Concluding Remarks and Perspectives
9. Concluding Remarks and Perspectives

9.1 General Conclusions and outlook on the bistetrazole-based spin-transition compounds.

9.1.1 Effect of a bulky substituent on the aliphatic spacer linking the tetrazole units.

Chapters 3, 4 and 5 in this thesis deal with spin-crossover bistetrazole-based compounds, with the report on five new members of this remarkable family. In chapter 3, the complexes [Fe(btzmp)$_2$µ-(btzmp)$_2$](ClO$_4$)$_2$ and [Fe$^{II}$(btzpol)$_{1.8}$(btzpol-OBF$_3$)$_{1.2}$](BF$_4$)$_{0.8}$, obtained from ligands bearing substituted alkyl spacers, are described. In both cases, the substituents are intended to favour a greater rigidity to the overall structure upon coordination, which is required to obtain more cooperative transitions. In the case of the btzmp ligand, steric effects due to the methyl groups are expected to generate a more rigid coordination network. This anticipation is based on the crystal packing$^1$ observed for [Fe(btzp)$_3$](ClO$_4$)$_2$. For [Fe$^{II}$(btzpol)$_{1.8}$(btzpol–OBF$_3$)$_{1.2}$](BF$_4$)$_{0.8}$, the alcohol function of the bistetrazole ligand was expected to form hydrogen-bonding interactions. Such H-bond networks are known to be responsible for the cooperative character of some spin-transition materials.$^2$ However, for both compounds, important unexpected results have been obtained, as summarised below.

[Fe(btzmp)$_2$µ-(btzmp)$_2$](ClO$_4$)$_2$ consists of a 1D polymer with a double bridge instead of the classical triple bridge usually observed with this type of bistetrazole-based 1D polymers. In fact, two monodentate btzmp ligands are coordinated at the axial positions of the Fe$^{II}$ octahedron. A similar situation is observed with [Fe$^{II}$(btzpol)$_{1.8}$(btzpol–OBF$_3$)$_{1.2}](BF_4)_{0.8}$, where the partial reaction of the alcohol functions of btzpol ligands with the anion yields a slightly modified and bulkier ligand. This modification of the btzpol ligands gives rise to the formation of a double bridge (similar to btzmp) along one of the crystallographic axes. In addition, the third bistetrazole unit now acts as a bis-monodentate ligand, and bridges the metal centres along a perpendicular axis, producing the first example of a bistetrazole-based 2D spin-transition coordination polymer. The presence of a bulky group on the linker has two consequences: a probable intra-ligand steric hindrance, which diminishes the free rotation of the tetrazole ring along the N–C bond, and a steric hindrance generated through the formation of the complex. Both constraints are most likely involved in the different crystal packings observed, compared to previously reported 1D bistetrazole-based polymers.

These two compounds exhibit distinct magnetic behaviours. Similarly to other spin-transition bistetrazole-based polymers, [Fe$^{II}$(btzpol)$_{1.8}$(btzpol-OBF$_3$)$_{1.2}](BF_4)_{0.8}$ shows an incomplete and gradual magnetic susceptibility curve.$^1,3$ The additional alcohol function has not resulted in the desired intermolecular interactions, that would enhance cooperativity. This gradual spin-transition is probably due to an overall lack of rigidity within the solid-state structure, resulting from the presence of voids, the flexibility of the ligand, and the lack of intermolecular interactions. The increase of dimensionality (from 1D to 2D) has not resulted in an enhancement of the cooperativity between the SCO centres. In contrast, [Fe(btzmp)$_2$µ-(btzmp)$_2$](ClO$_4$)$_2$ shows a spin-transition with hysteresis, as observed for two earlier reported bistetrazole-based compounds.$^4,5$ This behaviour can arise from a highly cooperative system, or from a structural phase transition. Although there are some structural differences that may increase the rigidity, in this case, the presence of an order-disorder transition seems to be the origin of the 4 K hysteresis loop. Nevertheless, the observed order/disorder transition of the
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anion is probably caused by the noticeable change of the [Ttz-centroid]–N4–Fe angle upon the spin transition.

9.1.2 Effect of the counterion on the SCO properties of the cation [Fe(btxz)\textsubscript{3}]\textsuperscript{2+}.

Chapter 4 deals with the study of the effect of the counterion on the SCO properties of the [Fe(btxz)\textsubscript{3}]\textsuperscript{2+} cation. In the bistetrazole family, the variation of the anion often results in a drastic change of the magnetic properties. For the only bistetrazole-based cation reported with structurally different anions, [Fe(btzb)\textsubscript{3}]\textsuperscript{2+}, the degree of completion of the transition is strongly affected by the choice of the counterion. This behaviour is observed again for the [Fe(btxz)\textsubscript{3}]\textsuperscript{2+} cation. Due to the fact that the characteristics of the anion are crucial to obtain single crystals suitable for X-ray diffraction, the details of the crystal structure of [Fe(btzb)\textsubscript{3}](ClO\textsubscript{4})\textsubscript{2} are still unknown, and thus no magneto-structural correlation for this behaviour has been possible up to now. In the present study, the two solved X-ray structures of the [Fe(btxz)\textsubscript{3}]\textsuperscript{2+} cation reveal several structural features responsible for the different magnetic behaviours observed. Both the transition temperature (\(T_{1/2}\)) and the degree of completion are influenced by the proximity of the anion, which affects the tilting freedom of the tetrazole rings. It appears that a closer contact between the anion and the tetrazole ring results in a greater distortion of the coordination sphere. As a result, a stabilisation of the HS state (over the LS state) is observed. The lack of influence of the nature of the anion on the cooperativity suggests that the cooperative nature of these systems arises from intrapolymeric interactions. However, the absence of an effect on the steepness of the transition due to the ...HS-LS-HS... pattern observed in the triflate derivative is not in agreement with this suggestion. The presence of a hysteresis loop detected by recent LITH (Light Induced Thermal Hysteresis) measurements on [Fe(btxz)\textsubscript{3}](CF\textsubscript{3}SO\textsubscript{3})\textsubscript{2} (see Figure 9.1), indicates that indeed cooperativity is present in this compound.\textsuperscript{6} Thus, the gradual slope in the \(\chi_m T\) vs. \(T\) curve observed for this material is apparently due to the macroscopic compensation of the long-range interactions by some counteracting short-range interactions.\textsuperscript{7} The same explanation can be proposed for the hexafluorophosphate and the perchlorate derivatives, although this needs to be confirmed.

A relationship between structural features of bistetrazole-based spin-transition polymers and their spin-crossover behaviours is pointed out in Chapter 5. The compilation and analysis of the structural data of these systems have resulted in a better understanding of the (mutual) influence of all chemical building blocks (ligand, metal, anion and solvent) on the resulting different crystallographic features (intrapolymeric distances, anion–π interactions, metal-to-ligand bond length, octahedron distortion...). Moreover, the comparison of these data for the HS and LS states reveals certain common behaviours of these bistetrazole-based systems when undergoing the spin transition. Some characteristics follow general tendencies observed for SCO systems, while other features are more specific to this type of coordination compounds. The tilting freedom of the coordinated tetrazole rings seems to be closely related to the capacity of the iron(II) centre to undergo the spin transition and to the temperature of the transition. This “tilting-freedom” is affected by the substituents on the aliphatic spacers (see 9.1.1) and, in 1D polymers, by the proximity of the anion to the metal...
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The effect of the anion observed for the 1D systems is opposite to that observed for 1,2,4-triazole-based materials. However, the effect of the anion can be explained as the steric effect exerted by any group close to the metal centre (in this case the anion), as noticed for other SCO compounds, such as the mononuclear pyrazolyl-borate-based systems or in the “trim” systems (trim = 4-(4-imidazolylmethyl)-2-(2-imidazolylmethyl)imidazole). This analogy with borate derivatives is probably due to the necessity for the azole rings to tilt and modify their spatial position to compensate the modification of the Fe–N distances caused by the spin transition. The distinct behaviour of the 1,2,4-triazole-based compounds is ascribed to their rigid bridge and to strong coordinative interactions, which restrict the tilting of the azole ring. The variations occurring with bistetrazole-based complexes upon spin transition are strongly dependent on the spacer used, and it is thus difficult to predict the behaviour of future compounds. New spacers (with bulky substituents close to the tetrazole rings) are needed to increase the number of examples in this family; this would allow the proposal of a clear magneto-structural relationship.

![Figure 9.1. \(\chi_mT\) vs. \(T\) curve under constant irradiation (green light, 520 nm) at two different rates: full squares (0.5 K/min) and empty squares (0.3 K/min).](image)

9.2 General Conclusions and outlook for triazine-based spin-transition compounds.

9.2.1 Dpyatriz as ligand for the preparation of spin-transition materials.

The triazine ring has proved to be an outstanding building unit for the synthesis of more intricate molecular building blocks, which are in turn necessary for the creation of new materials. Dpyatriz, a simple symmetric ligand based on the triazine unit, has been previously used with different metals, giving rise to diverse structures. The reaction of dpyatriz with Co(NO₃)₂ yields a dinuclear system. A tetrnnuclear complex is achieved with Zn(NO₃)₂, while the coordination with Cu(NO₃)₂ results in a polymeric species. These results clearly show the versatility of dpyatriz. Its nitrogen-based coordination sites made it a good candidate for the design and preparation of new spin-transition materials. Accordingly, the reaction of dpyatriz with different Fe²⁺ salts applying different reaction conditions has resulted in
mononuclear, dinuclear and polynuclear systems exhibiting various types of magnetic properties.

The related dinuclear entities discussed in chapter 6 of this thesis have shown that the reaction of dpyatriz with Fe\textsuperscript{II} salts tends to produce complexes of which the metal centres are bridged by two dpyatriz ligands. Each iron centre of the dinuclear unit is coordinated by two dipyridyldiamine moieties of two different dpyatriz ligands, leaving two free coordination sites to be completed by solvent and/or water molecules. The magnetic properties of the dinuclear complexes are largely dependent on these terminal ligands. In the case of the spin-transition dinuclear compound, the solvent molecules (acetonitrile) have proven to be labile, so that the complex is sensitive to chemical modification via exchange with atmospheric water. This instability of the material results in the loss of the spin-transition properties, yielding paramagnetic species. The use of a coordinating counterion and the application of solvothermal conditions allow the preparation of a stable system with no coordinated solvent molecules. This complex shows a slightly different coordination mode for dpyatriz, as one of the nitrogen atoms of the triazine ring is coordinated to the Fe\textsuperscript{II} centre. This feature, not commonly observed with triazine-containing ligands, brings about changes in the magnetic properties with respect to the two other dinuclear compounds previously obtained. The ferromagnetic behaviour observed for this new compound has been assigned to a polarisation of the triazine ring caused by its coordination to the metal. Interestingly, the isostructural cobalt and nickel compounds exhibit different magnetic behaviours, compared to the iron(II) derivative. The slight differences observed for the C–N triazine bond distances in the different complexes may affect the degree of ring polarisation induced by the different metals, resulting in different magnetic behaviours.

Another structural feature that characterises Fe\textsuperscript{II} dpyatriz-based complexes synthesised in normal conditions (room temperature and atmospheric pressure) is the available potential ligand-binding units. Indeed, only two of the three dipyridyldiamine moieties of the dpyatriz ligand are involved in the coordination to the metal centres. Consequently, these dinuclear compounds may be used as starting materials for the formation of more complex structures. In this sense, the application of solvothermal conditions has resulted in a 1D extended polymeric system, in which all potential coordination sites of dpyatriz are occupied by metal centres. Similarly to the dinuclear complexes, the polymeric species are moisture sensitive, as a result of the accessibility of the metal centres (nanoporous framework) and the lability of the solvent molecules. However, in this case the initial spin-transition properties of the polymeric system can be recovered, which makes the process reversible. The propionitrile/water sorption-desorption process is accompanied by a structural phase transition which does not occur via an amorphous phase. The compound loses the spin-transition properties to turn into a paramagnetic system. For other guest molecules studied, the process does not involve a structural change, although the magnetic properties do change. Thus, the variations in optical and magnetic properties of the system are caused by the different electronic properties of the guest solvent molecules, and are not due to a structural modification (as observed for the case of water). The substitution of non-volatile guests results in the stabilisation of the material, which is no more solvent dependent. This system represents one of the few examples where the spin-transition temperature can be drastically modified by a simple change of solvent.
Moreover, this host-guest material represents the first example of a functional material whose spin-transition properties can be stabilised by means of non-volatile solvent molecules.

In an attempt to combine magnetic exchange coupling and spin-transition properties in order to create hybrid materials, the ferromagnetic dinuclear system has been used as a synthetic precursor (Chapter 7). The dinuclear entity has proven to be unstable during the reaction with cyanide-based ligands, thereby hampering this prospect. The resulting mononuclear entity shows spin-transition properties, with a transition temperature in the range expected for thiocyanate-based materials. As for the thiocyanate derivative, the cyanoborohydride and dicyanamide complexes have both yielded spin-transition materials. The magnetic behaviour of the cyanoborohydride compound is very similar to the thiocyanate derivative, while that of dicyanoamide is completely different. The only changes in the spin-transition properties of the cyanoborohydride derivative with respect to the thiocyanate derivative are a higher transition temperature and a slightly lower cooperativity. The dicyanamide derivative shows a multi-step spin crossover, which may originate from the presence of crystallographically independent Fe$^{II}$ centres, or from the stabilisation of like-spin domains such as [HS-LS] pairs.

9.2.2 The design of new triazine-based units: the building block.

One of the main advantages of using the s-triazine as building unit to design new ligands is their straightforward synthesis. Considering that only two of the three dipyridylamino moieties of dpyatriz are involved in the binding of metal centres, the third moiety may be replaced by any other desired functional group. Presumably, this new function will not influence the coordination mode of the “modified” dpyatriz ligand and thus, the spin-transition properties should be retained. In this respect, the simplest dpyatriz derivative is 2-chloro[4,6-(dipyridin-2-ylamino)]-[1,3,5]-triazine, Cl-bdpat (Figure 9.2), where only two of the chloride atoms of the initial cyanuric chloride have been substituted by dipyridylamine.$^a$

As expected, the use of this ligand has resulted in a spin-transition compound (sensitive to atmospheric water) with a higher transition temperature and slightly steeper transition, compared to the corresponding dpyatriz dinuclear SCO complex (Figure 9.3). Unfortunately, this spin-transition compound could not be re-synthesised, and only the compound [Fe(Cl-bdpat)$_2$(H$_2$O)$_4$](ClO$_4$)$_2$·4H$_2$O that shows no spin transition (Figure 9.2) has been repetitively obtained.$^a$ Nevertheless, this result proves that Cl-bdpat coordinates to the metal ions in a similar manner as observed for dpyatriz. Therefore, the use of any substituent attached to the triazine ring by substitution of the chloride atom of Cl-bdpat, will certainly result in spin-transition materials with additional desired physical/structural properties. A large variety of new ligands may be designed, which, based on their goal, can be divided into two categories.

The first possibility is to use the third position of the triazine ring to improve the properties of the spin transition. In this sense, the main objective is to increase the cooperative nature of the spin transition. Highly cooperative systems based on the dpyatriz ligand have

$^a$ See chapter 2 for details on the experimental procedures for the preparation of all compounds discussed in this thesis.
not yet been achieved. The compound $[\text{Fe(dpyatriz)}_2(\text{NCS})_2]$ shows the steepest transition of all, but the cooperativity is still considered weak. The rest of the compounds exhibit similar degrees of cooperativity. A possible explanation for this lack of cooperativity is the flexibility of the dpyatriz ligand itself; and in particular the dipyridylamino moiety. Another interpretation is the small number of intermolecular interactions observed in dpyatriz-based compounds. Probably, the combination of both structural features is at the basis of the lack of cooperativity. To increase intermolecular interactions, two new ligands have been synthesised using a microwave reactor, namely 1-aminopyrene-[4,6-(dipyridin-2-ylamino)]-[1,3,5]-triazine, $\text{pe-bdpat}$, and 2-phthalimide-4-ylamino [4,6-(dipyridin-2-ylamino)]-[1,3,5]-triazine, $\text{ph-bdpat}$ (Figure 9.2). $\text{pe-bdpat}$ is potentially able to create $\pi-\pi$ interactions, while $\text{ph-bdpat}$ presents an acceptor–donor–acceptor hydrogen bonding pattern. Preliminary results have shown that reaction of $\text{pe-bdpat}$ with Fe(SCN)$_2$ (formed from the reaction of KSCN and Fe(SO$_4$)$_2$) produces a spin-transition complex with an unknown structure and chemical composition. As observed in Figure 9.3, the spin transition is even more gradual than those previously obtained with triazine-based spin-transition compounds. Thus, the inclusion of the 1-aminopyrene moiety has not resulted in the expected increase of cooperativity. The next logical step would be to replace the dipyridylamino moiety by a different coordinating entity aimed at enhancing the rigidity of the bridge.

![Figure 9.2](image)

**Figure 9.2.** a) Ligands mentioned in this chapter. $\text{Cl-bdpat}$, 2-chloro[4,6-(dipyridin-2-ylamino)]-[1,3,5]-triazine; $\text{pe-bdpat}$, 1-aminopyrene-[4,6-(dipyridin-2-ylamino)]-[1,3,5]-triazine; $\text{octadecyl-bdpat}$, octadecyl-1-amine-[4,6-(dipyridin-2-ylamino)]-[1,3,5]-triazine $\text{ph-bdpat}$, 2-phthalimide-4-ylamino-[4,6-(dipyridin-2-ylamino)]-[1,3,5]-triazine. b) Crystal structure of $[\text{Fe(Cl-bdpat)}_2(\text{H}_2\text{O})_4](\text{ClO}_4)_2$·4H$_2$O. Solvent molecules and anions are omitted for clarity.
Another potential aim is the use of the third position of the triazine ring to incorporate an additional function in the material. This may lead to hybrid building blocks, i.e. two functions (or even more) included in the same ligand. In this sense, the anchoring of 1-aminopyrene to the triazine confers luminescent properties to the new \textit{pe-bdpat} ligand. The luminescence is apparently quenched upon coordination of \textit{pe-bdpat} to Fe$^{II}$, most likely via relaxation through a non-emitting pathway. Another possibility is to attach a long alkyl chain (Figure 9.2) and, for instance, combine the spin-transition phenomenon with liquid-crystal properties. Such spin-transition/liquid crystal hybrid materials have already been achieved with 4-substituted 1,2,4-triazole-based ligands.\textsuperscript{14} Coordination experiments with the ligand \textit{octadecyl-bdpat} are currently performed, and initial results indicate that the use of this ligand does lead to spin-transition complexes with solvent-dependent properties (similarly to \textit{dpyatriz}). The liquid-crystal properties of the compounds so far prepared have not yet been investigated. Based on the aforementioned research prospects, many more bi-functional building blocks may be designed and easily synthesised. Research fields such as anti-cancer drug-discovery, catalysis or molecular magnets may now all be combined with the inherent switching capacity of spin-transition materials.
9.3 References


