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Grau de Química

# Treball Final de Grau

## Effect of Ionic Liquids on the synthesis and reactivity of manganese complexes with carboxylate ligand.

## Efecte dels Líquids Iònics en la síntesi i reactivitat de complexos de manganès amb lligand carboxilat.

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B:KC Barcelona Knowledge Campus
Campus d'Excel·lència Internacional

*Hubo un tiempo en que caminaste sola, escribiste sola, estudiaste sola y te vestiste sola. Recuerda ese momento.*

Monique Wittig

Primer de tot, agrair la inestimable ajuda de la Dra. Montserrat Corbella. L'aprenentatge en el grup ha estat molt intens, i alhora molt enriquidor. Moltes gràcies per tots els consells, interès i dedicació prestada en tot moment.

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A tots els amics i a la meva família, per recolzar-me sempre que ho he necessitat.

# REPORT

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# 1. SUMMARY

In order to mimic the active site of the Mn-catalase enzyme, the syntheses of three manganese(II) (**1**-**3**) and four manganese(III) (**4**-**7**) compounds have been studied, and the effect that an Ionic Liquid (1-Butyl-3-methylimidazolium Chloride, BmimCl) and another chloride salt ($Bu_4NCl$) had caused on the syntheses.

For manganese(II) compounds, stoichiometric amounts of $Mn(2\text{-}NO_2C_6H_4COO)_2$ (previously synthesized) and 2,2'-bipyridine were used, and different reaction conditions (solvent and presence of BmimCl or $Bu_4NCl$ in solution) were tested. The dinuclear compounds obtained **1** and **2** have general formula $[\{Mn(bpy)(2\text{-}NO_2C_6H_4COO)(L_1)\}(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2\{Mn(bpy)(2\text{-}NO_2C_6H_4COO)(L_2)\}]$, where for **1** $L_1$ = EtOH, $L_2 = H_2O$ and for **2** $L_1 = L_2 = H_2O$. Analogous compounds had been synthesized by the research group previously. Compound **3** $[Mn(bpy)(H_2O)_2(2\text{-}NO_2C_6H_4COO)_2]_n$ could be a more complex system that will need to be studied in more detail.

Manganese(III) compounds were obtained from the comproportionation reaction between a manganese(II) salt (nitrate or perchlorate) and $Bu_4NMnO_4$. The reaction conditions were also modified by adding BmimCl or $Bu_4NCl$ to the solutions, which led to the obtention of surprising compounds. Dinuclear compounds **4** and **7** (general formula $[\{Mn(H_2O)(bpy)\}_2(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2(\mu\text{-}O)](X)_2$, where X = $NO_3^-$ (**4**) or $ClO_4^-$ (**7**)) had already been obtained as well by the research group. The mixed-valence compounds $[Mn(bpy)Cl_2(H_2O)_2][\{Mn(bpy)Cl\}(\mu\text{-}2\text{-}NO_2C_6H_4COO)(\mu\text{-}O)_2\{Mn(bpy)(H_2O)\}]$ (**5**) and $[Mn(bpy)_2Cl_2][\{Mn(bpy)(H_2O)\}_2(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2(\mu\text{-}O)]Cl_3(ClO_4)$ (**6**) were only obtained by adding BmimCl or $Bu_4NCl$ to the solutions. These could also be more complex systems.

In this work, any crystal of good quality for X-ray diffraction has been obtained. However, the different compounds were characterized by IR spectroscopy, conductivity measurements, study of the magnetic behaviour and EPR spectroscopy. The molecular formulas of compounds **1-7** have been proposed from these studies.

Finally, an attempt to measure the catalase activity of the manganese(III) compounds **4-7** was performed, by the volumetric measurement of the $O_2$ evolved by the reaction of disproportion of $H_2O_2$. The compounds were poorly active, and the results have not been included in the memory.

**Keywords**: Manganese, Ionic Liquid, magnetic properties, EPR spectroscopy.

# 2. RESUM

Amb l'objectiu de mimetitzar el centre actiu de l'enzim Mn-catalasa, s'ha estudiat la síntesi de tres compostos de manganès(II) (**1**-**3**) i quatre compostos de manganès(III) (**4**-**7**), i l'efecte que han causat un Líquid Iònic (Clorur d'1-Butil-3-metillimidazol, BmimCl) i una altra sal de clorur ($Bu_4NCl$) en les síntesis.

Pels compostos de manganès(II), s'han utilitzat quantitats estequiomètriques de $Mn(2\text{-}NO_2C_6H_4COO)_2$ (sintetitzat prèviament) i 2,2'-bipiridina, i s'han variat les condicions de reacció (dissolvent i presència de BmimCl o $Bu_4NCl$ en solució). Els compostos dinuclears obtinguts **1** i **2** tenen fórmula general $[\{Mn(bpy)(2\text{-}NO_2C_6H_4COO)(L_1)\}(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2\{Mn(bpy)(2\text{-}NO_2C_6H_4COO)(L_2)\}]$, per **1** $L_1$ = EtOH, $L_2 = H_2O$ i per **2** $L_1 = L_2 = H_2O$. Anteriorment ja s'havien sintetitzat compostos anàlegs pel grup d'investigació. El compost **3** $[Mn(bpy)(H_2O)_2(2\text{-}NO_2C_6H_4COO)_2]_n$ podria tractar-se d'un sistema més complex que caldrà estudiar més detalladament.

Els compostos de manganès(III) s'han obtingut a partir de la reacció de comproporció entre una sal de manganès(II) (nitrat o perclorat) i $Bu_4NMnO_4$. També s'han variat les condicions de reacció afegint BmimCl o $Bu_4NCl$ a les solucions, el que va conduir a l'obtenció de compostos sorprenents. Els compostos dinuclears **4** i **7** (fórmula general $[\{Mn(H_2O)(bpy)\}_2(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2(\mu\text{-}O)](X)_2$, on X = $NO_3^-$ (**4**) o $ClO_4^-$ (**7**)) ja s'havien obtingut també pel grup d'investigació. Els compostos de valència mixta $[Mn(bpy)Cl_2(H_2O)_2][\{Mn(bpy)Cl\}(\mu\text{-}2\text{-}NO_2C_6H_4COO)(\mu\text{-}O)_2\{Mn(bpy)(H_2O)\}]$ (**5**) i $[Mn(bpy)_2Cl_2][\{Mn(bpy)(H_2O)\}_2(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2(\mu\text{-}O)]Cl_3(ClO_4)$ (**6**) només s'han obtingut afegint BmimCl o $Bu_4NCl$ a les solucions. Aquests també podrien tractar-se de sistemes més complexos.

En aquest treball no s'ha obtingut cap cristall de bona qualitat per fer difracció de raig X. No obstant, s'han caracteritzat els diferents compostos mitjançant espectroscòpia IR, mesures de conductivitat, estudi del comportament magnètic i espectroscòpia EPR. Les formules moleculars dels compostos **1**-**7** s'han proposat a partir d'aquests estudis.

Per últim, s’ha intentat mesurar l’activitat catalasa dels compostos de manganès(III) **4**-**7**, mitjançant la mesura volumètrica del $O_2$ emès per la reacció de desproporció de $H_2O_2$. Els compostos eren molt poc actius i els resultats no s’han inclòs en la memòria.

**Paraules clau**: Manganès, Líquid Iònic, propietats magnètiques, espectroscòpia EPR.

# 3. INTRODUCTION

The interest in the study of dinuclear complexes of manganese(II) and manganese(III) with carboxylate bridging ligand is due to their paper in some metalloenzymes. One of the most studied is the catalase enzyme, which is the responsible for catalysing the disproportion reaction of hydrogen peroxide into water and molecular oxygen:

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$$

There are two types of catalases, which can be classified according to their cofactor type: type I contains a hemo group in their active site, whereas type II contains two manganese ions bridged by carboxylate ligands (also called Mn-catalases). Two Mn-catalase enzymes have been isolated from *Lactobacilus plantarum*[1] and *Thermos thermophillus*[2], and their crystal structure has also been studied using X-ray diffraction[3–5]. Due to these works it has been possible to prove that there are two manganese ions in the active site of the enzyme. In the oxidized form ($Mn^{III}Mn^{III}$) both ions are bridged by a carboxylate, an oxide and a hydroxide, whereas in the reduced form ($Mn^{II}Mn^{II}$) they are bridged by a carboxylate, a hydroxide and a water. The coordination octahedron is completed with histidine and glutamate residues, or terminal water (**Figure 1**).

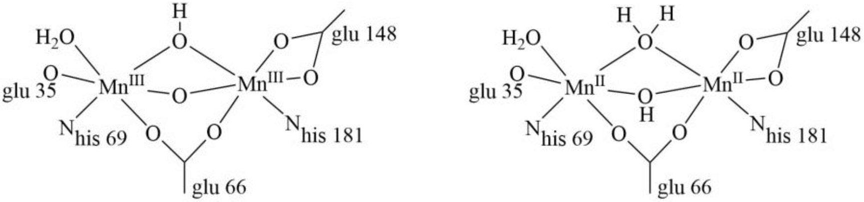


**Figure 1.** Structure of the oxidized form (left) and reduced form (right) of the active site of the catalase enzyme isolated from *Lactobacilus plantarum*[5].

The main function of the enzyme is its antioxidant capacity[6]. This is vital for many organisms, since hydrogen peroxide may end up forming hydroxyl radicals which can cause damage to cells, including their DNA for different mutagenic effects.

The catalytic cycle of Mn-catalase is not entirely known, although some estimations have been made thanks to circular dichroism, EPR and atomic absorption techniques. One of the proposed reaction mechanism for Mn-catalase enzyme in *Lactobacilus plantarum* is the following[5]:

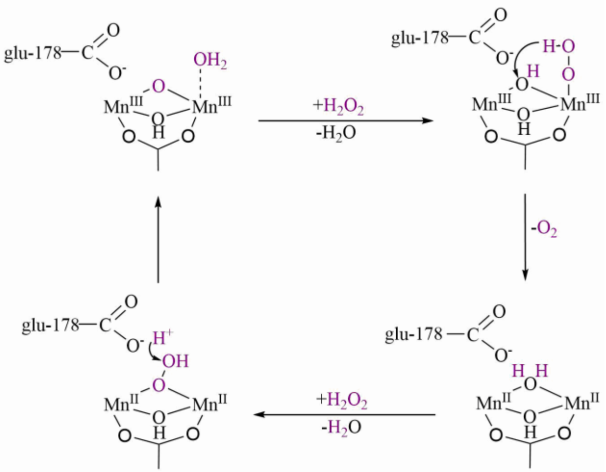


**Figure 2.** Proposed reaction mechanism of Mn-catalase enzyme for disproportion of $H_2O_2$ in *Lactobacilus plantarum*[5].

To be able to study in detail the active site of these enzymes and their functions, there have been synthesized model compounds with a similar structure to those. The research group "Models en bioinorgànica" has been focused on the synthesis and characterization of many variants of dinuclear manganese(II) and manganese(III) compounds with carboxylate bridging ligand.

The interest of these species is given by its antioxidant capacity in the disproportion of $H_2O_2$, and due to the versatility of their magnetic behaviour, specially of $Mn^{III}$ compounds. The interactions between $Mn^{III}$ ions can vary from ferro- to antiferromagnetic, with ground state $S = 4$ and $S = 0$, respectively[7]. These variations in magnetic behaviour may be due to structural changes caused by the elongation and distortion of the coordination octahedra of the ions[8].

The reaction between $Mn^{II}$ carboxylate and bidentate ligands (NN), such as 2,2'-bipyridine and 1,10-phenantroline leads to the formation of $Mn^{II}$ compounds with different nuclearity: mononuclear, dinuclear, trinuclear or 1D systems[9].

This work has been based on the study of the syntheses, reactivity and characterization of three $Mn^{II}$ compounds with 2-nitrobenzoate and 2,2'-bipyridine ligands ($[\{Mn(bpy)(EtOH)(2\text{-}NO_2C_6H_4COO)\}(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2\{Mn(bpy)(H_2O)(2\text{-}NO_2C_6H_4COO)\}]$ (**1**), $[\{Mn(bpy)(H_2O)(2\text{-}NO_2C_6H_4COO)\}_2(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2]$ (**2**), $[Mn(bpy)(H_2O)_2(2\text{-}NO_2C_6H_4COO)_2]_n$ (**3**)).

Moreover, the syntheses and characterization of two $Mn^{III}$ dinuclear compounds ($[\{Mn(bpy)(H_2O)\}(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2(\mu\text{-}O)\{Mn(bpy)(NO_3)\}](NO_3)$ (**4**), and $[[\{Mn(bpy)(H_2O)\}_2(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2(\mu\text{-}O)](ClO_4)_2$ (**7**)) and two mixed-valence Mn compounds $[Mn(bpy)Cl_2(H_2O)_2][Mn(bpy)Cl\}(\mu\text{-}2\text{-}NO_2C_6H_4COO)(\mu\text{-}O)_2\{Mn(bpy)(H_2O)\}]$ (**5**) and $[Mn(bpy)_2Cl_2][\{Mn(bpy)(H_2O)\}_2(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2(\mu\text{-}O)]Cl_3(ClO_4)$ (**6**)) has been studied.

In order to characterize the compounds, infrared spectroscopy spectra, elemental analysis, conductivity measurements, magnetism studies and EPR spectra (this latter only for $Mn^{II}$ compounds) have been used.

Furthermore, the role of an Ionic Liquid in the syntheses of the compounds has also been tested. Ionic Liquids (ILs) are defined as ionic organic substances (mostly quaternary ammonium or phosphonium salts) with melting point below 100 ºC, although the most commonly used are those with melting point close to room temperature[10].

The use of IL as a solvent is increasingly replacing VOC's (Volatile Organic Compounds). They are considered as a green alternative due to their low toxicity and thanks to some of these interesting properties[11]:

- They do not have vapour pressure (or it is negligible), therefore they do not evaporate and the inhalative exposure of workers is reduced.
- They have been shown to be non-flammable, so they are safer to manipulate.
- They are capable of dissolving metallic complexes, organic and organometallic compounds and gases.
- They are miscible in many organic solvents and water.

For this reasons, ILs have become a very important source of study in various fields of science. One of the applications that most attention is paid is the use of ILs in catalysed reactions. The reason for this is that metal catalysts could get immobilized in the ILs, and consequently they could have a rate acceleration effect on some reactions. In addition, the recovery and subsequent recycling of the immobilized catalyst would be facilitated.

In this work, the IL 1-Butyl-3-methylimidazolium Chloride (BmimCl) and another chloride salt ($Bu_4NCl$) have been used in some of the syntheses to test the effect they cause on the obtention of compounds.

The catalase activity of $Mn^{III}$ compounds **4-7** has also been tested by the volumetric measurement of the $O_2$ evolved by the reaction of disproportion of $H_2O_2$. The same measurements have also been tested with presence of triethylamine and the IL in the solution as well, to verify if it improves the catalytic efficiency of the compounds.

# 4. OBJECTIVES

- Mimic the active site of the Mn-catalase enzyme by synthesizing dinuclear compounds with 2-nitrobenzoate bridging ligand. Synthesis of manganese(II) compound $[\{Mn(bpy)(2\text{-}NO_2C_6H_4COO)\}_2(\mu\text{-}H_2O)(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2]$ (**A**), and manganese(III) compounds (already obtained by the research group[12,13]) with general formula $[\{Mn(H_2O)(bpy)\}_2(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2(\mu\text{-}O)](X)_2$, where X = $NO_3^-$ (**4**) or $ClO_4^-$ (**7**).
- Study the effect of the Ionic Liquid 1-Butyl-3-methylimidazolium Chloride (BmimCl) and $Bu_4NCl$ on the syntheses of the previous compounds.
- Characterize the synthesized species using magnetism and EPR techniques.
- Study the catalase activity of the $Mn^{III}$ compounds obtained by volumetric measurements of the $O_2$ evolved. Verify if the presence of Ionic Liquid in the solution affects their catalase activity.

# 5. SYNTHESIS AND CHARACTERIZATION

## 5.1. MANGANESE(II) COMPOUNDS

One of the targets of this work was to synthesize the manganese(II) compound [{Mn(bpy)(2-$NO_2C_6H_4COO$)}$_2$(μ-$H_2O$)(μ-2-$NO_2C_6H_4COO$)$_2$] (**A**) in order to mimic the active site of the catalase enzyme in its reduced form. Some other dinuclear compounds with general formula [{Mn(NN)(n-$RC_6H_4COO$)}$_2$(μ-$H_2O$)(μ-n-$RC_6H_4COO$)$_2$] (where NN = 2,2'-bipyridine or 1,10-phenantroline) have been reported in the literature previously[14–16], but none with R = 2-$NO_2$.

In this project it has not been possible to obtain the desired compound **A**. It can be discarded that this is due to the steric hindrance of the nitro group in *ortho* position, since one of the carboxylates used previously in compounds with aquo bridging ligand has been the anthracene carboxylate, which is very bulky.

The acidity of the carboxylate ligand could also be a determining factor to obtain compounds with water bridging ligand. In these compounds, there are some hydrogen bonds interacting between the carbonyl group of the monodentate carboxylate ligand and the aquo bridge, therefore the structure of the molecule is more rigid and gains stability[16].

The pKa values of the carboxylic acids of the compounds with water and carboxylate bridges previously reported are in the range 5.11-3.25[17,18], whereas the pKa value for 2-$NO_2C_6H_4COOH$ is 2.17. Its low pKa value could explain the non-formation of these hydrogen bonds, so the aquo bridge is not formed either.

In previous syntheses prepared by the research group with Mn(2-$NO_2C_6H_4COO$)$_2$, three types of polynuclear compounds of $Mn^{II}$ were obtained, depending on the stoichiometry of the reagents and the solvent used. The neutral dinuclear compound [{Mn(bpy)(EtOH)(2-$NO_2C_6H_4COO$)}$_2$(μ-2-$NO_2C_6H_4COO$)$_2$] (**B**) was obtained with the stoichiometric reaction between Mn(2-$NO_2C_6H_4COO$)$_2$ and 2,2'-bipyridine (bpy) and ethanol as solvent. The ionic dinuclear compound [{Mn(bpy)$_2$}$_2$(μ-2-$NO_2C_6H_4COO$)$_2$]($ClO_4$)$_2$ was obtained by adding $NaClO_4$ in the solution and bpy in 1:2 stoichiometry with the carboxylate in ethanol. Finally, the neutral trinuclear compound [$Mn_3$(bpy)$_2$(μ-2-$NO_2C_6H_4COO$)$_6$] was obtained by adding 2/3 of bpy and using acetonitrile as solvent[13].

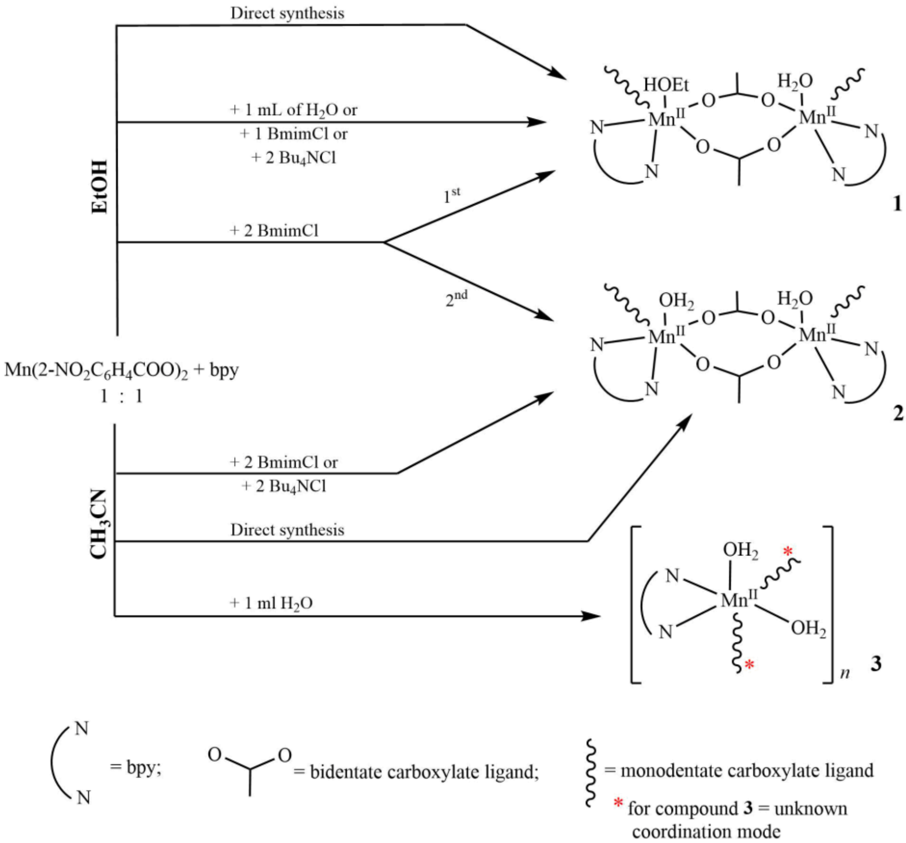
To favour the obtention of the dinuclear neutral compound **A**, stoichiometric amounts of the reagents were used. Then, the reaction conditions were varied as it is shown in the **Scheme 1**.

Manganese(II) carboxylate and bpy were mixed in ethanol or acetonitrile. In some syntheses also 1 mL of water was added to force the incorporation of the aquo bridge between $Mn^{II}$ ions. Furthermore, 1-Butyl-3-methylimidazolium Chloride (BmimCl) was used in 1:1 and 1:2 stoichiometry ($Mn(2\text{-}NO_2C_6H_4COO)_2$:BmimCl) in order to see the effect of Ionic Liquids on the syntheses. Finally, another organic chloride salt (tetrabutylammonium chloride, $Bu_4NCl$) was also used to verify if it causes the same effect as the IL.

Before starting the syntheses, it is necessary to prepare the manganese(II) carboxylate since it is not commercially available. This can be easily obtained by reacting the corresponding carboxylic acid and $Mn(AcO)_2$, using water as solvent and heating the solution[14]:

$$Mn(AcO)_2 + 2\ 2\text{-}NO_2C_6H_4COOH \xrightarrow{\Delta} Mn(2\text{-}NO_2C_6H_4COO)_2 + 2\ AcOH$$

All the compounds obtained following these syntheses are very insoluble in their respective reaction media. They precipitated very fast and crystals were not suitable for X-ray diffraction, therefore it has not been possible to solve their crystal structure. In the following sections the deduction of the proposed formulas of the compounds will be discussed.



**Scheme 1.** Syntheses scheme of $Mn^{II}$ compounds.

The proposed formulas have been based on IR spectra, elemental analysis, conductivity measurements, studies of magnetism and EPR spectra.

The formation of $[\{Mn(bpy)(EtOH)(2\text{-}NO_2C_6H_4COO)\}(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2\{Mn(bpy)(H_2O)(2\text{-}NO_2C_6H_4COO)\}]$ (**1**) was highly favoured when the syntheses were performed in ethanol, whereas $[\{Mn(bpy)(H_2O)(2\text{-}NO_2C_6H_4COO)\}_2(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2]$ (**2**) formation was favoured in acetonitrile. Although they have very similar structure, IR spectra of compounds **1** and **2** have slight differences that will be discussed later.

It seems that the addition of BmimCl or $Bu_4NCl$ to the mixtures did not cause any relevant effect on the obtained products: elemental analysis and magnetism studies indicate that $Cl^-$ is not in the complexes. It is worth mentioning that when BmimCl was added to the syntheses, the products were mostly crystalline, but they were covered by a layer of oil that had to be removed with water. This made the separation of the crystals more difficult. The obtention of compound **2** in the second fraction of the synthesis performed in ethanol and BmimCl:Mn(2-$NO_2C_6H_4COO)_2$ in 2:1 stoichiometry is not surprising, since each manganese has a labile position where either a water or ethanol molecule of the solvent can get coordinated.

Compounds **1** and **2** would have similar structure to the above-mentioned compound **B**. In its crystal structure, both $Mn^{II}$ ions are bridged by carboxylate ligands in *syn-anti* conformation mode. Crystal structure of compound **B** is shown in **Figure 3**[13]. The general formula for compounds **1**, **2** and **B** is [{Mn(bpy)(2-$NO_2C_6H_4COO$)($L_1$)}(μ-2-$NO_2C_6H_4COO)_2${Mn(bpy)(2-$NO_2C_6H_4COO$)($L_2$)}], where for **1** $L_1$ = EtOH, $L_2$ = $H_2O$; for **2** $L_1$ = $L_2$ = $H_2O$; and for **B** $L_1$ = $L_2$ = EtOH. Hereinafter, the three dinuclear compounds of manganese(II) will be labelled as $Mn^{II}_2$-EW (**1**), $Mn^{II}_2$-WW (**2**) and $Mn^{II}_2$-EE (**B**), according to their labile ligands $L_1$ and $L_2$.

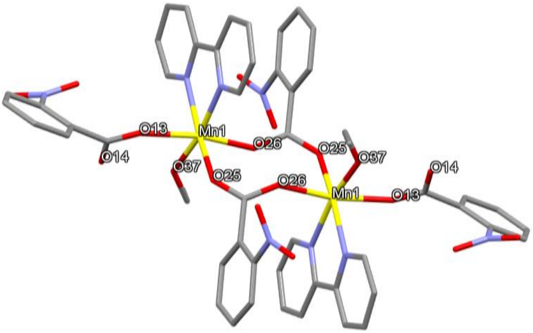
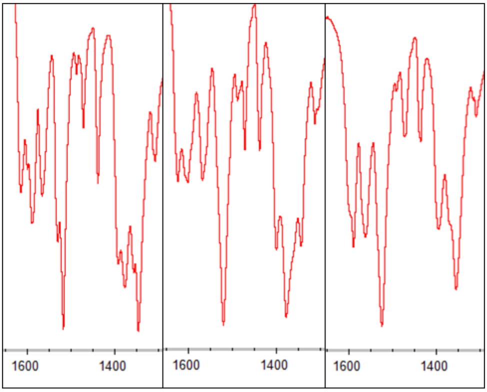


**Figure 3.** Crystal structure of the neutral compound [{Mn(bpy)(EtOH)(2-$NO_2C_6H_4COO$)}$_2$ (μ-2-$NO_2C_6H_4COO)_2$] (**B**)[13]. Hydrogen atoms have been omitted for clarity.

Furthermore, when the synthesis was performed in acetonitrile and 1 mL of water was added ($CH_3CN$:$H_2O$ 10:1) compound **3** [Mn(bpy)$(H_2O)_2$(2-$NO_2C_6H_4COO)_2]_n$ ($Mn^{II}_n$) was obtained. Elemental analysis, magnetism and EPR studies fit with the proposed formula, but it has not been possible to determine the coordination mode of the carboxylate ligands. Deductions indicate that it could be an *n*D (*n* = 1, 2 or 3) system of manganese(II) ions bridged by carboxylate ligands, or a *n*D system of mononuclear complexes interacting by hydrogen bonds. Some extended $Mn^{II}$ systems have been reported in literature[9,19], but none fits with our characterization.

The characterization using Infrared Spectroscopy[20] (IR) is an useful technique to identify different compounds according to their functional groups. The most characteristic bands of the 2,2'-bipyridine appear at 1600-1400 $cm^{-1}$ and 850-600 $cm^{-1}$ intervals. Carboxylate groups have two very intense bands which correspond to asymmetric and symmetric vibrations at 1620-1550 and 1410-1380 $cm^{-1}$, respectively. Moreover, the nitro group of the benzoate ligand displays asymmetric vibrations at 1470-1370 $cm^{-1}$ and symmetric ones at 1340-1320 $cm^{-1}$. As seen, many of these bands might appear overlapped in the spectra and makes it difficult to identify each compound properly.

Although the proposed structures for $Mn^{II}_2$-EW (**1**) and $Mn^{II}_2$-WW (**2**) are very similar, their IR spectra have slight differences in the carboxylate vibrations region. Probably the differences between the coordinated monodentate ligands, especially their steric hindrance, affect the carboxylate coordination modes and it is reflected in the IR spectra. Compound **3** ($Mn^{II}_n$) also presents some differences in 1650-1500 and 1400-1350 $cm^{-1}$ intervals with respect to **1** and **2**. In **Figure 4** some differences can be appreciated between all them in the range 1650-1300 $cm^{-1}$. This has been one of the determining factors to propose that there were three different manganese(II) compounds synthesized in this work.



$Mn^{II}_2$-EW (**1**) $Mn^{II}_2$-WW (**2**) $Mn^{II}_n$ (**3**)

**Figure 4.** IR spectra for compounds **1**, **2**, and **3** in the range 1650-1300 $cm^{-1}$.

## 5.2. MANGANESE(III) COMPOUNDS

Another objective of this work was to synthesize dinuclear manganese(III) compounds with general formula $[\{Mn(bpy)(H_2O)\}_2(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2(\mu\text{-}O)](X)_2$, where X = $NO_3^-$ (**4**) or $ClO_4^-$ (**7**). Hereinafter, both dinuclear compounds of manganese(III) will be labelled as $Mn^{III}_2\text{-}NO_3$ (**4**) and $Mn^{III}_2\text{-}ClO_4$ (**7**), according to their counterions. The syntheses, magnetic properties, X-ray structures and catalase activity for compounds **4** and **7** have already been described in the literature[12,13].

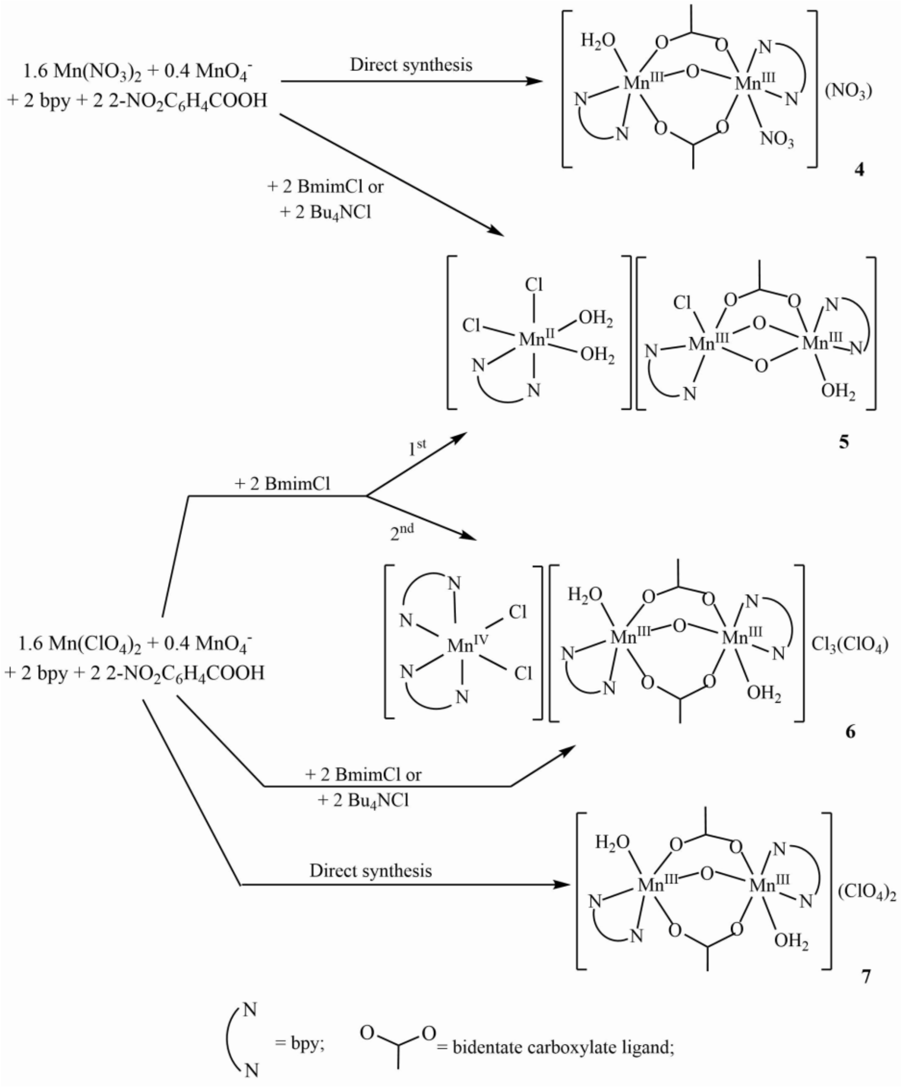
$Mn^{III}$ dinuclear compounds were obtained from the comproportionation reaction between a $Mn^{II}$ salt and $Bu_4NMnO_4$ in presence of bpy and $2\text{-}NO_2C_6H_4COOH$, as it shows the following equation[21]:

$$1.6\ Mn(X)_2\cdot n\ H_2O + 2\ 2\text{-}NO_2C_6H_4COOH + 2\ bpy + 0.4\ Bu_4NMnO_4 \rightarrow$$

$$\rightarrow [\{Mn(H_2O)(bpy)\}_2(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2(\mu\text{-}O)](X)_2 + 0.4\ Bu_4NX + 0.8\ HX + m\ H_2O$$

The syntheses were carried out in acetonitrile since ethanol can be oxidized to ethanal due to the presence of $Bu_4NMnO_4$ or $Mn^{III}$ compounds[22]. BmimCl and $Bu_4NCl$ were also added in some of the syntheses to test the effect they cause on the final compounds. As it is shown in the **Scheme 2**, a large variety of products were obtained depending on the $Mn^{II}$ salt used.

As it happened for manganese(II) compounds, the crystals obtained from these products are not suitable for X-ray diffraction, therefore it has not been possible to obtain their crystal structure. The deduction of the proposed formulas will be discussed in the following sections.



**Scheme 2.** Syntheses scheme of $Mn^{III}$ compounds. All the syntheses were performed in acetonitrile.

The proposed formulas have been based on IR spectra, elemental analysis, conductivity measurements and studies of magnetism and EPR (this latter only for the mixed-valence $Mn^{II}Mn^{III}_2$ compound **5**).

Regarding to the direct synthesis with $Mn(NO_3)_2$ as reagent, $[\{Mn(bpy)(H_2O)\}(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2(\mu\text{-}O)\{Mn(bpy)(NO_3)\}](NO_3)$ (**4**) was obtained. Our characterization concludes that this product is the same as the one synthesized previously by the research group[12].

$Mn^{III}_2\text{-}NO_3$ (**4**) is very insoluble in acetonitrile and precipitates in few minutes. However, when BmimCl or $Bu_4NCl$ were added to the suspension the redissolution of the solid was observed, and 30 minutes later a new precipitate appeared. The first hypothesis was that a dinuclear neutral compound with the same general formula for **4** and **7**, with chloride ligand in the labile positions $[\{Mn(Cl)(bpy)\}_2(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2(\mu\text{-}O)]$ was obtained.

Its elemental analysis does not fit with this formula and the conductivity measurements indicate that it was a neutral compound. Magnetic susceptibility measurements also did not fit with a dinuclear $Mn^{III}$ compound. Finally, EPR studies were a clear indicative that at least one $Mn^{II}$ was part of this product. Therefore, the proposed formula that best fits our analysis and the magnetic data is the $Mn^{II}Mn^{III}_2$ mixed-valence compound $[Mn(bpy)Cl_2(H_2O)_2][\{Mn(bpy)Cl\}(\mu\text{-}2\text{-}NO_2C_6H_4COO)(\mu\text{-}O)_2\{Mn(bpy)(H_2O)\}]$ (**5**), composed by two neutral complexes: a mononuclear $Mn^{II}$ and a dinuclear $Mn^{III}$.

The obtention of this compound is surprising since $Mn^{III}$ is a polarizing cation and is more attracted by hard ligands such as nitrate or water, despite this it seems that chloride got coordinated. It can also be concluded that the obtention of the compound is not due to the use of an IL, but to the presence of chloride ions in solution.

Now regarding to the direct synthesis with $Mn(ClO_4)_2$ as reagent, $[\{Mn(bpy)(H_2O)\}_2(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2(\mu\text{-}O)](ClO_4)_2$ (**7**) is obtained. This compound is much more soluble in acetonitrile than its analogue with $NO_3^-$ anion. Previously in the research group[13] the same compound was obtained by slow diffusion of *n*-hexane (precipitant) to an acetonitrile solution of **7** layered with dichloromethane. In the synthesis performed in this work, dichloromethane was added to the acetonitrile solution of **7** (1:1) and it was kept under *n*-hexane atmosphere for 30 days. Finally, it was necessary to left it in slow evaporation at air to obtain the desired product.

In both compounds $Mn^{III}_2\text{-}NO_3$ (**4**) and $Mn^{III}_2\text{-}ClO_4$ (**7**) manganese(III) ions are bridged by one oxo and two carboxylate ligands in *syn*-*syn* coordination mode (**Figure 5**). The hexacoordination polyhedron of each $Mn^{III}$ ion is completed with a bpy and a monodentate ligand. For compound **4** the labile ligands are $NO_3^-$ and $H_2O$, and for compound **7** two $H_2O$ ligands, resulting a cationic complex in both cases[12,13].

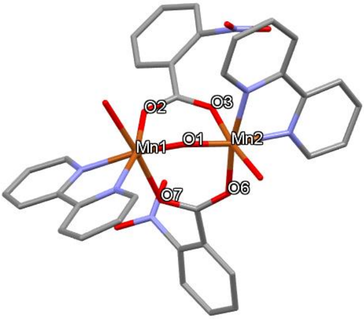


**Figure 5.** Crystal structure[13] of the core of the cationic complex [{Mn(bpy)($L_1$)}(μ-2-$NO_2C_6H_4COO$)$_2$(μ-O){Mn(bpy)($L_2$)}]$^{n+}$. For compound **4**: $L_1 = H_2O$ and $L_2 = NO_3^-$. For compound **7**: $L_1 = L_2 = H_2O$. Hydrogen atoms have been omitted for clarity.

Regarding to the syntheses with perchlorate salt, a mixture of $Mn(ClO_4)_2$, 2-$NO_2C_6H_4COOH$, $Bu_4NMnO_4$ and bpy was left in constant agitation and 30 minutes later BmimCl was added. Almost immediately, a new dark-brown precipitate appeared. Its IR spectra was recorded, and it could be observed that it was the same spectrum as the one for compound **5**.

In this way, it was concluded that when chloride ions were added to the above-mentioned mixture, these were coordinated much faster than $NO_3^-$ or $ClO_4^-$ anions and the compound [Mn(bpy)$Cl_2$($H_2O$)$_2$][{Mn(bpy)Cl}(μ-2-$NO_2C_6H_4COO$)(μ-O)$_2${Mn(bpy)($H_2O$)}] (**5**) was formed.

After the first precipitate was filtered, the mother liquor was kept and a new precipitate, this time crystalline, appeared a few days later. The presence of $ClO_4^-$ in this compound could be confirmed thanks to its characteristic band in the IR spectra at 1100 cm$^{-1}$. Then, this compound must be different to **5**. Elemental analysis and magnetism studies confirmed this fact. Finally, the proposed general formula that most suited the analysis and the magnetic measurements was the $Mn^{IV}Mn^{III}_2$ mixed-valence compound [Mn(bpy)$_2L_2$][{Mn(bpy)(L)}(μ-2-$NO_2C_6H_4COO$)$_2$(μ-O){Mn(bpy)(L)}](X)$_n$, where L = $Cl^-$, $ClO_4^-$ or $H_2O$ and X = $Cl^-$ or $ClO_4^-$.

The proposed formula for this new compound consists of a mononuclear $Mn^{IV}$ complex and a dinuclear $Mn^{III}$ complex with analogous structure to **4** and **7**. Since the crystalline structure of the compound has not been solved, it cannot be determined which ligands occupy the labile positions of the complexes. The formula of the mixed-valence $Mn^{IV}Mn^{III}_2$ compound

$[Mn(bpy)_2Cl_2][\{Mn(bpy)(H_2O)\}_2(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2(\mu\text{-}O)]Cl_3(ClO_4)$ (**6**) has been proposed according to the conductivity measurements[23].

The synthesis with $Mn(ClO_4)_2$ was repeated but this time changing the order in which the reagents were added. Firstly, BmimCl and bpy were added into a mixture of $Mn(ClO_4)_2$, $2\text{-}NO_2C_6H_4COOH$, $Bu_4NMnO_4$. Secondly, the same process was repeated but with $Bu_4NCl$ instead of BmimCl. In these attempts, only compound **6** was obtained.

It can be said that there is a certain competitiveness of $ClO_4^-$ and $Cl^-$ ions in solution for getting coordinated to $Mn^{III}$ ions, but it has not been possible to control it. A hypothesis is that factors such as the order in which the reagents are added, the agitation time or the room temperature could favour the formation of **5** or **6**.

Previously in manganese(II) section, some of the most characteristic bands of the ligands in the IR spectrum have been commented. For manganese(III) compounds, oxo bridge and counterions bands should also be considered. $Mn\text{-}O_{bridge}\text{-}Mn$ bonds arise between 740 and 560 $cm^{-1}$. $NO_3^-$ and $ClO_4^-$ present a very intense and broad band at 1380 and 1100 $cm^{-1}$, respectively. Especially $ClO_4^-$ band has been very useful to identify this ligand in some compounds, as explained above.

# 6. MAGNETIC PROPERTIES

Magnetic susceptibility data of the compounds **1-7** were recorded in the range 300-2 K. The fit of the experimental data ($\chi_M T$ versus $T$) was performed with PHI[24] program. The program uses the spin Hamiltonian $H = -2JS_1 \cdot S_2$ for dinuclear compounds $Mn^{II}_2$-EW (**1**), $Mn^{II}_2$-WW (**2**), $Mn^{III}_2$-$NO_3$ (**4**), $Mn^{III}_2$-$ClO_4$ (**7**) and $H = -2JS_1 \cdot S_2 + S_3$ for the mixed-valence compound $Mn^{II}Mn^{III}_2$ (**5**), considering magnetic coupling constant ($J$) and the spin operator ($S_i$). The experimental data of manganese(II) compound $Mn^{II}{}_n$ (**3**) and mixed-valence compound $Mn^{IV}Mn^{III}_2$ (**6**) has not been fitted due to its complex behaviour.

Magnetization ($M$) measurements at low temperatures (2 K) and strong magnetic fields ($H$) ($M$/N$\mu_\beta$ versus $H$ graph, N = Avogadro Number) are an useful tool to know the number of unpaired electrons of the spin ground state of the compound. In addition, magnetization measurements varying temperature (1.8-6.7 K) and magnetic field ($M$/N$\mu_\beta$ versus $HT^{-1}$ graph) are a good technique to determine the axial anisotropy parameter ($D_{Mn}$). This splits the spin states $S$ into levels $M_s$ = ± 0, 1, …, $n$/2 for non-fractional $S$ and into $M_S$ = ± 1/2, 3/2, …, $n$/2 for fractional $S$ values ($n$ = number of unpaired electrons). 2$J$ value indicates the energy gap between the spin ground state and the first excited state for a dinuclear compound with antiferromagnetic coupling (shown below in page 30). The rhombic anisotropy parameter ($E_{Mn}$) split the positive and negative $M_S$ levels[25].

It is worth mentioning the difference between the Zero-Field Splitting (ZFS) parameters of the ion ($D_{Mn}$ and $E_{Mn}$) and the ZFS parameters for the spin states ($D_S$ and $E_S$), which are related to the ion ones. For a mononuclear compound there is only one possible spin state, therefore the ion parameters and the spin state parameters will be the same. Nevertheless, for polynuclear compounds there are more than one possible spin state, so $D_S$ and $E_S$ will have different value for each spin state of the system.

The value of the ZFS parameter $D_{Mn}$ of the manganese(II) ion is very low ($|D_{Mn}| < 0.3$ cm$^{-1}$)[26] since $Mn^{II}$ ions do not manifest Jahn-Teller effect. Therefore, this parameter has been omitted in the fit of the magnetic susceptibility data. For $Mn^{III}$ ion this parameter is much greater ($|D_{Mn}|$ = 2-5 cm$^{-1}$) and in some cases its effect can be observed in magnetism graphs. For this reason, for $Mn^{III}$ ions the ZFS parameter $D_{Mn}$ has been included in the fit. Also, Jahn-Teller axis (Euler $\beta$ angle) will only be considered for $Mn^{III}$ dinuclear compounds. The crystal structures solved previously by the research group[12,13] for the dinuclear compounds $Mn^{III}_2$-$NO_3$ (**4**) and $Mn^{III}_2$-$ClO_4$

(**7**) indicate that the relative orientation of the two coordination octahedra are near perpendicularity. For analogous compounds with $[Mn_2(\mu\text{-}O)(\mu\text{-}n\text{-}RC_6H_4COO)_2]^{2+}$ core it has been verified that the alignment of the axes must be considered to fit of the magnetic susceptibility data, since otherwise it would lead to erroneous results[27].

## 6.1. MAGNETIC BEHAVIOUR OF MANGANESE(II) DINUCLEAR COMPOUNDS 1 AND 2

Compounds **1**, **2**, and **B** have the same general formula $[\{Mn(bpy)(2\text{-}NO_2C_6H_4COO)(L_1)\}(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2\{Mn(bpy)(2\text{-}NO_2C_6H_4COO)(L_2)\}]$, where for **1** $L_1$ = EtOH, $L_2$ = $H_2O$; for **2** $L_1$ = $L_2$ = $H_2O$; for **B** $L_1$ = $L_2$ = EtOH. Then, their magnetic behaviour should be similar.

For compound **1** $\chi_M T$ remains almost constant between 8.3-9.0 cm$^3$ mol$^{-1}$ K until ~100 K, which is close to the expected value for two uncoupled Mn$^{II}$ ions (8.75 cm$^3$ mol$^{-1}$ K). Below this temperature $\chi_M T$ decreases until approximately 1.5 cm$^3$ mol$^{-1}$ K at 2 K. This behaviour is characteristic for an antiferromagnetic coupling (spin ground state $S$ = 0). Compound **2** has practically the same trend. This coincides with the proposed formulas since they only differ in a monodentate ligand, therefore their $\chi_M T$ versus $T$ values should be similar (**Figure 6**).

Regarding to the $\chi_M$ versus $T$ graph, it can be observed that in both compounds the trend of $\chi_M$ at temperatures below 10 K does not describe the expected maximum which is typical for antiferromagnetic compounds. This phenomenon may be due to a paramagnetic impurity that only manifests at low temperatures. In the $\chi_M T$ graph is not possible to appreciate it.

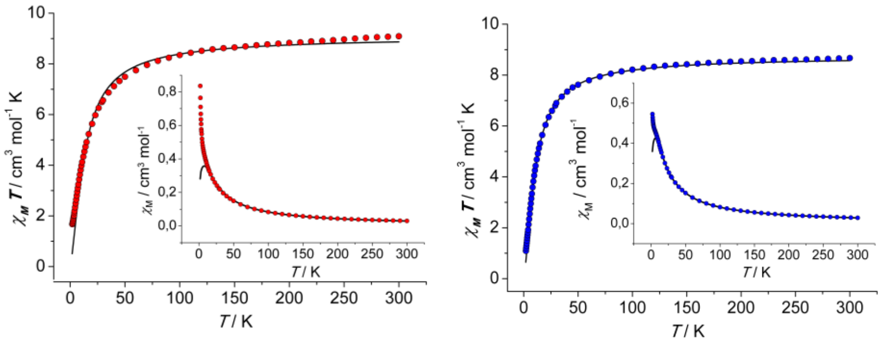


**Figure 6.** $\chi_M T$ versus $T$ and $\chi_M$ versus $T$ (inset) for Mn$^{II}_2$-EW (**1**, left) and Mn$^{II}_2$-WW (**2**, right) in the range 2-300 K. The solid line represents the simulation of the graphs with the parameters found in the best fit to the experimental data in the range 2-300 K.

The fit of the experimental data has been done in the range 10-300 K for $Mn^{II}_2$-EW (**1**) and 8-300 K for $Mn^{II}_2$-WW (**2**). The parameters obtained from the fit with PHI[24] program are shown in the **Table 1**.

It has been performed a simulation of the $\chi_M T$ and $\chi_M$ trend for compounds **1** and **2** in the range 2-300 K with the parameters found in the best fit to the experimental data. In the $\chi_M$ graph, the maximum described by the simulation at low temperatures confirms the presence of paramagnetic impurities in compounds **1** and **2**.

**Table 1.** Parameters obtained from the fit of $\chi_M T$ in the range 10-300 K for $Mn^{II}_2$-EW (**1**) and 8-300 K for $Mn^{II}_2$-WW (**2**) using the spin Hamiltonian $H = -2JS_1 \cdot S_2$.

| Compound | $2J$ / cm$^{-1}$ | *g* | *R* |
|---|---|---|---|
| **1** | -1.8 | 2.04 | $3.5 \cdot 10^{-4}$ |
| **2** | -1.5 | 2.00 | $3.5 \cdot 10^{-5}$ |

For both compounds $2J$ have negative low values, which indicates weak antiferromagnetic interaction. These values are very similar to those described in the literature[13] for $Mn^{II}_2$-EE (**B**) ($2J$ = -1.6 cm$^{-1}$), which has analogous structure to **1** and **2**.

## 6.2. MAGNETIC BEHAVIOUR OF MANGANESE(II) COMPOUND 3

The results of $\chi_M T$ for $[Mn(bpy)(H_2O)_2(2\text{-}NO_2C_6H_4COO)_2]_n$ (**3**) are surprising and difficult to explain without having its crystalline structure (**Figure 7**).

The trend of $\chi_M T$ is practically constant at 4.3-4.5 cm$^3$ mol$^{-1}$ K between 300-14 K, which is close to the expected value for one $Mn^{II}$ ion (4.4 cm$^3$ mol$^{-1}$ K). The shape of the graph suggests that it could be a mononuclear compound, or a system with very weak ferromagnetic interactions. Parameters obtained from the fit of $\chi_M T$ have not been calculated since experimental data is not clear.

The field dependence of the magnetization at 2 K graph ($M/N\mu_\beta$ versus $H$) in **Figure 7** shows that when the applied field is above 3.5 T, $M/N\mu_\beta$ exhibits an indicative value of 5 unpaired electrons (spin ground state $S$ = 5/2). This result can be due to a mononuclear $Mn^{II}$ compound, but also to a more complex system with this spin ground state.

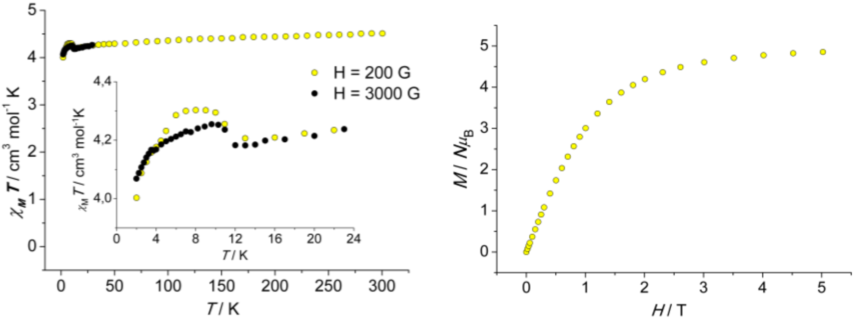


**Figure 7.** $\chi_M T$ versus $T$ at 200 and 3000 G (2-300 K, left) and $M/N\mu_\beta$ versus $H$ (0-5 T, right) for $Mn^{II}_n$ (**3**).

However, in the $\chi_M T$ graph there is something contradictory with the expected values for a mononuclear complex at low temperatures: $\chi_M T$ values at high field (3000 G) and low field (200 G) do not coincide. Then, the phenomenon of magnetic ordering caused by spin canting could occur, which is typical of network or chain structures (*n*D systems) with long-distance interactions. It is characterized by a small net magnetic moment resulting from a collection of atomic magnetic moments that do not cancel each other out due to the canting of the spins[28]. As stated, it manifests at low temperatures when different magnetic fields are applied to the sample, and different values of $\chi_M T$ are measured.

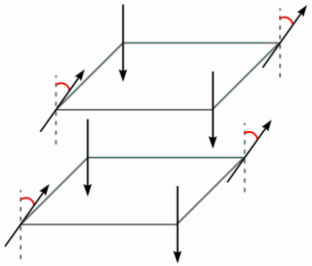


**Figure 8.** Spin canting scheme in *n*D systems.

The magnetic behaviour of the compound cannot be guaranteed or justified without its crystalline structure. In any case, the results indicate that it could be a *n*D system of $Mn^{II}$ ions with carboxylate bridging ligands and very weak ferromagnetic coupling. Another possible option is that it could be a *n*D system of mononuclear $Mn^{II}$ compounds united by strong hydrogen bonds and long-distance interactions, therefore there would not be magnetic coupling between the $Mn^{II}$ ions.

## 6.3. MAGNETIC BEHAVIOUR OF MANGANESE(III) DINUCLEAR COMPOUNDS 4 AND 7

Due to their analogue structure $[\{Mn(bpy)(H_2O)\}_2(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2(\mu\text{-}O)](X)_2$, where X = $NO_3^-$ (**4**) and $ClO_4^-$ (**7**), manganese(III) compounds **4** and **7** are expected to have similar magnetic behaviour. Magnetic studies for both compounds have been already reported in literature[12,13].

$Mn^{III}_2$-$NO_3$ (**4**) shows a $\chi_M T$ value of 6.2 $cm^3\ mol^{-1}$ K at 300 K, which fits with the expected value for two uncoupled $Mn^{III}$ ions (6.0 $cm^3\ mol^{-1}$ K). $Mn^{III}_2$-$ClO_4$ (**7**) shows 5.8 $cm^3\ mol^{-1}$ K at 300 K . When the temperature decreases, the $\chi_M T$ value falls until reaching 4.2 $cm^3\ mol^{-1}$ K for **4** and 2.1 $cm^3\ mol^{-1}$ K for **7** at 2 K, indicating a non-negligible population in the first excites states (**Figure 9**). This trend is characteristic for antiferromagnetic coupling (spin ground state $S = 0$).

The $M/N\mu_\beta$ versus $H$ graph (inset) recorded at 2 K for both compounds does not have an antiferromagnetic trend. This fact reaffirms that the antiferromagnetic interaction is weak and that there are more than one spin state populated at low temperature (**Figure 9**).

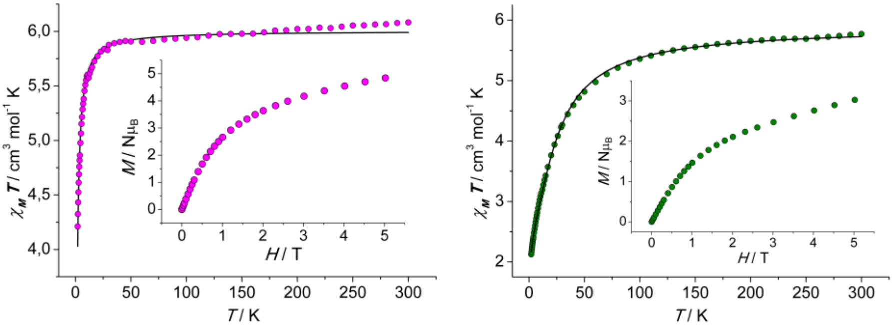


**Figure 9.** $\chi_M T$ versus $T$ (2-300 K) and $M/N\mu_\beta$ versus $H$ (0-5 T, inset) for $Mn^{III}_2$-$NO_3$ (**4**, left) and for $Mn^{III}_2$-$ClO_4$ (**7**, right). The solid lines correspond to the best fit of the experimental data in the range 2-300 K.

$\chi_M T$ versus $T$ values have been fitted with the PHI[24] program in the temperature range 2-300 K. The parameters obtained from the fit are shown in the **Table 2**.

**Table 2.** Parameters obtained from the fit of $\chi_M T$ in the range 2-300 K for $Mn^{III}_2$-$NO_3$ (**4**) and $Mn^{III}_2$-$ClO_4$ (**7**) using the spin Hamiltonian $H = -2JS_1 \cdot S_2$.

| Compound | $2J$ / $cm^{-1}$ | $D_{Mn}$ / $cm^{-1}$ | $g$ | $R$ |
|---|---|---|---|---|
| **4** | -0.1 | 1.10 | 2.00 | $8.5 \cdot 10^{-5}$ |
| **7** | -3.0 | -2.25 | 1.98 | $4.7 \cdot 10^{-5}$ |

$2J$ value for $Mn^{III}_2$-$NO_3$ (**4**) and $Mn^{III}_2$-$ClO_4$ (**7**) are of similar magnitude to the analogue compounds reported in the literature (-0.08 and -4.6 $cm^{-1}$, respectively)[12,13]. Magnetic coupling constants for both compounds are negative, and for compound **7** is greater than **4**, which coincides with the behaviour reported in the bibliography.

## 6.4. MAGNETIC BEHAVIOUR OF MIXED-VALENCE MANGANESE(II-III) COMPOUND 5

$\chi_M T$ versus $T$ graph of compound $[Mn(bpy)Cl_2(H_2O)_2][\{Mn(bpy)Cl\}(\mu\text{-}2\text{-}NO_2C_6H_4COO)(\mu\text{-}O)_2\{Mn(bpy)(H_2O)\}]$ (**5**) does not correspond to the expected for dinuclear $Mn^{III}$ compound (**Figure 10**). It shows a $\chi_M T$ value of 11,7 $cm^3$ $mol^{-1}$ K at 300 K and 17,7 $cm^3$ $mol^{-1}$ K at 2 K. The expected value of $\chi_M T$ for two $Mn^{III}$ and one $Mn^{II}$ uncoupled ions is 10.4 $cm^3$ $mol^{-1}$ K. The formula that best fits the experimental data is composed by a dinuclear $Mn^{III}$ complex with ferromagnetic coupling (spin ground state $S = 4$) and a mononuclear $Mn^{II}$ complex that does not interact with the $Mn^{III}$ ions.

Magnetization data was collected between 1.8-6.7 K applying magnetic in the range 0.5-5 T. $M/N\mu_\beta$ versus $HT^{-1}$ graph shows the superimposition of the various isofield lines, which is indicative of a spin ground state with low value of ZFS.

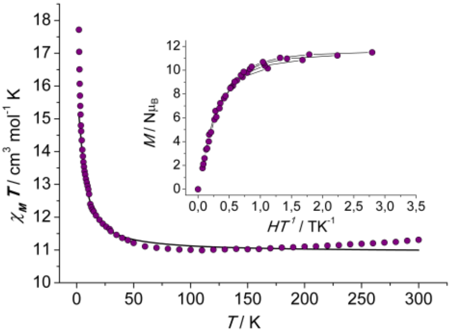


**Figure 10.** $\chi_M T$ versus $T$ (2-300 K) and $M$/N$\mu_\beta$ versus $HT^{-1}$ (0-5 T, 1.8-6.7 K, inset) for Mn$^{II}$Mn$^{III}_2$ (**5**). The solid line represents the simulation of the graph with the parameters found in the best fit to the experimental data in the range 2-300 K.

$\chi_M T$ versus $T$ values have been fitted with the PHI[24] program in the temperature range 8-300 K. The parameters obtained from the fit are shown in **Table 3**. 2$J$ value indicates ferromagnetic coupling between both Mn$^{III}$ ions. The $D_{Mn}$ value obtained in the fit was negligible.

**Table 3.** Parameters obtained from the fit of $\chi_M T$ in the range 8-300 K for Mn$^{II}$Mn$^{III}_2$ (**5**) using the spin Hamiltonian H = $-2JS_1 \cdot S_2 + S_3$.

| Compound | 2J / cm$^{-1}$ | g | R |
|---|---|---|---|
| **5** | 1.0 | 2.09 | $1.1 \cdot 10^{-4}$ |

EPR studies were carried out as well to confirm the presence of a Mn$^{II}$ ion in the compound. For a Mn$^{III}$ ion no signal is expected due to its great value of axial anisotropy parameter $D_{Mn}$. Nevertheless, its EPR spectrum shows a medium intensity signal near g ≈ 2 typical of Mn$^{II}$ compounds. Therefore, the proposed formula that best fits our analysis is [Mn(bpy)Cl$_2$(H$_2$O)$_2$][{Mn(bpy)Cl}(μ-2-NO$_2$C$_6$H$_4$COO)(μ-O)$_2${Mn(bpy)(H$_2$O)}] (**5**).

## 6.5. MAGNETIC BEHAVIOUR OF MIXED-VALENCE MANGANESE(IV-III) COMPOUND 6

Like for $[Mn(bpy)(H_2O)_2(2\text{-}NO_2C_6H_4COO)_2]_n$ (**3**), the magnetic behaviour for the mixed-valence $Mn^{IV}Mn^{III}_2$ compound **6** is difficult to explain without having its crystalline structure (**Figure 11**).

It is shown in the graph that $\chi_M T$ value decreases slightly from 8.5 $cm^3\ mol^{-1}$ K at 300 K to 7.8 $cm^3\ mol^{-1}$ K at 40 K. The expected $\chi_M T$ value for two $Mn^{III}$ and one $Mn^{IV}$ uncoupled ions is 7.9 $cm^3\ mol^{-1}$ K. At low temperatures, $\chi_M T$ value starts increasing until reaching a maximum at 2 K. The shape of the graph is indicative of a very weak magnetic interaction. Moreover, in the range 2-12 K, $\chi_M T$ values at high field (3000 G) and low field (200 G) do not coincide. This might be caused again by long-distance magnetic ordering.

The non-superimposition of the various isofield lines in the reduced magnetization graph ($M/N\mu_\beta$ versus $HT^{-1}$) is indicative of non-negligible value of ZFS in the spin ground state (**Figure 11**).

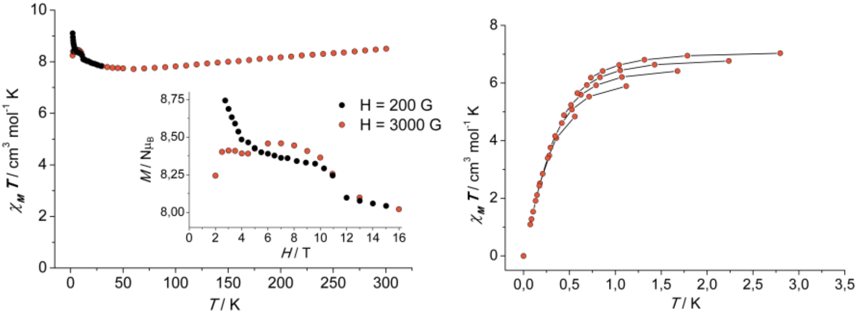


**Figure 11.** $\chi_M T$ versus $T$ at 200 and 3000 G (2-300 K, left) and $M/N\mu_\beta$ versus $HT^{-1}$ (0-5 T, 1.8-6.7 K, right) for $Mn^{IV}Mn^{III}_2$ (**6**).

The parameters obtained from the fit of $\chi_M T$ have not been calculated since experimental data is not clear.

The formula that best fits with this behaviour is $[Mn(bpy)_2Cl_2][\{Mn(bpy)(H_2O)\}_2(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2(\mu\text{-}O)]Cl_3(ClO_4)$ (**6**), with weak magnetic interaction between manganese(**III**) ions. Magnetic ordering caused by spin canting could be explained by long-distance hydrogen bond interactions, although it cannot be confirmed without its crystalline structure.

# 7. EPR SPECTROSCOPY

When a magnetic field $H$ is applied to the sample, the degenerated $M_S$ levels split due to Zeeman effect according to the Zeeman Hamiltonian $H = g\mu_B HS$, where $g \approx 2$ for a free electron (Lande factor), $\mu_B$ is the Bohr magneton, $H$ is the applied magnetic field and $S$ is a spin operator (**Figure 12**). Consequently, the levels population will not be the same as when they were degenerated, according to the Boltzmann distribution.

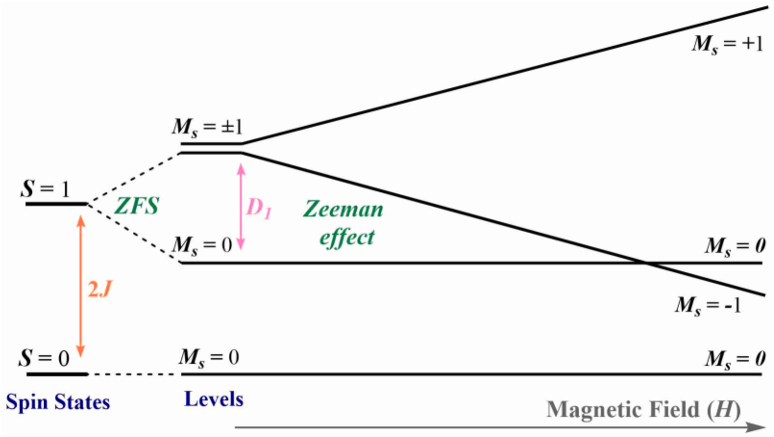


**Figure 12.** Qualitative representation of the Zero-Field Splitting (ZFS) and Zeeman effect of the spin ground state and first excited for an antiferromagnetic compound with significant $D_1$.

Then, the goal for Electron Paramagnetic Resonance (EPR) is studying the energetic transitions between electronic levels $M_S$ when a suitable frequency is applied.

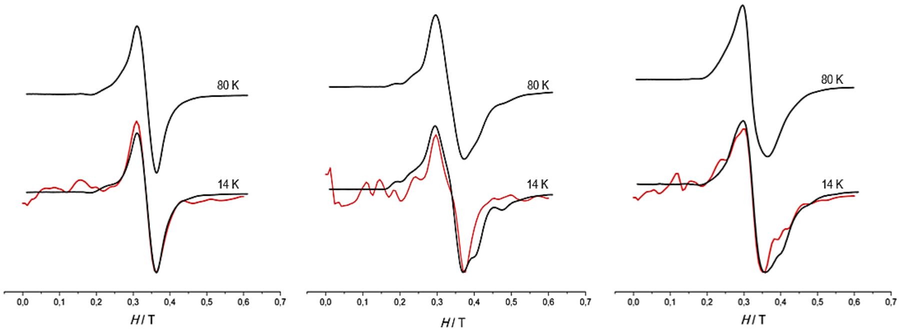
EPR allows us to study molecules with small ZFS value ($D_{Mn}$ and $E \approx h\nu$), like $Mn^{II}$ ions. Normally the frequency applied corresponds to microwave radiation, approximately 9.4 GHz.

For isotropic systems where $D_{Mn} = 0$, the Zeeman plots are the same for the three directions of the magnetic field ($x = y = z$), and only one symmetric band at $g \approx 2$ is expected. On the other hand, for systems with greater value of $D_{Mn}$, the Zeeman plot in $z$ direction is different from $y$ and $x$ ($x = y \neq z$). This fact is important to consider which transitions can take place: according to the selection rules, only transitions with $\Delta M_S = \pm 1$ are allowed. However, when axial anisotropy ($D_{Mn}$) becomes relevant, the $M_s$ levels mix and transitions that should be forbidden as $\Delta M_s = \pm 2$ might appear, making the EPR spectrum more difficult to interpret.

In the spectra, the splitting of the signals is related to the ZFS parameters of the spin ground state $D_S$ and $E_S$. Hence, for dinuclear systems with weak antiferromagnetic interactions, the splitting of the signals is related mostly to $D_1$ and $E_1$.

In this way, simulations of EPR spectra of the three manganese(II) compounds were performed with the PHI[24] program in order to find the ZFS parameters. For this, the values of $2J$ and $g$ previously found in magnetism studies were used for Mn$^{II}_2$-EW (**1**) and Mn$^{II}_2$-WW (**2**). Magnetism data of Mn$^{II}_n$ (**3**) could not be fitted due to its strange behaviour, and its EPR data has been simulated considering a Mn$^{II}$ mononuclear compound.

The X-band EPR spectra for manganese(II) compounds **1**, **2**, and **3** were recorded on powdered samples at 14 and 80 K (**Figure 13**).



Mn$^{II}_2$-EW (**1**) Mn$^{II}_2$-WW (**2**) Mn$^{II}_n$ (**3**)

**Figure 13.** Variable-temperature X-band EPR spectra for compounds **1**, **2** and **3**. The red lines correspond to the best simulation of the experimental data.

At 80 K, all of them show a band centred at $g \approx 2$. However, when the temperature falls to 14 K the spectra become more complicated due to the features that appear around the broad band. It is worth mentioning the not symmetric band at $g \approx 2$ for Mn$^{II}_2$-WW (**2**). This is because there is more than one allowed transition at this applied field, therefore the bands appear overlapped.

For dinuclear compounds $Mn^{II}_2$-EW (**1**) and $Mn^{II}_2$-WW (**2**) the shape of the spectra also depends on their magnetic behaviour. Both compounds have antiferromagnetic coupling between the manganese(II) ions (spin ground state $S = 0$), therefore no signal is expected on EPR spectra. Nevertheless, the low $2J$ value allows the excited states $S = 1$ and $S = 2$ to be populated at 14 K, so energetic transitions will be observed.

The EPR spectra for 1D systems[9] with two carboxylate bridges present a single narrow band at $g \approx 2$. The EPR spectrum of $Mn^{II}_n$ (**3**) does not have this shape, but this possibility cannot be discarded since its crystal structure has not been solved.

Spectra recorded at 14 K were simulated with PHI[24] program, using the magnetic coupling constant $J$ obtained from the fit of the magnetic data. Several simulations were performed by screening different values and sign of $D_{Mn}$ and $E_{Mn}$ within the logical range that one may expect for hexacoordinated manganese(II) ions (**Table 4**). For all the simulations it was tried to reproduce the $g \approx 2$ band. Features around them were difficult to adjust.

**Table 4.** Parameters used in the simulations of EPR spectra of $Mn^{II}_2$-EW (**1**), $Mn^{II}_2$-WW (**2**) and $Mn^{II}_n$ (**3**). $\Delta H_{P-P}$ are experimental values measured in the EPR spectra.

| Compound | $g$ | $D_{Mn}$ / cm$^{-1}$ | $\|E_{Mn}\|$ / cm$^{-1}$ | $\|E_{Mn}\|/\|D_{Mn}\|$ | $\Delta H_{P-P}$ / G |
|---|---|---|---|---|---|
| **1** | 2.05 | -0.28 | 0.02 | 0.07 | 520 |
| **2** | 2.03 | -0.33 | 0.01 | 0.03 | 750 |
| **3** | 2.08 | 0.05 | 0.01 | 0.2 | 610 |

The $D_{Mn}$ values obtained from these simulations are consistent with manganese(II) ions with distorted octahedral geometry[29]. Based on the simulations it is concluded that the sign of $D_{Mn}$ changes the shape of the spectra, whereas $E_{Mn}$ sign does not affect. For this reason, it has not been possible to determine it.

Compounds **1** and **2** have very similar ZFS parameters, as it was expected due to their analogue proposed formula $[\{Mn(bpy)(2\text{-}NO_2C_6H_4COO)(L_1)\}(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2\{Mn(bpy)(2\text{-}NO_2C_6H_4COO)(L_2)\}]$, where for **1** $L_1$ = EtOH, $L_2 = H_2O$ and for **2** $L_1 = L_2 = H_2O$. $|E_{Mn}|/|D_{Mn}|$ value is related to the distortion of $Mn^{II}$ environment. It is considered that if $|E_{Mn}|/|D_{Mn}| = 0$ it has axial distortion, and if $|E_{Mn}|/|D_{Mn}| \sim 0.3$ it has a rhombic distortion. For these compounds it is observed that **1** and **2** have axial distortion, while **3** has rhombic.

# 8. STUDY OF THE CATALASE ACTIVITY OF MANGANESE(III) COMPOUNDS

As already explained in the introduction, the research group “Models en Bioinorgànica” is focused on the syntheses of manganese(III) dinuclear compounds to mimic the active site of the Mn-catalase enzyme.

Studies of the catalase activity with a large variety of $Mn^{III}$ dinuclear compounds with general formula $[\{Mn(NN)(H_2O)\}_2(\mu\text{-}n\text{-}RC_6H_4COO)_2(\mu\text{-}O)](X)_2$ have been carried out previously in the group, in order to study the effect of the nature and position of the substituent in the aromatic ring of the carboxylate bridging ligand[12–14,22,30].

In this work, the catalase activity of the different $Mn^{III}$ compounds obtained was studied as well. In this way, solutions of compounds $Mn^{III}_2\text{-}NO_3$, $Mn^{II}Mn^{III}_2$, $Mn^{IV}Mn^{III}_2$, $Mn^{III}_2\text{-}ClO_4$ (**4-7**) with concentration $10^{-3}$ M and acetonitrile as solvent were prepared. Then, volumetric measurements of the $O_2$ evolved by the disproportionation reaction of $H_2O_2$ catalysed by the $Mn^{III}$ compounds were made. Moreover, the same measurements were made with BmimCl ($10^{-3}$ M) and triethylamine ($1.4\cdot10^{-4}$ M) in the reaction medium.

The results of the evolution of the $O_2$ evolved have been omitted since the synthesized compounds were poorly active. The presence of BmimCl in the reaction medium did not improve the catalase activity of the compounds. However, in basic medium the reaction rate increased as expected[31].

# 9. EXPERIMENTAL SECTION

## 9.1. MATERIALS AND METHODS

Infrared Spectra were recorded in solid state in the range 4000-400 $cm^{-1}$ with ATR iD7 Thermo Nicolet iS5 FT-IR spectrometer.

Elemental analysis of C, H, N and Cl were carried out in “Serveis Cientifico-Tècnics” of the Universitat de Barcelona and in the Microanalysis Service of the Institute for Advanced Chemistry of Catalonia.

Conductivity measurements of solutions with concentration $10^{-3}$ M were carried out with a HACH HQ40d instrument at room temperature.

Magnetic susceptibility measurements in the range 2-300 K and magnetization measurements at 2 K in the range 0-5 T and in the ranges 1.8-6.7 K and 0.5-5 T were carried out in a SQUID magnetometer Quantum Design Magnetometer MPMS XL5 at the “Unitat de Mesures Magnètiques” of the Universitat de Barcelona. Two different magnetic fields were used for the susceptibility measurements, 200 (2-28 K) and 3000 G (2-300 K). Pascal’s constants were used to estimate the diamagnetic corrections for the compounds. The fit was performed by minimizing the function $R = \Sigma [(\chi_M T)_{exp} - (\chi_M T)_{calcd}]^2 / \Sigma [(\chi_M T)_{exp}]^2$.

Solid-state EPR spectra were recorded with X-band (9.4 GHz) frequency using a Bruker ESP-300E spectrometer at 90 and 14 K at the “Unitat de Mesures Magnètiques” of the Universitat de Barcelona.

## 9.2. SYNTHESES OF COMPOUNDS

All manipulations were carried out at room temperature under aerobic conditions. Reagents and solvents were obtained from commercial sources and used without further purification. $Bu_4NMnO_4$ was prepared as described in the literature[32]. Yields were calculated from the stoichiometric reaction. ***Caution!*** Perchlorate salts of compounds containing organic ligands are potentially explosive. Only small quantities of these compounds should be prepared and handled behind suitable protective shields.

### 9.2.1. Synthesis of manganese(II) carboxylate $Mn(2\text{-}NO_2C_6H_4COO)_2{\cdot}4H_2O$

3.2 g (13 mmols) of $Mn(AcO)_2{\cdot}4H_2O$ and 4.4 g (26 mmols) of $2\text{-}NO_2C_6H_4COOH$ were dissolved in 20 mL of water. The previous mixture was heated with constant agitation for 10 minutes. After that it was concentrated until the volume was reduced to 10 mL. The resulting mixture was cooled at room temperature and an ivory white precipitate of $Mn(2\text{-}NO_2C_6H_4COO)_2{\cdot}4H_2O$ was formed. Finally the solid was filtered, washed in ether and dried at air. It is important to wash it properly since there may be remains of acetic acid in the product. Yield: 5.29 g (86%). Anal. calc. for $C_{14}H_{16}O_{12}N_2Mn$ (459.22): C, 36.62; H, 3.51; N, 6.10 %. Found: C, 34.60; H, 3.13; N, 6.70 %. IR $\nu_{max}/cm^{-1}$: 3353 (m), 3383 (br), 3112 (br), 1677 (w), 1594 (s), 1567 (s), 1519 (vs), 1439 (m), 1351 (vs), 1303 (m), 860 (m), 777 (m), 701 (vs), 634 (vs).

### 9.2.2. Synthesis of $[\{Mn(bpy)(EtOH)(2\text{-}NO_2C_6H_4COO)\}(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2\{Mn(bpy)(H_2O)(2\text{-}NO_2C_6H_4COO)\}]$ (1)

0.12 g (0.77 mmols) of 2,2'-bipyridine were added to a solution of 0.53 g (1.15 mmols) of $Mn(2\text{-}NO_2C_6H_4COO)_2{\cdot}4H_2O$ dissolved in 15 mL of ethanol. The mixture was stirred until a yellow precipitate appeared. The solid was filtered and dried at air. The mother liquor was kept in order to recover more product. One day later more precipitate appeared, and this was filtered and dried at air. Yield: 0.52 g (77%). Anal. calc. for $C_{50}H_{40}O_{18}N_8Mn_2$ (1150.77): C, 52.19; H, 3.50; N, 9.74 %. Found: C, 50.53; H, 2.74; N, 9.50 %. IR $\nu_{max}/cm^{-1}$: 1621 (vs), 1593 (s), 1570 (s), 1524 (s), 1471 (m), 1493 (m), 1396 (vs), 1347 (s), 1308 (m), 1153 (w), 1051 (m), 1011 (m), 862 (m), 833 (m), 789 (m), 775 (s), 736 (s), 694 (m), 647 (m).

### 9.2.3. Synthesis of $[\{Mn(bpy)(H_2O)(2\text{-}NO_2C_6H_4COO)\}_2(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2]$ (2)

0.27 (0.58 mmol) of $Mn(2\text{-}NO_2C_6H_4COO)_2{\cdot}4H_2O$ were dissolved in 10 mL of acetonitrile. Then 0.09 g (0.58 mmol) of 2,2'-bipyridine were added to the previous solution. The mixture was stirred and few minutes later a yellow precipitate appeared. This was filtered and dried at air and mother liquor was kept. One day later more precipitate appeared, this was filtered and dried at air too. Yield: 0.17 g (50%). Anal. calc. for $C_{48}H_{36}O_{18}N_8Mn_2$ (1122.72): C, 51.35; H, 3.23; N, 9.98 %. Found: C, 52.22; H, 3.28; N, 10.08 %. IR $\nu_{max}/cm^{-1}$: 1626 (m), 1608 (m), 1566 (m), 1524 (vs), 1478 (m), 1439 (m), 1402 (m), 1379 (vs), 1343 (m), 1309 (m), 1150 (w), 1070 (w), 1011 (m), 768 (s), 731 (s), 691 (s), 649 (s).

### 9.2.4. Synthesis of $[Mn(bpy)(H_2O)_2(2\text{-}NO_2C_6H_4COO)_2]_n$ (3)

0.27 g (0.58 mmols) of $Mn(2\text{-}NO_2C_6H_4COO)_2{\cdot}4H_2O$ were dissolved in 10 mL of acetonitrile. A white precipitate appeared in few minutes. Then 1 mL of water was added to the previous suspension and the precipitate was easily redissolved. After that 0.09 g (0.58 mmols) of 2,2'-bipyridine dissolved in 5 mL of acetonitrile were added to the above-mentioned solution (total volume ∼16 mL). The mixture was stirred for some minutes, and a pale-yellow precipitate was formed. This was filtered and dried at air. The mother liquor was kept and 10 days later more product was obtained. This was filtered and dried at air too. Yield: 0.26 g (79%). Anal. calc. for $C_{24}H_{20}O_{10}N_4Mn$ (579.37): C, 49.75; H, 3.48; N, 9.67 %. Found: C, 48.68; H, 3.63; N, 9.39 %. IR $\nu_{max}/cm^{-1}$: 3366 (br), 3097 (br), 2458 (w), 1968 (w), 1594 (s), 1558 (s), 1535 (vs), 1472 (m), 1439 (m), 1399 (s), 1357 (vs), 1152 (w), 1023 (w), 790 (m), 768 (vs), 734 (vs).

### 9.2.5. Synthesis of $[\{Mn(bpy)(H_2O)\}(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2(\mu\text{-}O)\{Mn(bpy)(NO_3)\}](NO_3)$ (4)

$Mn(NO_3)_2{\cdot}4H_2O$ (0.32 g, 1.28 mmols) and $2\text{-}NO_2C_6H_4COOH$ (0.28 g, 1.6 mmols) were dissolved in 20 mL of acetonitrile. Then, 0.11 g of $Bu_4NMnO_4$ (0.32 mmols) dissolved in 10 mL of the same solvent were added to the above-mentioned mixture, previously filtered. Finally, 0.25 g of 2,2'-bipyridine (1.6 mmols) dissolved in 10 mL of acetonitrile were also added (total volume ∼40 mL). The resulting dark brown suspension was stirred for a few minutes, filtered, washed with ether and dried at air. To obtain a crystalline product the same amount of reagents were used, but dissolved in different solvents: $Mn(2\text{-}NO_2C_6H_4COO)_2{\cdot}4H_2O$ and $2\text{-}NO_2C_6H_4COOH$ in 20 mL of acetonitrile; $Bu_4NMnO_4$ in 20 mL of acetonitrile; 2,2'-bipyridine in 20 mL of ethanol (total volume ∼60 mL. $CH_3CN$:EtOH 40:20). Yield: 0.48 g (64%). Molar conductivity in $CH_3CN$: 119 $cm^2\ \Omega^{-1}\ mol^{-1}$. Molar conductivity in $CH_3CN:H_2O$ (9:1): 202 $cm^2\ \Omega^{-1}\ mol^{-1}$. Anal. calc. for $C_{34}H_{26}O_{16}N_8Mn_2$ (912.49): C, 44.75; H, 2.87; N, 12.28 %. Found: C, 43.27; H, 2.80; N, 12.16 %. %. IR $\nu_{max}/cm^{-1}$: 3207 (br), 1603 (s), 1567 (m), 1529 (s), 1498 (m), 1469 (m), 1444 (m), 1328 (vs), 1291 (vs), 1170 (m), 1159 (m), 1107 (m), 1057 (m), 1031 (m), 842 (m), 765 (vs), 728 (vs), 694 (s), 649 (s).

### 9.2.6. Synthesis of $[Mn(bpy)Cl_2(H_2O)_2][\{Mn(bpy)Cl\}(\mu\text{-}2\text{-}NO_2C_6H_4COO)(\mu\text{-}O)_2\{Mn(bpy)(H_2O)\}]$ (5)

0.16 g (0.64 mmols) of $Mn(NO_3)_2{\cdot}4H_2O$ and 0.14 g (0.8 mmols) of $2\text{-}NO_2C_6H_4COOH$ were dissolved in 10 mL of acetonitrile. Then, 0.055 g of $Bu_4NMnO_4$ (0.16 mmols) dissolved in 10 mL of the same solvent were added to the above-mentioned mixture, previously filtered. Finally, a mixture of 0.13 g of 2,2'-bipyridine (0.8 mmols) and 0.30 g of $Bu_4NCl{\cdot}H_2O$ (1mmol) dissolved in 10 mL of acetonitrile was also added (total volume ~30 mL). The dark brown solution was stirred and some minutes later a brown precipitate appeared. This was filtered, washed with ether and dried at air. Yield: 0.24 g (86%). Molar conductivity in $CH_3CN$: 20.4 $cm^2\ \Omega^{-1}\ mol^{-1}$. Molar conductivity in $CH_3CN:H_2O$ (9:1): 227.5 $cm^2\ \Omega^{-1}\ mol^{-1}$. Anal. calc. for $C_{37}H_{34}O_9N_7Cl_3Mn_3$ (991.88): C, 44.80; H, 3.46; N, 9.88; Cl, 10.72 %. Found: C, 46.12; H, 3.00; N, 10.14; Cl, 10.92 %. IR $\nu_{max}/cm^{-1}$: 1597 (s), 1569 (m), 1529 (s), 1492 (w), 1465 (w), 1441 (m), 1369 (vs), 1307 (m), 1247 (w), 1154 (w), 1055 (w), 1028 (m), 1016 (w), 832 (w), 766 (vs), 730 (vs), 697 (s), 648 (s).

### 9.2.7. Synthesis of $[Mn(bpy)_2Cl_2][\{Mn(bpy)(H_2O)\}_2(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2(\mu\text{-}O)]Cl_3(ClO_4)$ (6)

$Mn(ClO_4)_2{\cdot}6H_2O$ (0.23 g, 0.64 mmols) and $2\text{-}NO_2C_6H_4COOH$ (0.14 g, 0.8 mmols) were dissolved in 10 mL of acetonitrile. Then, 0.055 g of $Bu_4NMnO_4$ (0.16 mmols) dissolved in 10 mL of the same solvent were added to the above-mentioned mixture, previously filtered. Finally, a mixture of 0.13 g of 2,2'-bipyridine (0.8 mmols) and 0.30 g of $Bu_4NCl{\cdot}H_2O$ (1mmol) dissolved in 5 mL of acetonitrile was also added (total volume ~25 mL). The solution was stirred and a dark-brown precipitate appeared immediately. This was filtered and the mother liquor was kept in order to recover more product. A week later, some black crystals appeared in the second fraction. These were filtered and dried at air. Yield: 0.21 g (63%). Molar conductivity in $CH_3CN$: 383.2 $cm^2\ \Omega^{-1}\ mol^{-1}$. Molar conductivity in $CH_3CN:H_2O$ (9:1): 444.2 $cm^2\ \Omega^{-1}\ mol^{-1}$. Anal. calc. for $C_{54}H_{44}O_{15}N_{10}Cl_6Mn_3$ (1450.52): C, 44.71; H, 3.06; N, 9.66; Cl, 14.50 %. Found: C, 44.60; H, 2.95; N, 9.70; Cl, 14,93 %. IR $\nu_{max}/\ cm^{-1}$: 1602 (s), 1570 (m), 1528(s), 1491 (m), 1468 (m), 1443 (s), 1406 (m), 1370 (s), 1316 (m), 1308 (m), 1274 (w), 1246 (m), 1218 (w), 1167 (m), 1156 (m), 1078 (s), 1154 (m), 1028 (m), 1014 (m), 831 (w), 764 (vs), 737 (m), 730 (vs), 698 (m), 671 (m), 649 (s), 619 (m).

### 9.2.8. Synthesis of [{Mn(bpy)($H_2O$)}$_2$(μ-2-$NO_2C_6H_4COO$)$_2$(μ-O)]($ClO_4$)$_2$·$CH_2Cl_2$·4$H_2O$ (7)

$Mn(ClO_4)_2 \cdot 6H_2O$ (0.23 g, 0.64 mmols) and 2-$NO_2C_6H_4COOH$ (0.14 g, 0.8 mmols) were dissolved in 10 mL of acetonitrile. Then, 0.055 g of $Bu_4NMnO_4$ (0.16 mmols) dissolved in 5 mL of the same solvent were added to the above-mentioned mixture, previously filtered. Finally, a mixture of 0.13 g of 2,2'-bipyridine (0.8 mmols) dissolved in 5 mL of acetonitrile was also added (total volume ∼20 mL). To favour the precipitation, 20 mL of dichloromethane were mixed with the remaining solution ($CH_3CN$:$CH_2Cl_2$ 1:1). This was kept under *n*-hexane atmosphere for 30 days. Finally, it was left in slow evaporation at air. Yield: 0.36 g (76%). Molar conductivity in $CH_3CN$: 368.0 $cm^2\,\Omega^{-1}\,mol^{-1}$. Molar conductivity in $CH_3CN$:$H_2O$ (9:1): 333.9 $cm^2\,\Omega^{-1}\,mol^{-1}$. Anal. calc. for $C_{35}H_{38}O_{23}N_6Cl_4Mn_2$ (1162.39): C, 36.16; H, 3.30; N, 7.23 %. Found: C, 37.43; H, 3.66; N, 7.14 %. %. IR $v_{max}$/$cm^{-1}$: 3457 (br), 2961 (w), 2874 (w), 1600 (m), 1526 (w), 1469 (w), 1447 (w), 1396 (m), 1068 (vs), 7794 (m), 726 (m), 624 (s).

# 10. CONCLUSIONS

The conclusions that can be drawn from this work are:

1) The stoichiometric reaction between $Mn(2\text{-}NO_2C_6H_4COO)_2$ and 2,2'-bipyridine in ethanol or acetonitrile led to the formation of dinuclear $Mn^{II}$ compounds with general formula $[\{Mn(bpy)(2\text{-}NO_2C_6H_4COO)(L_1)\}(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2\{Mn(bpy)(2\text{-}NO_2C_6H_4COO)(L_2)\}]$, where for **1** $L_1$ = EtOH, $L_2$ = $H_2O$ and for **2** $L_1$ = $L_2$ = $H_2O$. The presence of BmimCl or $Bu_4NCl$ in their syntheses did not affect the obtention of the products; it seems that chloride ions are not coordinated in any of the compounds. Both compounds **1** and **2** show very similar antiferromagnetic behaviour and EPR spectra.
2) The stoichiometric reaction between $Mn(2\text{-}NO_2C_6H_4COO)_2$ and 2,2'-bipyridine in acetonitrile:water 9:1 did not lead to the formation of dinuclear $Mn^{II}$ compounds. Instead, a mononuclear compound or an extended system of $Mn^{II}$ ions was obtained. The proposed formula for this compound was $[Mn(bpy)(H_2O)_2(2\text{-}NO_2C_6H_4COO)_2]_n$ (**3**). Its magnetic susceptibility graph at different applied fields allowed us the observation of certain magnetic order at low temperatures, typical of compounds with long-distance interactions.
3) The syntheses of dinuclear $Mn^{III}$ compounds with general formula $[\{Mn(H_2O)(bpy)\}_2(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2(\mu\text{-}O)](X)_2$, where X = $NO_3^-$ (**4**) or $ClO_4^-$ (**7**) have been reproduced as already reported in the literature. Magnetic studies indicated that both compounds have antiferromagnetic interaction between $Mn^{III}$ ions.
4) In the above-mentioned syntheses with $Mn(NO_3)_2$, when BmimCl or $Bu_4NCl$ were added to the solution, Cl- ions got coordinated to $Mn^{III}$ ions leading to the obtention of the mixed-valence $Mn^{II}Mn^{III}_2$ compound $[Mn(bpy)Cl_2(H_2O)_2][\{Mn(bpy)Cl\}(\mu\text{-}2\text{-}NO_2C_6H_4COO)(\mu\text{-}O)_2\{Mn(bpy)(H_2O)\}]$ (**5**). When the same syntheses were performed with $Mn(ClO_4)_2$ and BmimCl or $Bu_4NCl$ were added, mixed-valence $Mn^{II}Mn^{III}_2$ and $Mn^{IV}Mn^{III}_2$ compounds **5** and **6** ($[Mn(bpy)_2Cl_2][\{Mn(bpy)(H_2O)\}_2(\mu\text{-}2\text{-}NO_2C_6H_4COO)_2(\mu\text{-}O)]Cl_3(ClO_4)$) could be obtained. Magnetic data for **5** suggests that there is a ferromagnetic coupling between $Mn^{III}$ ions, whereas for **6** there is a very weak magnetic interaction and certain magnetic order at low temperatures.

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# 12. ACRONYMS

AcO: acetate

bpy: 2,2’-bipyridine

BmimCl: 1-butyl-3-methylimidazolium chloride

EPR: electron paramagnetic resonance

EtOH: ethanol

IL: ionic liquid

IR: infrared

L: monodentate ligand

ZFS: zero-field splitting