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Appendix (Supporting Information)

In this Appendix we will give an example of the calculations that we have carried out to estimate the kinetic rate constants of the chemical steps involved in the proposed mechanism. The Specfit program allows the calculation of the parameters not reported previously in literature, as well as the spectra of the unknown species that better fit the temporal evolution of the spectra. In order to do so, the program requires the initial concentrations of all the reactants and initial values to all the constants in the proposed mechanistic scheme. These constants can be used as fixed or fitting parameters; the latter will be changed in the iterative procedure. When available, we can add as a restriction the known spectrum of some of the species; the spectrum of the other species will be calculated in the procedure.

a) The Reaction of R_4 with One Equivalent of Peroxydisulfate (Figures SI 2 and SI 4). To avoid making the calculation too slow, we calculated the equilibrium concentrations in the formation dissociation equilibrium of the binuclear complex, starting from the analytical concentrations employed. To explain the dynamics of this reaction we propose a mechanistic scheme comprising reactions 1, 3, 4, 6, 8, 11 and 13 (Table 2).

$$[(NH_3)_5Ru^{II}4NCpy]^{2+} + [S_2O_8]^{2-} \rightarrow [(NH_3)_5Ru^{III}4NCpy]^{3+} + [SO_4]^{2-} + [SO_4] \cdot k_{11}$$
(11)

$$[(NC)_{5}Fe^{II}pyC(O)NHRu^{III}(NH_{3})_{5}]^{-} + H_{2}O \leftrightarrow$$

$$[Fe^{II}(CN)_{5}H_{2}O]^{3-} + [Ru^{III}(NH_{3})_{5}NHC(O)py]^{2+} \qquad k_{13}(13)$$

We have not included the reactions of the radical $[SO_4]$ because we assume them to be diffusion controlled process, with $k \sim 1 \ge 10^9 M^{-1} s^{-1}$. Their inclusion would make the numerical integration of the equation too slow. Instead, we have considered that the peroxydisulfate ion reacts with an effective double concentration. The numerical simulation of both models show that in the conditions of our experiments this is a reasonable approximation.

We have used as fixed parameters the concentrations for the measured values of the kinetic rate constants of reactions 1, 10 and 14 and the kinetic rate constants for reaction 4, estimated through the Marcus cross relation.³⁷

When the global analysis was performed without any spectral restriction, the output showed unreasonable spectra for the different species, namely too high absorbance values or large negative numbers. This result reflects the covariance between the type of parameters involved in the calculation: the spectra and the kinetic constants. To solve this problem Specfit, allows to impose restrictions on the two types or parameters. In our case, we have obtained very good results by including as a restriction in the calculation the known spectra of all the mononuclear species.

Using theses procedures we found the reported values for the unknown constants. The predicted spectral evolution follows qualitatively all the features of the experimental traces (Figure 2a). The standard deviation of predicted values with respect to the experimental ones is 2.8 10⁻².

To fit the experiment with addition of $Mepz^+$ (Figure SI 3), we have used the same set of reactions, but with the addition of reaction 5.

b) The Reaction of R_4 with Excess of Peroxydisulfate. The simplest model that we can apply to this reaction involves reactions 1, 3, 8, 10 and 11. In this model we are not considering the hydrolysis reactions, so we should expect that it to be valid only at short times. By assuming the kinetic constants for reactions 1, 3 and 11 as fixed parameters, a bad fitting for the spectral evolution at 820 nm is obtained. Besides, the spectrum of M_4 shows an unexpected shoulder at 550 nm, suggesting that the program is assigning some of the absorbance of R_4 to M_4 , or in other words, that R_4 is decreasing too fast.. The concentration profiles for R_4 , M_4 and O_4 in this calculation predict that the three species coexist during the run time, suggesting the inclusion of reaction 7. We calculate the rate constants for this step using the Marcus cross relation assuming that the precursor complex is formed by the approach of the ruthenium of one of the species to the iron of the other and using the parameters as for the calculation of the rate constants for equation 4.

With these modifications, we found satisfactory agreement between the predicted and the experimental results in several experiments with different initial concentrations of peroxydisulfate (Table SI 1).

The previous results show that the proposed mechanism reproduces the successive spectra of the mixtures of R_4 with peroxydisulfate. Because of the strong correlation between the spectra and the kinetic constants, the dispersion in the calculated values for different experiments is larger than the one found for systems with simpler mechanisms. To estimate the error in the proposed values of kinetic constants of reactions 4 and 7, we have tested which are the values that introduce significant error in the fitting. In this way we have been able to estimate an upper (or lower) limit for these parameters. The spectra of M_4 obtained in different fittings are very similar; however, higher uncertainties appeared in the spectrum of Ox_4 ; therefore, this spectrum can only be presented qualitatively.

Supporting Information

[S ₂ O ₈] ²⁻	[(NH ₃) ₅ Ru ^{II} 4Cp] ²⁺	[Fe ^{II} (CN)5H2O] ³⁻	[R ₄]	k ₁₀	
4.97 10 ⁻⁵	3.63 10 ⁻⁶	3.62 10 ⁻⁶	8.66 10 ⁻⁶	6.0 10 ²	3.6 10 ²
6.39 10 ⁻⁵	3.63 10-6	3.62 10 ⁻⁶	8.66 10 ⁻⁶	7.0 10 ²	$3.5 \ 10^2$
3.10 10 ⁻⁵	3.64 10 ⁻⁶	3.75 10 ⁻⁶	8.96 10 ⁻⁶	6.5 10 ²	4.0 10 ²
1.07 10 ⁻⁴	5.8 10 ⁻⁶	4.78 10 ⁻⁶	1.82 10 ⁻⁵	7.3 10 ²	4.6 10 ²

Table 1. Kinetics constants calculated for the reaction of R_4 with excess of peroxydisulfate, with different initial concentrations of reactants.

All concentrations are expressed as M. The constants are expressed in $M^{-1} s^{-1}$.

Supporting Information Figure Captions

SI Figure 1. (a) Cyclic voltagrams for the $[(NC)_5Fe^{II}-4pyCN-Ru^{II}(NH_3)_5]^-$ in buffer edta-sodium acetate pH =5.5, I = 0.1 M, t 25° C, (NaCl). (b) Same as before for the $[(NC)_5Fe^{II}-3pyCN-Ru^{II}(NH_3)_5]^-$.

SI Figure 2. Spectral changes observed in the reaction of $[(NC)_5Fe^{II}-4pyCN-Ru^{II}(NH_3)_5]^-$ with one equivalent of peroxydisulfate. $[Fe^{II}] = 1.04 \times 10^{-4} \text{ M}$; $[Ru^{II}] = 0.98 \times 10^{-4} \text{ M}$; $[S_2O8^{2-}] = 0.5 \times 10^{-4} \text{ M}$; pH = 5.5; I = 0.1 M; $T = 25^{\circ} \text{ C}$. (a) Spectral changes between 0 and 90 s with steps of 4 s between spectra (b) 60-600 s with steps of 40 s (c) 600-2200 s with steps of 80 s. (d) Spectral changes observed in the reaction of $[Fe^{III}(CN)_5H_2O]^{2-}$ and $[Ru(NH_3)_54NCpy]^{2+}$. $[Fe^{III}] = 2.09 \times 10^{-4} \text{ M}$; $[Ru^{II}] = 1.97 \times 10^{-4} \text{ M}$; pH = 5.5; I = 0.1 M; $T = 25^{\circ} \text{ C}$.

SI Figure 3. Spectral changes observed in the reaction of $[(NC)_5Fe^{II}-4pyCN-Ru^{II}(NH_3)_5]^-$ with one equivalent of peroxydisulfate in the presence of an excess of methyl-pirazinium ion. $[Fe^{II}] = 1.04 \times 10^{-4} \text{ M}$; $[Ru^{II}] = 0.98 \times 10^{-4} \text{ M}$; $[S_2O8^{2-}] = 0.5 \times 10^{-4} \text{ M}$; $[Mepz^+] = 2.3 \times 10^{-2} \text{ M}$; pH = 5.5; I = 0.1 M; $T = 25^{\circ} \text{ C}$. (a) Spectral changes between 0 and 120 s with steps of 40 s between spectra (b) 120-600 s with steps of 40 s (c) 600-2200 s with steps of 160 s.

SI Figure 4. Spectral changes observed in the reaction $[(NC)_5Fe^{II}-3pyCN-Ru^{II}(NH_3)_5]^-$ with one equivalent of peroxydisulfate . $[Fe^{II}] = 5.4 \times 10^{-5} \text{ M}; [Ru^{II}] = 5.3 \times 10^{-5} \text{ M}; [S_2O8^{2-}] = 2.6 \times 10^{-5} \text{ M}; I = 0.1 \text{ M}, T = 25^{\circ} \text{ C}.$ (a) Spectral changes between 0 and 72 s with steps of 12 s between spectra (b) 120-600 s with steps of 48 s.

SI Figure 5. Spectral changes observed in the reaction of $[(NC)_5Fe^{II}-4pyCN-Ru^{II}(NH_3)_5]$ with excess of peroxydisulfate. $[Fe^{II}] = 1.3 \times 10^{-5} \text{ M}$; $[Ru^{II}] = 1.3 \times 10^{-5} \text{ M}$; $[S_2O8^{2-}] = 3.1 \times 10^{-5} \text{ M}$; I = 0.1 M, $T = 25^{\circ} \text{ C}$. (a) Spectral changes between 0 and 70 s with steps of 7 s between spectra (b) 70-154 s with steps of 7 s (c) 154-378 s with steps of 35 s.

SI Figure 6. Consecutive spectra in the reaction $[(NC)_5Fe^{II}-4pyCN-Ru^{II}(NH_3)_5]^{-1}$ with one equivalent of peroxydisulfate. $[Fe^{II}] = 2.4 \ 10^{-4} \ M$; $[Ru^{II}] = 2.4 \ 10^{-4} \ M$; $[S_2O8^{2-}] = 8.4 \ 10^{-5} \ M$. I= 0.1 M, T= 25° C. (a) Spectral changes between 0 and 15 s with steps of 1.5 s between spectra (b) 15-120 s with steps of 6 s.

SI Figure 1 0,2 0,6 0,8 -0,2 0,0 0,4 1,0 1,2 а ļ 5µA b -0,2 0,0 0,2 0,4 0,6 0,8 1,2 1,0

E (V vs NHE)

SI Figure 2



SI Figure 3



SI Figure 4





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SI Figure 5





