

# Investigating the stability of carbonyl triruthenium carboxylates and the photodissociation of the functional ligand CO

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Many scientific researchers have shown that depending on concentration the carbon monoxide (CO - monoxide oxide) present several functions in the body, such as neurotransmitter or a blood vessel relaxant<sup>1</sup>. Studies have shown that ruthenium derivatives exhibit photochemical characteristics that stimulate the development of CO releasing compounds in biological conditions (CO-RMs - CO-releasing molecules)<sup>1</sup>. The CO molecule coordinated to a trinuclear ruthenium carboxylate has become target of research, because under appropriate conditions occur the controlled release of CO<sup>2,3</sup>. This work presents the study of CO release from the complexes **(1)** [Ru<sub>3</sub>O(OAc)<sub>6</sub>(4-acpy)<sub>2</sub>(CO)] and **(2)** [Ru<sub>3</sub>O(OAc)<sub>6</sub>(4-tbpy)<sub>2</sub>(CO)] (where 4-acpy = 4 -acetylpyridine and 4-tbpy = 4-tert-butylpyridine). These complexes were previously synthesized in our research group. In this study, it was evaluated the effect of acetonitrile and phosphate buffer solution (pH = 7.4 for simulates biological conditions) on the stability of the compounds and on the photoinduced CO release (10<sup>-5</sup> mol L<sup>-1</sup>). For photoinduced reaction it was used laser irradiation at a wavelength of 377 nm and the quantum yield of CO release was determined by reineckate chemical actinometry<sup>3</sup>. The stability of the complexes was verified by recording spectra in a time interval of 50 minutes in the same solutions, but in the absence of laser irradiation. In these complexes the coordination of a single CO to one of three ruthenium centers forms a valence-trapped Ru<sub>3</sub>(II,III,III) core, because the  $\pi$ -accepting character of CO. Analyzing the absorption spectra of the complexes **(1)** and **(2)** after irradiation, it can be observed a reduction of the band around 600 nm and the appearance of a new band around 900 nm. The spectral changes are accompanied by isosbestic points (706 nm in acetonitrile and 695 nm in phosphate buffer solution). The quantum yield ( $\Phi$ ) of CO release in acetonitrile solution is higher to complex **(2)** ( $\Phi$ =0.011) than to complex **(1)** ( $\Phi$ =0.0012). Also, these values are higher in aqueous phosphate buffer solution ( $\Phi$ =0.024 and 0.0044, respectively) than in acetonitrile. Since CO release is triggered by irradiation at a charge transfer band, the excited state has an oxidized character (core Ru<sub>3</sub>III,III,III). For complex **(2)** we observed the influence of the 4-tbpy ligand that present  $\sigma$ -donor characteristic and this strongly contributes to the stability of the excited state. On the other hand, the more polar property of the phosphate buffer can stabilize the charge-separation excited state due to more favorable solvation interactions, and this effect leads to an increase of CO release from the complexes. According to the data obtained, these complexes are promising to release molecules of biological interest. In the next steps of this work, kinetics aspects of CO releases will be investigated.

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