

*Title:* **Preparation of a mixed-valence Co(III)-Fe(II) cubic complex and kinetic study of its redox reactivity with peroxodisulfate.**

*Student:* Aina Queral Beltran

*Date:* June 2019

*Supervisor/s:* Dr. Manuel Martínez López  
*Departament of Química Inorgànica i Orgànica*

The oxidation of Fe<sup>II</sup> in the newly prepared and characterised mixed-valence complex  $[\{Co^{III}(Me_3TACN)_4\}(\mu-NC)_3\{Fe^{II}(CN)_6\}_4]^{4-}$  has been studied as a function of pH and the concentration of the oxidizing agent. The oxidation reaction has been carried out with peroxodisulfate and consists of a fourth-step process with the participation of solvent-assisted outer-sphere complexes, as a result of the establishment of hydrogen bonds that involve the oxo groups of the oxidant (peroxodisulfate), the water molecule of the reaction medium and the terminal cyanido ligands of the octametallal cube. The reduction reaction, by hydroxide ions, of the fully oxidized  $[\{Co^{III}(Me_3TACN)_4\}(\mu-NC)_3\{Fe^{III}(CN)_6\}_4]$ , takes place producing hydrogen peroxide from water even at neutral or slightly acidic pH. The kinetic parameters for the oxidation reaction have been determined and are indicative of above mentioned outer-sphere precursor formation. While for the oxidation of the initial mixed-valence  $\{Co^{III}/Fe^{II}\}_4^{4-}$  and partially oxidized  $\{Co^{III}_4/Fe^{II}_3Fe^{III}\}^{3-}$  complexes, the outer-sphere precursor formation equilibrium constants,  $K_{OS}$ , are large enough for the observation of limiting kinetics in their oxidation reaction rate-determining steps, for the oxidation of the intermediate  $\{Co^{III}_4/Fe^{II}_2Fe^{III}_2\}^{2-}$  and  $\{Co^{III}_4/Fe^{II}Fe^{III}_3\}$  complexes the buildup of outer-sphere precursor complexes with peroxodisulfate has not been detected.

**Keywords:** Cobalt / Iron / Mixed-valence complexes / Redox processes.