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Synthesis and characterization of a new tricarbonyl Mn(I) complex containing an imidazole as ancillary ligand

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Efforts have been made to develop eco-friendly catalysts based on the first-row transition metal series. In this work, we present the synthesis and structural characterization of a new metal complex based on Mn(I), *fac*-$Mn(CO)_3$(pbiH)Br, where pbiH = 2-(2-pyridyl)benzimidazole, aiming at the application on electrochemical CO_2 reduction reaction (CO_2RR). The *fac*-$Mn(CO)_3$(pbiH)Br complex was synthesized and initially characterized by ^{1}H NMR and FTIR. The ^{1}H NMR spectrum is characterized by peaks in the aromatic region and are attributed to the protons of the pbiH ligand. The signals are downfield relative to those observed for the free ligand due to interaction with the Mn(I) center. Additionally, a small broad singlet signal at 14 ppm corresponding to the amine proton is observed, evidencing the acidic character of this proton. FTIR spectrum is characterized by the ν_{N-H} m(3068 cm^{-1}), $\nu_{C\equiv O}$ s(2017, 1910 and 1883 cm^{-1}), and ν_{Mn-N} w(268 cm^{-1}) stretches, corresponding respectively to the NH group in the pbiH ligand, the *facial* geometry of the carbonyl groups in the complex, and the Mn(I)-N coordination bond. Cyclic voltammetry was carried out in argon-deaerated anhydrous CH_3CN with NH_4PF_6 (0.1 mol L^{-1}) as supporting electrolyte at 500 mV s^{-1}. Two irreversible oxidation potentials at 0.78 and 1.14 V (*vs.* Fc/Fc^+) were found, while quasi-reversible reduction potentials were observed at -2.10 and -2.65 V (*vs.* Fc/Fc^+). This profile agrees well with similar manganese complexes reported in the literature [1]. UV-Vis spectrum was recorded in CH_3CN to investigate the electronic transitions present in this complex. It shows two bands with maxima at 220 and 240 nm attributed to fully allowed intraligand (IL $_{\pi\rightarrow\pi^*}$) transitions with $\varepsilon = 4.0 \times 10^4$ and 2.5×10^4 L mol^{-1} cm^{-1}, respectively. At smaller energies, a broad band between 260 and 390 nm is observed and it is attributed to a mixture of IL $_{\pi\rightarrow\pi^*}$ and metal-to-ligand charge transfer (MLCT) transitions (ε=1.8 x 10^4 L mol^{-1} cm^{-1}). In conclusion, the proposed structure was successfully synthesized as evidenced by ^{1}H NMR and FTIR. Spectra. The new species is electrochemically active and holds potential applicability as CO_2RR catalyst, in which the role of the imidazole proton will be investigated.

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