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Synthesis and characterization of potential CO-releasing molecules based on oxo-centered triruthenium clusters with imidazole ligands

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Carbon monoxide (CO) is a diatomic gaseous molecule biologically generated by the human physiology that has important biological roles in anti-inflammatory and apoptosis processes.[1] Therefore, over the years scientists have been developing carbon monoxide releasing molecules (CORMs) which are molecules produced to deliver CO in order to be use as treatment for diseases.[1] Considering all these molecules, the ruthenium complexes CORM-2 ($Ru_2Cl_4(CO)_6$) and CORM-3 ($[Ru(glycinato)Cl(CO)_3]$) are the most studied having anticancer and vasodilation properties.[1] Based on this use of ruthenium complexes as CORMs the LABiQSC[2] research group aimed to study the carbonyl complexes from the oxo-centered triruthenium cluster class. Hence, this work will present the spectroscopic properties of the $[Ru_3O(CH_3COO)_6(L)_2CO]$ complexes where L = imidazole (**1**) and its derivates benzimidazole (**2**), 1-methylimidazole (**3**) and 1-(2-hidroxyethyl)imidazole (**4**), being the last three new complexes. It was observed in the absorption spectra (Figure 1a) that the main band (intra-cluster band) has a bathochromic shift from the complex with **3** (571 nm) to **2** (581 nm). In the infrared spectrum, the complexes showed υ_{CO} stretching band from 1948 cm^{-1} for **1** to 1919 cm^{-1} for **4**, indicating that in these series the ligand exchange play a significative role in the CO bond strength with the ruthenium. For all the complexes the ^1H NMR chemical shift for the acetate (CH_3 (a), labels in Figure 1a) are the same (1.85 ppm), while the CH_3(b) are 1.59 ppm for **1** and **3**, 1.61 ppm for **4** and 1.66 ppm for **2**. All the spectroscopic data are compatible with the literature analogs.[2,3] The CO delivery reaction of these complexes with biological oxidant hydrogen peroxide (Figure 1b) were studied and k_{obs} results were $5.3 \times 10^{-4} s^{-1}$, $9.4 \times 10^{-4} s^{-1}$, $1.26 \times 10^{-3} s^{-1}$ and $1.51 \times 10^{-3} s^{-1}$ for the complexes with **2**, **1**, **3** and **4**, respectively, showing that the CO release constant rates follow the inverse pattern from υ_{CO} stretching bands. The solvato complex correspond the product of the CO release.[2,3]

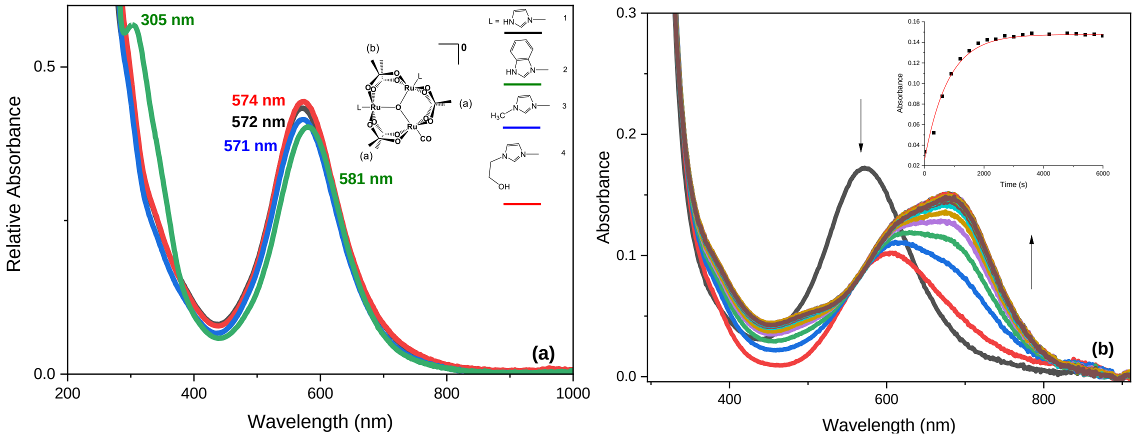

Figure 1. Absorption spectrum of the carbonyl complexes in dimethyl sulfoxide (a) 1-MeIm (4.2×10^{-5} mol/L) complex reaction with hydrogen peroxide (1.24 mol/L) in acetonitrile (b)

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