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Structural effects in $[M(L_A)_2(L_B)]^{2+}$ type complexes in controlled Proton-coupled electron transfer processes

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Proton-coupled electron transfer (PCET) reactions are fundamental in various chemical and biological processes, including photosynthesis, some enzymatic reactions and energy devices[1,2]. The origin of the interdependence of proton and electron transfer is thermodynamic, where the reduction potential shifts with protonation/deprotonation[2-3]. In this work, a series of complexes of the $[M(L_A)_2(L_B)]^{2+}$ type were synthesized, characterized, as shown in figure 1, and the Pourbaix diagrams for all the complexes were constructed in the pH range 0-8, where the first two oxidation processes of these species under different pH conditions were described, in order to verify the influence of structural changes in the auxiliary ligands, the metal center and the structure of the bisbenzoimidazole, which acts as a proton donor site and can also act as a redox ligand; and to understand how these changes affect the thermodynamics of these reactions in this series. For all the complexes, a PCET region was observed in the Pourbaix diagrams for both oxidations, showing a linear slope with increasing pH, consistent with the Nernstian slope expected for a $1e^-/1H^+$ process on diagrams. The $[Ru(NHCpy)_2(BiBimH_2)]^{2+}$ complex was used as a reference for the comparisons. When MC was replaced by iron, there was an increase in the pK_a values of the complex (pK_{a1}-3.16→5.31 and pK_{a2} 6.07→9.42), a reduction of 370 mV in their potential of the 1st oxidation potential, and for the 2nd potential process was maintained. When the auxiliary ligands are modified, it can be seen that the complex with carbene ligand 1,2-bpy has the first potential 130 mV lower that others complexes, while the value of the second process is slightly lower. When methyl groups are added to L_b, we observe that the pK_a values presented by the complex decrease (pK_{a1}-3.16→7.06 and pK_{a2} 6.07→9.30), the first oxidation remains at potentials close to the reference compound, but the second process occurs 200 mV at lower potentials.

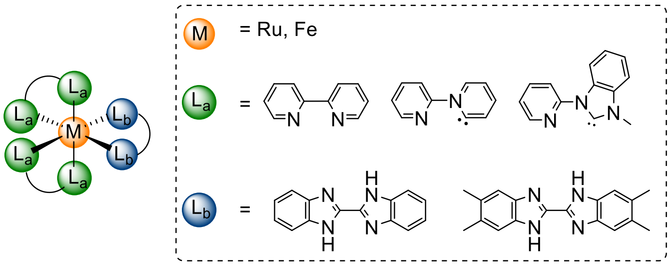

Figure 1 : Complexes synthesized for this study

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