metal ions [10,13,14,19]. Such coordination properties have been used in the present contribution to tune the ligand field strength in a new series of neutral complexes prepared with Fe(II) and the abpt co-ligand: the polynitrile anions bearing one negative charge led us to the new SCO series formulated as $[Fe(abpt)_2X_2]$ (X = tcm$^-$, tcnome$^-$, tcnoet$^-$, tcnopr$^-$, tcnoetOH$^-$, tncopr3OH$^-$, tcnopr2OH$^-$ and tcnsme$^-$). In this series, the single charge on the anion induces a terminal coordination mode for the polynitrile unit, resulting in neutral discrete SCO complexes. The use of a dianionic polynitrile anion in combination with Fe(II) and the abpt ligand, has led to the first cyanocarbanion based chain compound presenting a spin crossover transition. This compound showed a HS metastable state at low temperature induced by light (LIESST effect) with a limit temperature of ca. 35 K (T_{LIESST}). A further advantage of the polynitrile anions is the possibility to be reduced or oxidized to generate neutral or anionic radicals that, besides their high ability to coordinate and bridge metal atoms, can transmit the magnetic coupling between them in a much more effective way [29]. Attempts to prepare metal complexes presenting SCO with polynitrile ligands using electrochemical and chemical redox processes are underway.

3. Other strategies: spin crossover (SCO) system based on macrocyclic ligands

The design of new SCO complexes is still of a greatest interest since improvement of the SCO properties needs studies on various different molecular systems. In the previous section, we have shown that the polynitrile anions constitute an interesting tool to prepare new multidimensional systems exhibiting SCO phenomenon. In our ongoing work on the design of new molecular systems based on new ligands that can be fine-tuned *via* chemical changes, another promising way which has been developed recently in our group concerns the use of new neutral polydentate ligands which are able to tune the ligand field energy around the metal centre [30].

Up to now, most of the SCO Fe(II) complexes involve polydentate ligands combining both N-heterocyclic and amino-aliphatic groups [31]. In this context, the use of polydentate ligands such as polyazamacrocycles derivatives (Scheme 2) could constitute an efficient way to design new SCO systems since the ligand field of the fully saturated polydentate macrocycle ligands may be fine-tuned *via* their N-functionalization with adequate potentially coordinating or chelating groups such as pyridine or poly-N-donating heterocyclic groups (see the selected examples depicted in Scheme 2).

Furthermore, most of the SCO complexes studied to date require two or more appropriate ligands which generally make difficult to control the synthesis and to avoid the formation of mixtures of polymorphic systems. Therefore, the use of macrocyclic ligands involving at least six N-donor atoms should open an original way to design new SCO complexes exhibiting desirable molecular structures (Scheme 2). It is well known that the fully saturated polydentate macrocyclic ligands such as cyclen, cyclam or their C-hexamethyl derivatives form very stable complexes with transition metal ions [32–34]; however, in the case of Fe(II) most of them are either LS or HS [33,34]. To the best of our knowledge, only two examples have been reported as SCO complexes: the $[FeL(NCS)_2]$ complex (L = meso-5,5,7,12,12,14-hexamethyl-1,4,8,11-teraazacyclotetradecane) with a $T_{1/2}$ around 350 K [34], and the $[Fe(Me_3\text{-}[9]aneN_3(MeCN)_3](CF_3\text{–}SO_3)_2$ complex (Me_3-[9]aneN_3 = 1,4,7-trimethyl-1,4,7-triazacyclonane) with a $T_{1/2}$ of ca. 320 K [35]. In the case of the unsaturated macrocycle rings, Busch et al. reported in 1972 the complex $[FeL'(phen)](ClO_4)_2$ [36] (L′ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-teraazacyclotetradeca-4,11-diene; phen = o-Phenanthroline) as a new example exhibiting SCO behaviour with a $T_{1/2}$ of ca. 250 K. It is expected that the total or selective partial N-functionalization of these ligands by pendant donor groups such as N-donating heterocyclic groups will yield novel and unusual coordination modes and, therefore, new coordination spheres for which the ligand field energy could be fine-tuned by varying the size of the fully saturated hetero-cycle or the number and the nature of the substituting groups. In this context, Hendrickson and co-workers [37] reported in 1986 a detailed study on the Fe(II) complexes of triazamacrocycles involving three pendant pyridylmethyl groups. In the case of the 9-membered ring system (tp[9]aneN_3), the Fe(II) complex is LS while the Fe(II) complex of the larger 12-membered ring system (tp[12]aneN_3) shows an HS magnetic state. Using the 10-membered ring system (tp[10]aneN_3) having an intermediate size ring, McGarvey and co-workers [38] prepared, few years latter, the complex $[Fe(tp[10]aneN_3]^{2+}$. In the solid state the perchlorate salt exhibits a LS state at room temperature, while in acetonitrile solution the complex shows a relaxation of the $^1A_1 \leftrightarrow {}^5T_2$ spin equilibrium after perturbation by a pulsed laser. In the present section, we report the structural and magnetic properties of two new Fe(II) complexes based on the cyclen and cyclam N_4-macrocycle rings bearing two pyridylmethyl arms. The complex based on the substituted cyclen ligand: $[Fe(L1)](BF_4)_2$ (**19**) (L1 = 1,7-bis(2′-pyridylmethyl)-1,4,7,10-tetraazacyclododecane) shows an unusual trigonal prismatic coordination sphere with an HS state in the whole temperature range studied, whereas the cyclam-derivative $[Fe(L2)](BF_4)_2{\cdot}H_2O$ (**20**) (L2 = 1,8-bis(2′-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane) exhibits a SCO behaviour with a transition temperature ($T_{1/2}$) of ca. 150 K. To the best of our knowledge, complex **20** is the first SCO system based on a functionalized tetraazamacrocycle ligand.



Scheme 2. Examples of poly- and two-functionalized tetraazamacrocycles (L1 and L2 ligands).

3.1. Cyclen based system

The new iron(II) complex of formula $[Fe(L1)](BF_4)_2$ (**19**) (L1 = 1,7-bis(2′-pyridylmethyl)-1,4,7,10-tetraazacyclododecane) has been synthesized and characterized by variable temperature single crystal X-ray diffraction and variable temperature magnetic susceptibility measurements [30]. The crystal structure determinations of **19** reveal a discrete iron(II) monomeric structure in which the functionalized tetraazamacrocycles (L1) act as hexadentate ligands; the iron(II) ions are coordinated with six nitrogen atoms: four from the macrocycle and two from two pyridine groups occupying two *cis* positions around the metal ion. Careful examination of the N–Fe–N bond angles reveals that the six-coordinate geometry of the iron ion in **19** strongly differs from the distorted octahedron observed in transition metal complexes based on similar hexadentate macrocycle ligands [39] since the Fe(II) ion adopts an unusual distorted trigonal prismatic geometry. This

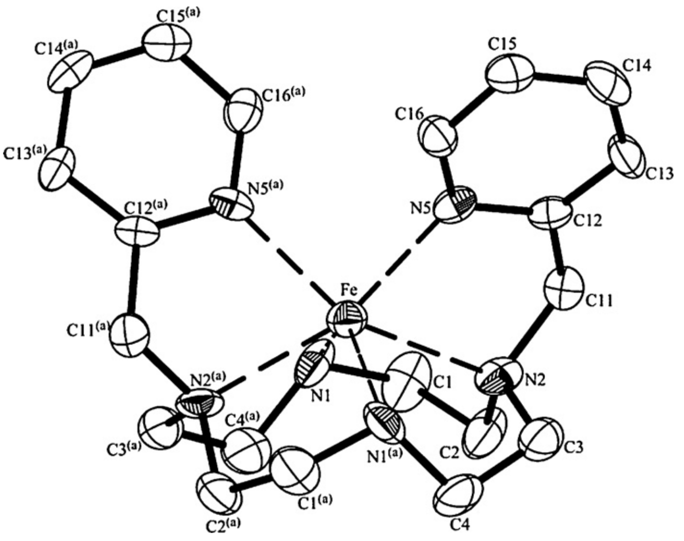


Fig. 8. ORTEP drawing of the cationic complex of **19**. Code of equivalent position: (a) −*x*, *y*, 1/2 − *z*.

unusual geometry is well characterized by the very high value of the trigonal distortion parameter [40] of 809(4)° compared to the observed range for the octahedral geometry (0–300°). However, as observed in parent M(II) complexes based on hexadentate poly-(pyridylmethyl)-cyclen ligands, the coordinated pyridyl groups are disposed in the same side of the basal macrocyclic ring. This fact results from the small size of the cyclen ring which precludes the Fe(II) ion to enter inside the ring and forces it to remain well above the mean ring plane. Such geometric requirements of the ligand impose a large deviation of the metal ion (1.0 Å) from the average plane through the four nitrogen atoms of the cyclen ring (Fig. 8).

The thermal dependence of the product of the molar magnetic susceptibility times the temperature ($\chi_m T$) for this complex is depicted in Fig. 9. The $\chi_m T$ product shows a room temperature value of 3.10 emu K mol^{-1} that remains constant down to ca. 20 K. This value, slightly higher than the spin only value calculated for an isolated metal ion with $S = 2$ (3.0 emu K mol^{-1}), indicates that complex **19** is essentially paramagnetic and presents the high-spin ($S = 2$) configuration in the whole temperature range. In agreement with the observed paramagnetic behaviour, the average of the six Fe–N distances at 293 K (2.218(6) Å) and at 90 K (2.209(2) Å) correspond well with distances observed for high-spin (HS) Fe^{II} complexes.

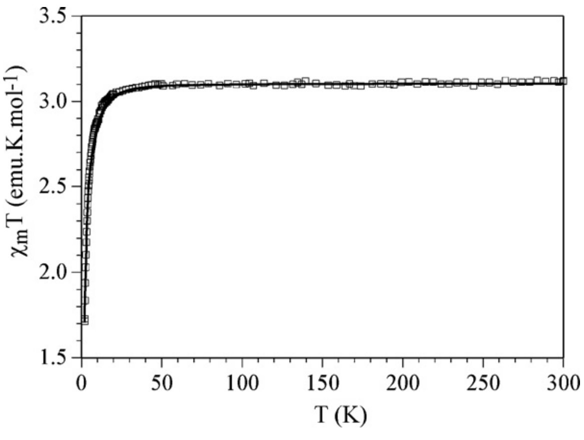


Fig. 9. Thermal variation of the $\chi_m T$ product for compound **19**.

The HS behaviour of this complex may be attributed to the nature and the geometry of the macrocycle ligand for which the cyclen ring is not sufficiently large to accommodate normal distorted octahedron geometry as shown by the huge value of the trigonal distortion parameter ($\Theta = 809(4)°$). Indeed, the distorted trigonal prismatic coordination sphere of this complex imposes relatively long Fe–N distances as described above and to the best of our knowledge all the hexacoordinated Fe^{II} complexes exhibiting SCO behaviours involve a distorted octahedron environment. Thus, such unusual coordination mode of **19** may induce low ligand field energy which explains the HS spin state in the whole studied temperature range.

3.2. Cyclam based system

The result obtained with the smaller cyclen-derivative ligand clearly suggests that the use of a larger macrocycle may allow a better insertion of the Fe(II) ion therefore, may lead to the formation of a octahedral complex that could present a SCO transition. Thus, we decided to use a larger cyclam-derivative instead of the cyclen one to prepare the iron(II) complex formulated as $[Fe(L2)](BF_4)_2 \cdot H_2O$ (**20**); (L2 = 1,8-bis(2′-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane). This compound has been characterized by variable temperature single crystal X-ray diffraction and variable temperature magnetic susceptibility measurements [30]. The molecular structure of this complex is similar to the cyclen-derivative one. However, in this case the Fe^{II} ion adopts a distorted octahedral geometry in which the six Fe–N distances at room temperature (average 2.197(4) Å) are in the range expected for HS Fe^{II} complexes [12,27]. The four amine nitrogen span two contiguous faces of the coordination polyhedron, and the pyridine nitrogen occupy the remaining pair of cis positions as observed in parent Ni(II) complexes based on similar macrocycle ligands (Fig. 10) [41]. As for complex **19**, the Fe(II) ion is displaced in the same direction than the methyl-pyridine groups from the mean plane of the four nitrogen atoms of the cyclam ring. However the deviation in **20** is slightly shorter (0.91 Å) than the corresponding one observed for **19**. This difference is probably due to the higher flexibility of the cyclam ring resulting from the two additional saturated aliphatic carbon atoms.

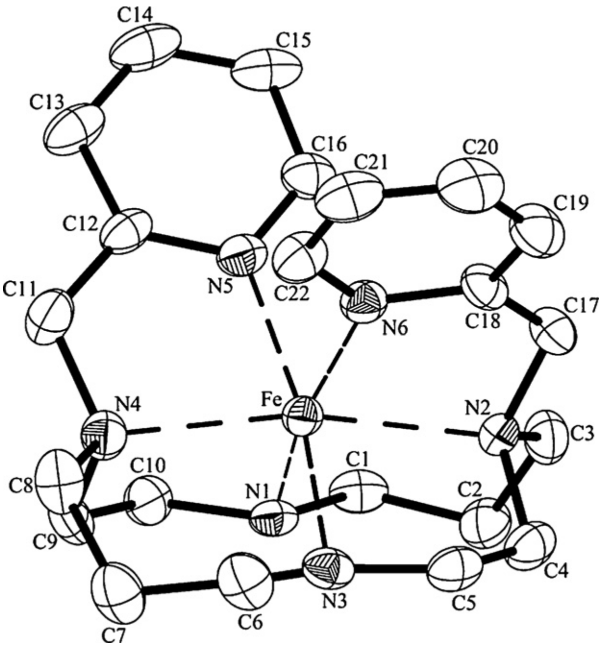


Fig. 10. ORTEP drawing of the cationic complex of **20**.

The magnetic measurements performed on compound **20** show that the thermal behaviour is very different from that of complex **19**. The $\chi_m T$ product for **20** decreases upon cooling and drops rapidly from a room temperature value of ca. 3.2 emu K mol^{-1} to reach a value close to zero at ca. 90 K (Fig. 11). This behaviour is characteristic of a HS ↔ LS SCO conversion. The temperature of the transition, $T_{1/2}$, is estimated to be around 150 K (Fig. 11).

In order to better understand the magnetic behaviour of complex **20**, variable temperature single crystal X-ray diffraction measurements were performed in the temperature range 293–90 K. The crystal structure solved at 90 K showed a strong modification of the iron coordination sphere in good agreement with the presence of a SCO from HS to LS. The average Fe–N distances and the trigonal distortion parameter (Θ) of the coordination sphere decrease significantly. This particular behaviour is the structural signature of the HS → LS transition. Surprisingly, the octahedron distortion parameter remains constant in both spin states ($\Sigma = 91(2)^\circ$) and the averaged Fe–N value (2.077(4) Å) at this temperature is higher than expected. This particularity cannot be solely explained by the incomplete transition at 90 K, as the magnetic data indicates almost 100% conversion at 90 K. Such a high octahedron distortion may be due to the constrained geometry induced by the macrocyclic ligand. It can be assumed that such a ligand imposes distorted geometries even in the LS state for Fe(II) SCO complexes. An additional proof of this distortion imposed by the macrocyclic ligand is the fact that the average Fe–N bond distances in the LS state are slightly longer than those usually observed in other LS Fe(II) complexes. Furthermore, the trigonal distortion parameter, Θ, significantly decreases during the HS to LS transition, confirming that the spin transition process is specifically accompanied by this type of twisting distortion from D_{3h} to O_h symmetry.

To understand how the crystal and the lattice parameters were affected by the magnetic transition, the temperature dependence of the lattice parameters of a single crystal of **20** were measured in the range 293–90 K. As it can be seen in Fig. 12, the *a* and *b* parameters show essentially linear and gradual decreases with a more gradual effect for the *b* parameter. In the temperature range 293–160 K the *c* parameter shows a gradual decrease similar to that of the *b* axis. Below 160 K, a relatively abrupt decrease, parallel to that described above for the magnetic behaviour, was observed at the same temperature than that of the magnetic transition (150 K). The thermal variation of the angular β parameter depicted in Fig. 12 does not show any anomaly down to 160 K, where a drop of about 2.5° occurs. This behaviour corresponds very well with a SCO transition also evidenced by an abrupt colour change from yellow to red observed in the single crystal as the temperature is decreased from 200 to 100 K (Fig. 12). These structural data show that the single crystal of **20** contracts anisotropically on cooling since the more significant changes occurs essentially along both *c* and β cell parameters. On heating the single crystal back to 200 K, no thermal hysteresis in lattice parameters is evident.

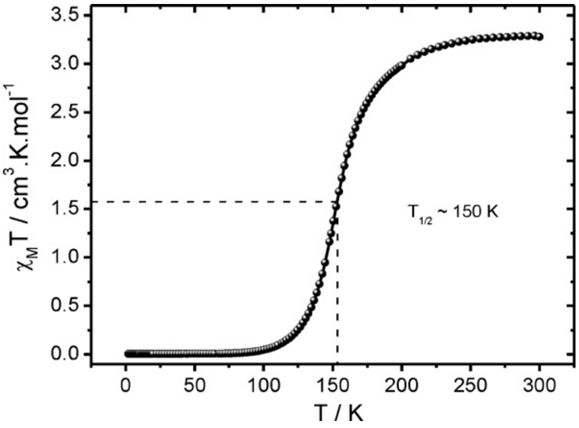


Fig. 11. Thermal variation of the $\chi_m T$ product for **20**. Inset shows the derivative of the $\chi_m T$ product vs. temperature.

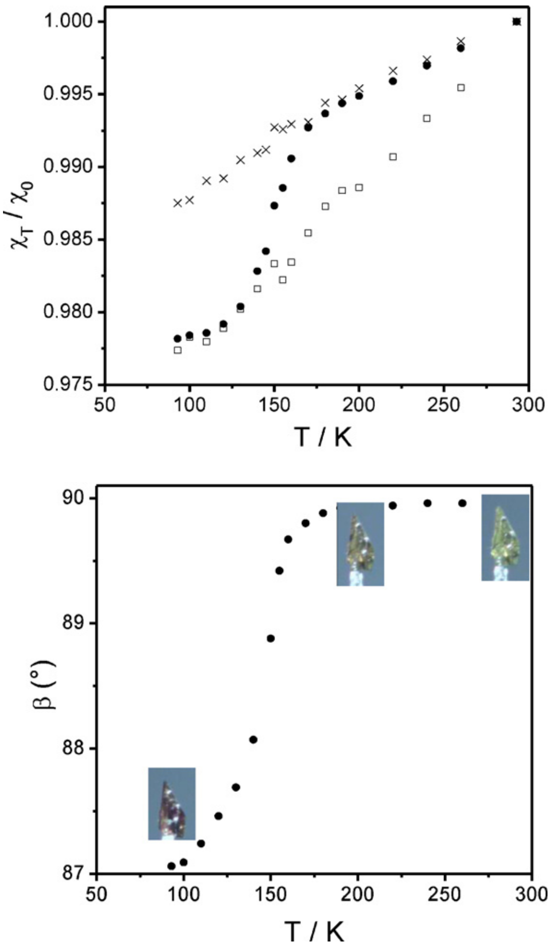


Fig. 12. Thermal variation of the lattice parameters of complex **20**; *a* (×), *b* (□) and *c* (●) parameters (top) and angular β parameter showing the anisotropic contraction of the crystal around the SCO transition (bottom).

3.3. Concluding remarks

In summary, two new iron(II) complexes: [Fe(L1)]$(BF_4)_2$ (**19**) and [Fe(L2)]$(BF_4)_2 \cdot H_2O$ (**20**), based respectively on functionalized cyclen (L1) and cyclam (L2) ligands, have been structurally and magnetically characterized. In both cases the structure consists of a discrete monomeric $[FeL]^{2+}$ cation and two uncoordinated $(BF_4)^-$ anions. The two complexes display different magnetic behaviours since **19** remains in the high-spin state in all the temperature range and does not undergo any spin transition, while complex **20** presents a SCO behaviour with a transition temperature of 150 K. As expected from the magnetic data, the crystal structure of **20** at 90 K shows a strong modification of the iron coordination sphere which is the structural signature of the spin-state transition from HS to LS. In addition, temperature dependence of the lattice parameters of a single crystal of **20** shows that the crystal contracts anisotropically on cooling since the most important structural changes occurs along the *c* axis and the β angle, and fit well the SCO magnetic behaviour.

These previous results indicate that the chemical flexibility of such ligands can be viewed as an excellent starting point for the design of new parent macrocycle ligands able to create moderate or strong intermolecular interactions which are crucial for new SCO cooperative systems. In this context, the many possible modifications of the macrocyclic ligands (number of atoms in the cycle, number and nature of the functionalizing groups, etc.) confer these novel systems as very promising ones to prepare new SCO systems. Moreover, the substitution of the counter anions may also play an important role on the magnetic behaviour as it was already observed with others polydentate ligands [42].

Acknowledgements

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