

Title: **Effect of Ionic Liquids on the synthesis and reactivity of manganese complexes with carboxylate ligand.**

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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 (Bu₄NCl) had caused on the syntheses.

For manganese(II) compounds, stoichiometric amounts of Mn(2-NO₂C₆H₄COO)₂ (previously synthesized) and 2,2'-bipyridine were used, and different reaction conditions (solvent and presence of BmimCl or Bu₄NCl in solution) were tested. The dinuclear compounds obtained **1** and **2** have general formula $[\{\text{Mn}(\text{bpy})(2\text{-NO}_2\text{C}_6\text{H}_4\text{COO})(\text{L}_1)\}\{\mu\text{-}2\text{-NO}_2\text{C}_6\text{H}_4\text{COO}\}_2\{\text{Mn}(\text{bpy})(2\text{-NO}_2\text{C}_6\text{H}_4\text{COO})(\text{L}_2)\}]$, where for **1** L₁ = EtOH, L₂ = H₂O and for **2** L₁ = L₂ = H₂O. Analogous compounds had been synthesized by the research group previously. Compound **3** [Mn(bpy)(H₂O)₂(2-NO₂C₆H₄COO)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 Bu₄NMnO₄. The reaction conditions were also modified by adding BmimCl or Bu₄NCl to the solutions, which led to the obtention of surprising compounds. Dinuclear compounds **4** and **7** (general formula $[\{\text{Mn}(\text{H}_2\text{O})(\text{bpy})\}_2(\mu\text{-}2\text{-NO}_2\text{C}_6\text{H}_4\text{COO})_2(\mu\text{-O})(\text{X})_2]$, where X = NO₃⁻ (**4**) or ClO₄⁻ (**7**)) had already been obtained as well by the research group. The mixed-valence compounds [Mn(bpy)Cl₂(H₂O)₂][{Mn(bpy)Cl}{μ-2-NO₂C₆H₄COO}(μ-O)₂{Mn(bpy)(H₂O)}] (**5**) and [Mn(bpy)₂Cl₂][{Mn(bpy)(H₂O)₂(μ-2-NO₂C₆H₄COO)₂(μ-O)]Cl₃(ClO₄) (**6**) were only obtained by adding BmimCl or Bu₄NCl 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 O₂ evolved by the reaction of disproportion of H₂O₂. The compounds were poorly active, and the results have not been included in the memory.

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