Chapter 7

Summary, conclusions and perspectives
7.1. Summary, conclusions and future perspectives

This last chapter deals with a brief overview and evaluation of all the herein described work and it provides some conclusions and suggestions for further research.

Numerous efforts have been undertaken to develop new molecular magnetic materials.\textsuperscript{1} To achieve such a task, it is necessary to understand the magnetic properties at the nanoscopic level. In coordination chemistry, the origin of the magnetic moments stems from the unpaired electrons of transition-metal ions or rare-earth ions. Nevertheless, the presence of organic ligands is required to bridge the metal ions and to stabilize the whole molecule. Therefore, the magnetic properties generally depend on the nature of the paramagnetic metal ion, on the ability of the ligand to propagate magnetic exchange interactions between the metal ions and on the different structural topologies imposed by the metal-ligand interactions.

In this thesis, the manganese(III) ion has been selected to study its coordination chemistry with a variety of new phenol-pyrazole ligands, because of its paramagnetic behaviour. The manganese(III) ion displays negative Ising-type of anisotropy, which often leads to interesting magnetic properties.\textsuperscript{1} Carboxylates and Schiff-base ligands are well known bridging ligands, able to stabilize the manganese ion in various oxidation states in polynuclear clusters.\textsuperscript{2,3} Therefore, efforts have been undertaken in the search for new types of ligands, which would preferentially give novel polynuclear systems with peculiar magnetic properties. The selection of the bridging ligand is crucial for the synthesis of novel molecules with the desired topology and magnetic properties; therefore in Chapter 1 a detailed bibliographic survey has been presented to understand the ability of the pyrazole to act as a bridging ligand capable to propagate the magnetic exchange interactions in polynuclear compounds. In this thesis project, a phenol group has been introduced as substituent on the pyrazole ring, to enhance the number of possible binding sites for the metal ions due to the oxygen-donor site. Therefore, a series of phenol-pyrazole ligands has been synthesized with variations in the 5-position of the pyrazole ring, \textit{i.e.} hydrogen, methyl, ethyl and phenyl, to investigate the role of the ligand in the formation of new complexes. Consequently, the aim of this PhD research work has been to explore the coordination chemistry of these new phenol-pyrazole based ligands towards mainly the manganese(III) ion and to study the formation of new complexes and their magnetic properties.

In Chapter 2, a family of mononuclear manganese(III) compounds is presented with the general formula \([\text{Mn(HphpzR)X}_2] \) \((R = \text{H, Me, Et, Ph and } \text{X}^{-} = \text{Cl}^{-}, \text{Br}^{-})\). All these compounds contain a square-pyramidal geometry for manganese(III). It is shown how the nature of the ligand determines the crystal packing, since the presence of small substituents in the 5-position of the pyrazole ring allows the formation of 1-D chains stabilized by hydrogen bonding, whereas bulky substituents in the 5-position of the pyrazole ring, \textit{i.e.} phenyl,
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Preclude the formation of such chains. Magnetic and thermal properties were studied, showing the importance of the crystal packing on the magnetic properties. The effect on the magnetic exchange interaction by the exchange of the halogen from chloride to bromide was also analyzed in this type of compounds. Compounds of formula \([\text{Mn}(\text{HphpzH})_2X]\) \((X^- = \text{Cl}^-, \text{Br}^-)\) form chains, which are stabilized by strong hydrogen bonding and the distances between the manganese(III) ions are small enough to form magnetic chains. The analysis of the magnetic data and the thermal studies, as reported in Chapter 2, indicated Heisenberg type of chains with \(XY\) (planar) anisotropy (positive sign of \(D\)). The presence of long-range ordering was observed at \(ca.\ 1.5\ \text{K}\) with specific heat studies. The finding of a planar type of anisotropy was a bit surprising, since the manganese(III) ion in most cases displays an Ising-type of anisotropy (negative \(D\)).

As described in Appendix A, HFEPR spectroscopy was therefore performed to determine more reliably the sign and magnitude of the zero-field splitting parameters, \(D\) and \(E\) of these two compounds. The HFEPR spectra of the compounds in their powder form are reported, revealing indeed a negative sign of \(D\) and in addition a large \(E\) parameter for both compounds. Probably the absence of the \(E\) term in the theoretical models available for the analysis of the specific heat data is at the origin of the discrepancy in the sign of the \(D\) term found in the two experiments. The additional HFEPR spectra, taken in solution, revealed drastic changes in the zero-field splitting parameters, indicating the low stability of these compounds in solution. In Appendix A a discussion of the sign and magnitude of the zero-field splitting parameters for other mononuclear manganese(III) compounds reported in the literature in relation to their crystal structure is also presented. The sign and the magnitude of the zero-field splitting parameter, \(D\), is found to depend mainly on the type of ligands at the axial positions. Therefore, the study of different monodentate ligands at the axial position can be of interest, especially the iodide ligand which might lead to a positive sign of \(D\). The replacement of the monodentate ligand \(X^-\) in compounds \([\text{Mn}(\text{HphpzH})_2X]\) can be interesting not only for the study of the zero-field splitting parameters, but also for the possible effect on the strength of the magnetic exchange interaction. For instance, the introduction of a smaller ligand, such as the fluoride ion, can be expected to increase the strength of the magnetic exchange interaction, similar as observed when bromide is replaced by chloride. The compounds \([\text{Mn}(\text{HphpzMe})_2X]\) \((X^- = \text{Cl}^-, \text{Br}^-)\) also form 1-D chains and an increase of the distance between the manganese(III) ions along the chain is imposed by the ligand \(\text{H}_2\text{phpzMe}\). As a consequence, weaker antiferromagnetic interactions are observed in comparison with the compounds \([\text{Mn}(\text{HphpzH})_2X]\) \((X^- = \text{Cl}^-, \text{Br}^-)\) and 1-D magnetic ordering is not observed above 2 K. The introduction of a bulky substituent in the pyrazole ring, such as a phenyl group, precludes the formation of 1-D chains, as observed in the compounds \([\text{Mn}(\text{HphpzPh})_2X]\) \((X^- = \text{Cl}^-, \text{Br}^-)\). Since the distances
between the manganese(III) ions are large, almost a paramagnetic behaviour is observed. A bulky phenol-pyrazole ligand induces weaker magnetic exchange interactions between the manganese(III) ions. To overcome this, the substitution of the halogen could be performed by other functional groups, such as azide, acetate or dicyanamide. Thus, 1-D chains oriented along the perpendicular direction of the plane formed by the phenol-pyrazole ligands and the manganese(III) would be formed. In such compounds, the new structural effects on the magnetic exchange interaction could be studied. In addition, the compounds \([\text{Mn(HphpzR}_2X]}\) can also be used for the synthesis of high nuclearity compounds, as shown in Chapter 3; the lability of the halogen, the empty position in the coordination sphere of the manganese(III) ion and the still empty coordination bonding site of the N–H group of the pyrazole ring allow the formation of interesting clusters. The investigation of these compounds as building blocks could be further explored with various other bridging ligands, such as cyanide, azide, dicyanamide, etc., or with preformed complexes to form new compounds with different topologies.³

Chapters 3 and 4 deal with oxide-centred trinuclear manganese(III) complexes.⁵,⁶ All of them contain the trinuclear core \([\text{Mn}_3(\mu_3-O)(\text{phpzR})_3]^+\), in which the three phenol-pyrazole ligands are in the plane formed by three manganese(III) ions and the axial positions are occupied by solvent molecules (methanol or ethanol) and bridging ligands (carboxylate and azide). As a result, in these chapters the influence of the type of phenol-pyrazole ligand and of the co-ligands on the structural symmetry of the \([\text{Mn}_3(\mu_3-O)(\text{phpzR})_3]^+\) and consequently, on its magnetic properties, have been carefully investigated. Apparently the role of the phenol-pyrazole ligand is to determine the type of structure that is formed, i.e. either an isolated trinuclear unit or a 1-D chain.⁵-¹⁰ In these 1-D chains, the trinuclear units can be linked by a bridging ligand, i.e. acetate and azide or by hydrogen bonding interactions. Substituents in the 4-position of the phenol ring allow the formation of 1-D chains.⁷-¹⁰ The introduction of these substituents do not create a distortion of the \([\text{Mn}_3(\mu_3-O)]^{7+}\) core and might control the separation between the 1-D chains. However, the substituents in the 5-position of the pyrazole ring, such as methyl or phenyl can generate a difference in the \([\text{Mn}_3(\mu_3-O)]^{7+}\) core and the dimensionality of the complex depending on the type of ligands at the axial positions of the three manganese(III) ions. The presence of substituents in the 5-position of the pyrazole ring, such as methyl or phenyl, drives the carboxylate to bind to two manganese(III) ions from the same trinuclear manganese(III) unit, instead of bridging the trinuclear units (Chapter 3 and 4). If the carboxylate ligand is small, i.e. acetate, these trinuclear units can form chains because of the hydrogen bonds established between the carboxylate and solvent molecules (compounds 11 and 13). If the carboxylate ligand is bulkier, such as benzoate, two carboxylates are binding to the two manganese(III) ions of the same trinuclear unit.
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(Compounds 14 and 15) and they become isolated. Consequently, in all these cases with carboxylate ligands, the Mn–O–Mn angle(s) in which the carboxylate ligand binds the manganese(III) ions from the same trinuclear unit is (are) found to deviate strongly from the value of 120° towards smaller values; whereas the remaining angle(s) is (are) distorted toward higher values. The coordinated solvent molecules are also found to be important. The number of solvent molecules bound to manganese(III) ions can vary. For example in compound 13 only one solvent molecule is coordinated (ethanol), instead of three methanol molecules in compound 11, thereby forcing the trinuclear units in the 1-D chain to be closer than when methanol is present. In all trinuclear manganese(III) compounds containing phenol-pyrazole ligands, predominant antiferromagnetic interactions are found between the manganese(III) ions in the trinuclear unit. For an equilateral triangle, the Mn–O–Mn angles are 120° and the oxide bridge lie in the plane formed by the three manganese(III) ions. In this geometry, antiferromagnetic interactions are indeed to be expected. However, when a distortion in the [Mn3(µ3-O)]7+ core is present, notably when the Mn–O–Mn angles become smaller than 120° and a concomitant displacement of the µ3-O2− from the plane formed by the three manganese(III) ions occurs, the type of magnetic interactions between the manganese(III) ions may change drastically. In the present project such examples were encountered with the compounds [Mn3(µ3-O)(phpzMε3)(MeOH)3(OAc)]·1.5MeOH (11) and [Mn3(µ3-O)(phpzMe)3(O2CMe)(EtOH)]·EtOH (13), in which a ferromagnetic interaction was deduced in relation to the uniquely distorted pathway. Since the most important structural parameter in the magnetic exchange path has been found to be the Mn–O–Mn angle, the distortion in the three angles should be responsible for the occurrence of predominant ferromagnetic interactions. Therefore, to achieve overall ferromagnetic behaviour in the triangle, the introduction of a suitable ligand able to distort the three Mn–O–Mn angles toward smaller values is needed. The introduction of a third carboxylate ligand might induce such distortion, since the presence of two carboxylate ligands induces the distortion in two Mn–O–Mn angles (Chapter 4). Another possible bridging ligand could be a group able to bind all the three manganese(III) ions together, i.e. a triol-based ligand, (HO)3CR′(R′ = CF3, etc). However, in both cases, the compound will need two positive counter ions to balance the total charge of the complex. Another option is the addition of a counter ion, i.e. perchlorate or tetraphenylborate in which the distortion of the [Mn3(µ3-O)]7+ core can be caused by electronic effects. The overall magnetic behaviour that have been found in the trinuclear manganese(III) units with phenol-pyrazole ligands are all antiferromagnetic so far.5-10 However, the dimensionality of the compounds and the packing of these trinuclear units is important to observe different magnetic exchange interactions between the trinuclear
manganese(III) units. The majority of the trinuclear compounds composed by phenol-pyrazole ligands forms 1-D chains, in which the trinuclear units are bridged by acetate, or azide ligands.\textsuperscript{5,7-10} In case of the introduction of a substituent in the 5-position of the pyrazole ring, such as methyl, the acetate ligand binds to two manganese(III) ions from the same trinuclear units (compound 11 and 13).\textsuperscript{5,6} As a consequence, the trinuclear units are forming 1-D chains stabilized by the hydrogen bonding established between the solvent molecules and the acetate ligand. In the case of a bulkier carboxylate ligands, such as benzoate, two carboxylate ligands are at the axial positions of the manganese(III) ions of the trinuclear units. Therefore, these trinuclear units become isolated (compounds 14 and 15). In most of the 1-D chains, ferromagnetic interactions are observed between the trinuclear units that form the chain.\textsuperscript{6-10} Therefore, different magnetic behaviours are observed, varying from single-chain magnet behaviour to long-range magnetic ordering.\textsuperscript{5-10} To elucidate the factors that determine the type of magnetic exchange interactions and the dimensionality of the magnetic ordering in trinuclear manganese(III) units, the synthesis of new 1-D chains formed by trinuclear complexes is needed. Variations in the bridging ligands, such as using formate, terephthalate or even nitrogen-donor ligands, like pyrazine can be applied to bridge the trinuclear manganese(III) units. Moreover, reactions with non-alcoholic solvents, like pyridine, could be tried to check if the [Mn\textsubscript{3}(μ\textsubscript{3}-O)(phpzR)\textsubscript{3}]\textsuperscript{+} core is retained. In addition, the trinuclear units can also be used as building blocks to obtain clusters of even higher nuclearities or other topologies as it has been performed with the basic carboxylates, [Mn\textsubscript{3}(μ\textsubscript{3}-O)(O\textsubscript{2}CR)\textsubscript{6}L\textsubscript{3}]\textsuperscript{+}.\textsuperscript{11}

Chapter 5 deals with the synthesis and characterization of high-nuclearity manganese(III) compounds. Additionally, Appendix B contains some crystallographic information of these compounds. Previously, the compound [Mn\textsubscript{8}(μ\textsubscript{4}-O\textsubscript{4})(phpzMe)\textsubscript{8}(thf)\textsubscript{4}] has been reported in our group.\textsuperscript{12} Therefore, in the present study the influence of different solvents on the stability of the [Mn\textsubscript{8}(μ\textsubscript{4}-O\textsubscript{4})(phpzR)\textsubscript{8}] core has been investigated. The [Mn\textsubscript{8}(μ\textsubscript{4}-O\textsubscript{4})(phpzR)\textsubscript{8}] core is preserved when the H\textsubscript{2}phpzH or the H\textsubscript{2}phpzMe ligands are employed even when using solvents, such as ethanol or acetonitrile. However, the use of a bulkier ligand such as H\textsubscript{2}phpzEt under suitable synthetic conditions induces the formation of a new type of core, probably due to the steric effects imposed by the ethyl group. Instead, a hexanuclear compound is obtained, [Mn\textsubscript{6}(μ\textsubscript{3}-O\textsubscript{4})(μ\textsubscript{3}-Br)\textsubscript{2}(HphpzEt)\textsubscript{6}(phpzEt)] (18). In the octanuclear manganese(III) compounds [Mn\textsubscript{8}(μ\textsubscript{4}-O\textsubscript{4})(phpzR)\textsubscript{8}(s)] (R = H, Me; s = solvent), strong antiferromagnetic interactions between the manganese(III) ions are present (Chapter 5 and ref. 12) leading to a ground state of \( S_T = 0 \). The solvent does not neither modify the type of structure, nor the magnetic properties, since the strong antiferromagnetism is due principally to the magnetic exchange interaction between the manganese(III) ions in the core and in the periphery and weak antiferromagnetic interactions are expected to be present between the
manganese(III) ions in the core. However, in the hexanuclear compound 18, weak ferromagnetic interactions are observed. Apparently, this new core favours the existence of weak ferromagnetic interactions. Due to the low symmetry of the cluster it is very difficult to quantify the magnetic exchange interaction. DFT studies would be appealing to determine the main magnetic paths to further modify the molecule and increase the strength of the magnetic exchange interactions. In addition, studies at lower temperatures (< 2 K) could be performed to check the type of magnetic ordering. Although non-coordinated solvents are present in the cluster, the synthesis in other solvents might lead to the same cluster or new complexes. Although the bromide atoms are weakly bonded to the manganese(III) ions and are not expected to provide a strong magnetic exchange path, it would be of interest to replace them by chloride or azide ligands.

Chapter 6 presents the coordination chemistry of the ligand H2phpzMe towards other transition metal ions, such as cobalt(III), copper(II) and nickel(II). The choice of the transition-metal ion can lead to different products. In the case of cobalt, a dinuclear cobalt(III) compound is formed by aerial oxidation of the cobalt(II) ion. This compound is diamagnetic and the four different binding modes of the ligand to cobalt(III) ion highlight the coordination versatility of the phenol-pyrazole ligands. In the case of nickel(II) and copper(II) ions, isostructural mononuclear compounds are formed. These compounds have been prepared by numerous synthetic routes, indicating their high stability. However, under specific conditions, clusters can also be formed.13,14 So, suitable synthetic conditions could lead to the formation of other new compounds. In the case of copper(II) ion, an excess of base would be enough to doubly deprotonate the H2phpzMe ligand and the copper(II) ions could be coordinated to the three possible binding sites since an octahedral geometry is also favoured by copper(II) ions. By contrast, in the case of nickel(II) ions this might be more difficult, since the nickel(II) ion, being diamagnetic, has a strong preference for the square-planar geometry.

7.2. References