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New Mn(II) complexes with benzoxazole-based ligands: synthesis, structure and their electrochemical behavior

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Graphical abstract

Abstract

Six complexes of various Mn(II) salts: $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ (**1**), $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (**2**), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (**3**) with 2-(1-methyl-2-(pyridin-2-ylmethylene)hydrazinyl)benzo[d]oxazole L^{A} (complexes **1A** – **3A**) and 2-(2-((1H-imidazol-4-yl)methylene)-1-methylhydrazinyl)benzo[d]oxazole HL^{B} (complexes **1B** – **3B**) have been synthesized. All complexes were obtained in 1:1 stoichiometry. Their structures have been established through analytical and spectroscopic (ESI-MS, IR, ^1H NMR and microanalyses) methods as well as by X-ray structure determinations. In order to gain some insights into the electron-richness of studied systems, the electrochemical properties of ligands L^{A} and HL^{B} and complexes **1A** and **1B** were investigated by cyclic voltammetry. Complexes **1A** and **1B** were chosen due to isostructurality what allows to the direct comparison of their behavior. The impact of pyridine and imidazole substituents on electrochemical behavior of synthesized systems was evaluated and showed that the presence of NH moiety in imidazole ring of HL^{B} does not feasible the adsorption on the bare gold electrode.

1. Introduction

The ongoing interest in well-defined stable systems exhibiting some distinct properties has led researchers to extensively explore the chemistry of Schiff-bases. They are common enzymatic intermediates where an amine reversibly reacts *in vivo* with an aldehyde or ketone of cofactor of substrate, e.g. the common enzyme cofactor PLP (pyridoxal 5'-phosphate) forms an intermediate imine with lysine residue and is transferred to the substrate [1]. Moreover, they participate in photosynthesis and oxygen transportation in living organisms [2]. The versatility of imines and their ability to coordinate metal ions has allowed one to create a great variety of potentially applicative materials. Many complexes of Schiff-base ligands with d-electron metal ions have been investigated as models for active sites of enzymes [3], antifungal [4] and antibacterial [5,6] as well as anticancer [7,8] drugs. Their biocompatibility enables biologists to develop new DNA-cleavage and repair systems [9-11]. They also provide some valuable magnetic properties which are useful in fabrication of novel electronic nano-devices [12,13]. They are already used as catalysts in multiple organic and metalorganic reaction such as, for instance, ring-opening olefin epoxidation [14] or alcohol oxidation [15] as well as in photocatalytic organic matter degradation processes [16]. Some d^{10} -electron metal ions (as Zn^{2+} , Cd^{2+} , Ag^+) coordinated by Schiff base type ligands display intense luminescence and exhibit high quantum yields thus may be utilized in design of new OLED's (Organic Light Emitting Diodes) or as components in WOLED's (White Organic Light Emitting Diodes) construction [17,18].

The coordination chemistry of Mn(II) has been extensively explored in recent years mainly due to its essential role in biological systems. For instance, Manganese ions act as cofactors of numerous enzymes, such as oxidoreductases, transferases, ligases or lyases [19]. Manganese is also present in eukaryotic mitochondria in the form of superoxide dismutase (Mn-SOD), which is responsible for deactivation of superoxide O_2^- formed from the one-

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