Electronic Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

Ru^{III}(edta) mediated oxidation of azide in presence of hydrogen peroxide. Azide versus peroxide activation†

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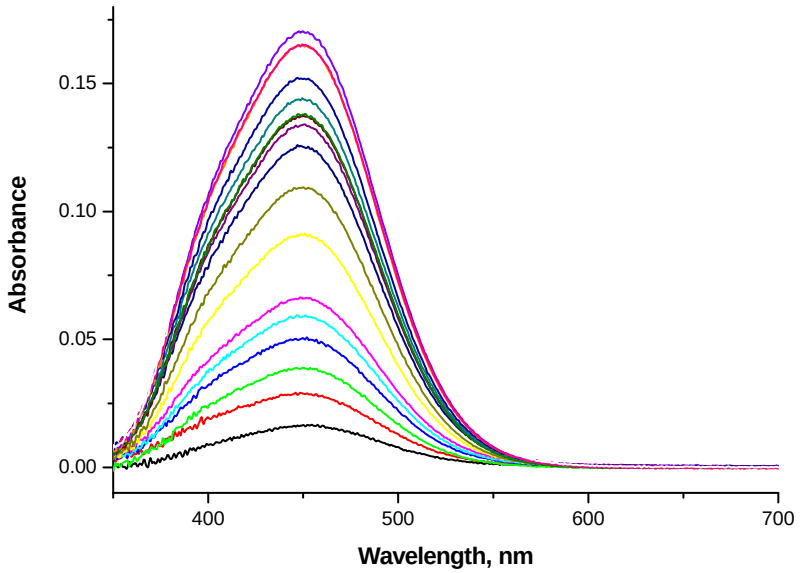


Figure S1. Difference spectra recorded during titration of 2 x 10^{-4} M $[Ru^{III}(edta)(H_2O)]^-$ with N_3^- (4 x 10^{-5} – 1 x 10^{-2} M) in 0.010 M acetate buffer at pH = 5.0 and 25 °C.

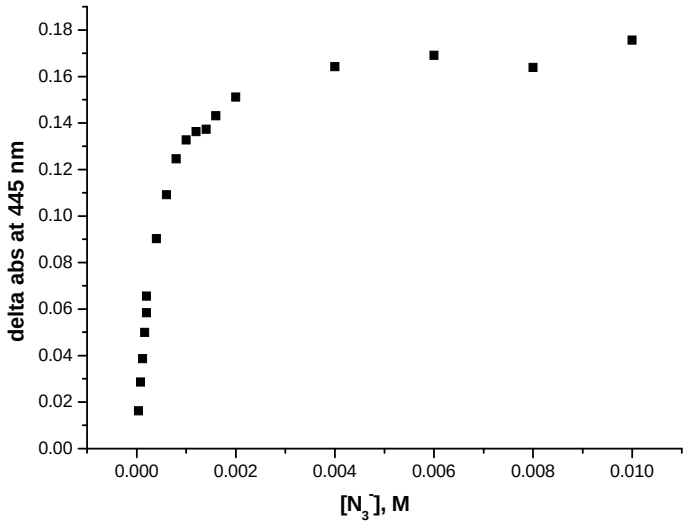


Figure S2. Plot of the relative absorbance at 445 nm versus the azide concentration constructed on the basis of data reported in Figure S1. Experimental conditions: see Figure S1.

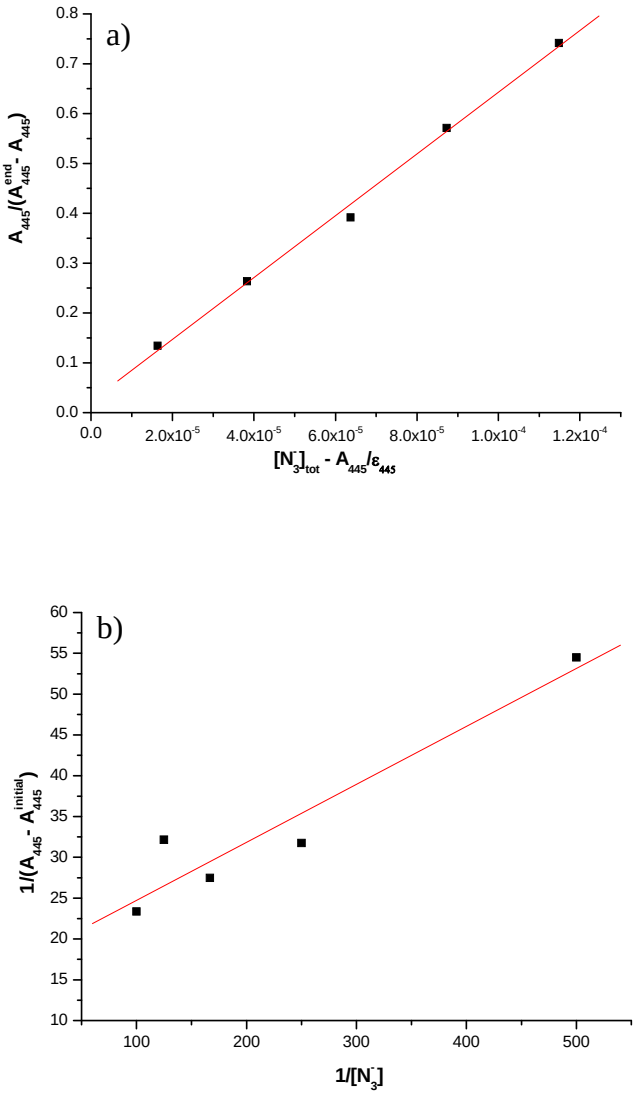


Figure S3. Determination of the values of K_1 (a) and K_2 (b) for the reversible binding of azide to $[Ru^{III}(edta)(H_2O)]^-$ based on the thermodynamic data shown in Figures S1 and S2.

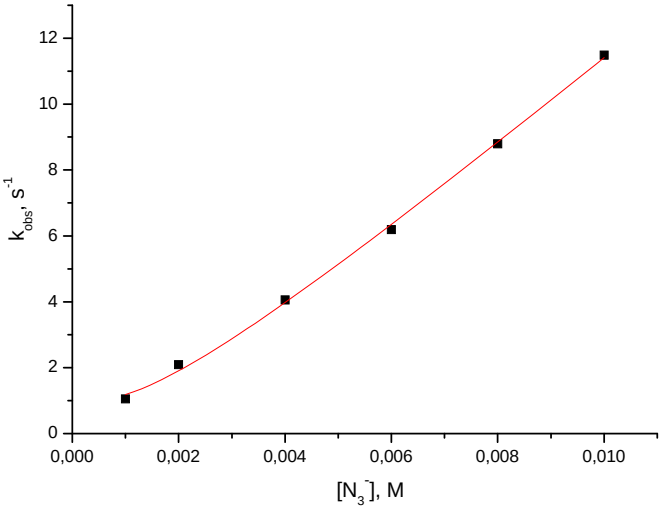


Fig. S4. Plot of k_{obs} vs. $[N_3^-]$ at 25 ^oC, pH 5.0 (10 mM acetate buffer), $[Ru^{III}] = 2 \times 10^{-4}$ M.

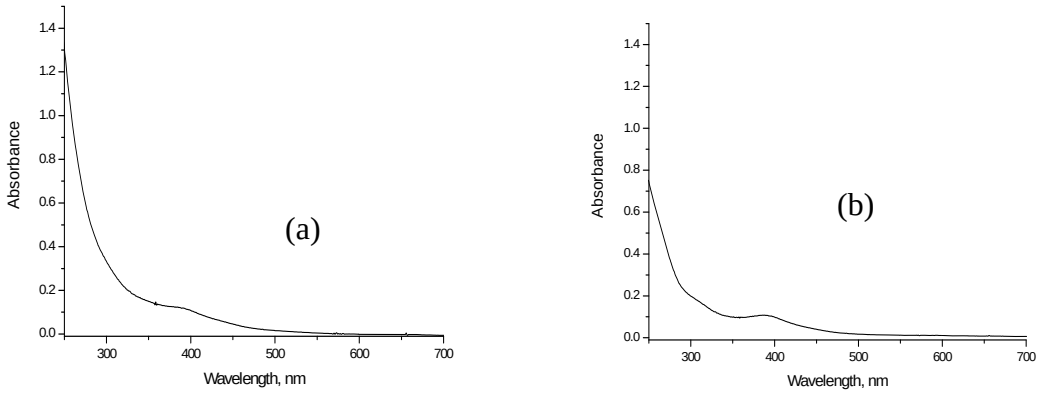


Figure S5. UV-Vis spectra of (a) final reaction mixture obtained after bleaching of the 445 nm band ($[Ru^{III}(edta)]$ = 2 x 10^{-4} M, $[N_3^-]$ = 1 x10^{-3} M and $[H_2O_2]$ = 0.02 M, pH 5.0) and (b) solution of $[Ru^{III}(edta)(NO)]^-$ (2 x 10^{-4} M) containing $[Ru^{V}(edta)O]^-$ complex (1 x 10^{-5} M) and a trace of nitrite.

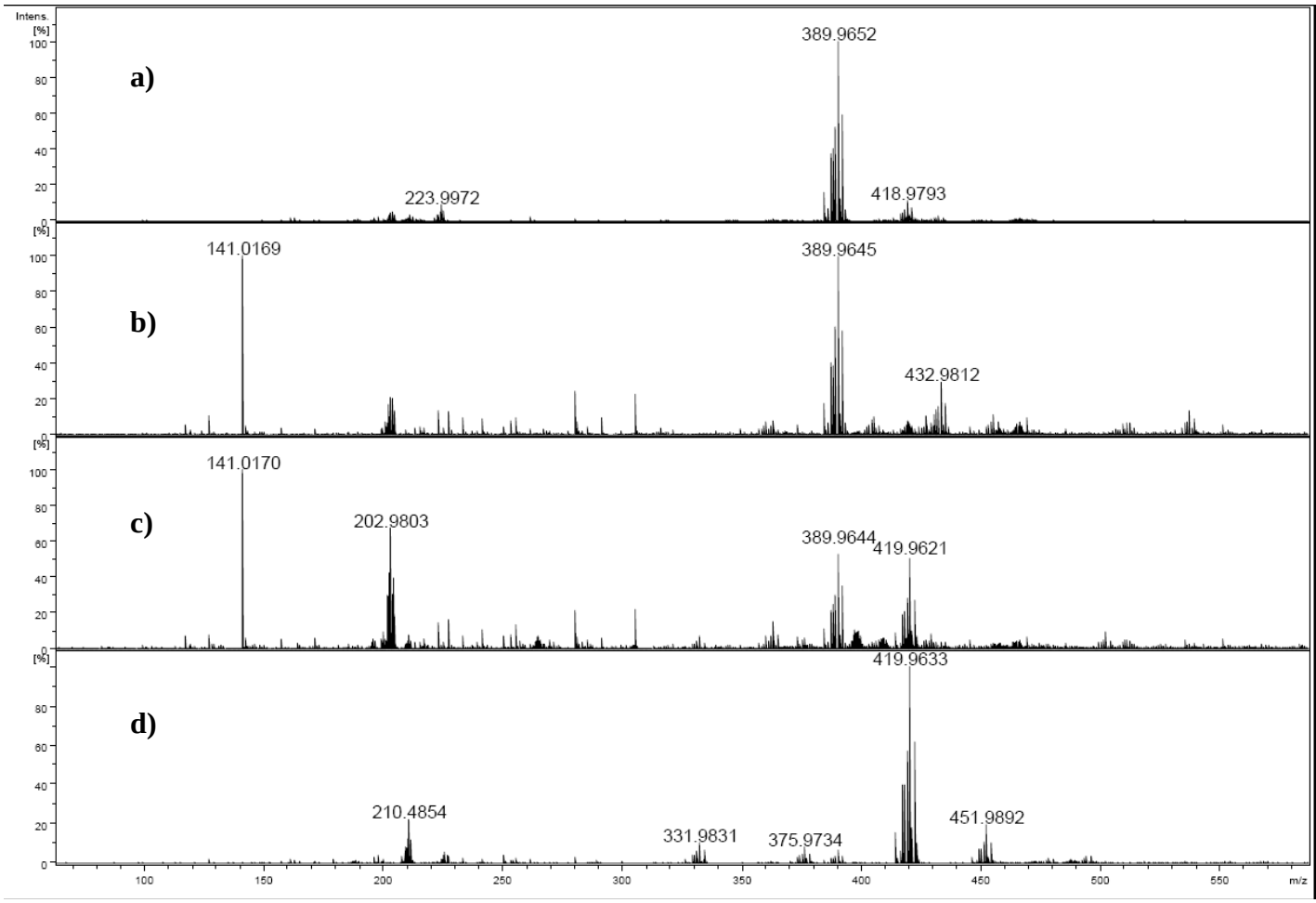
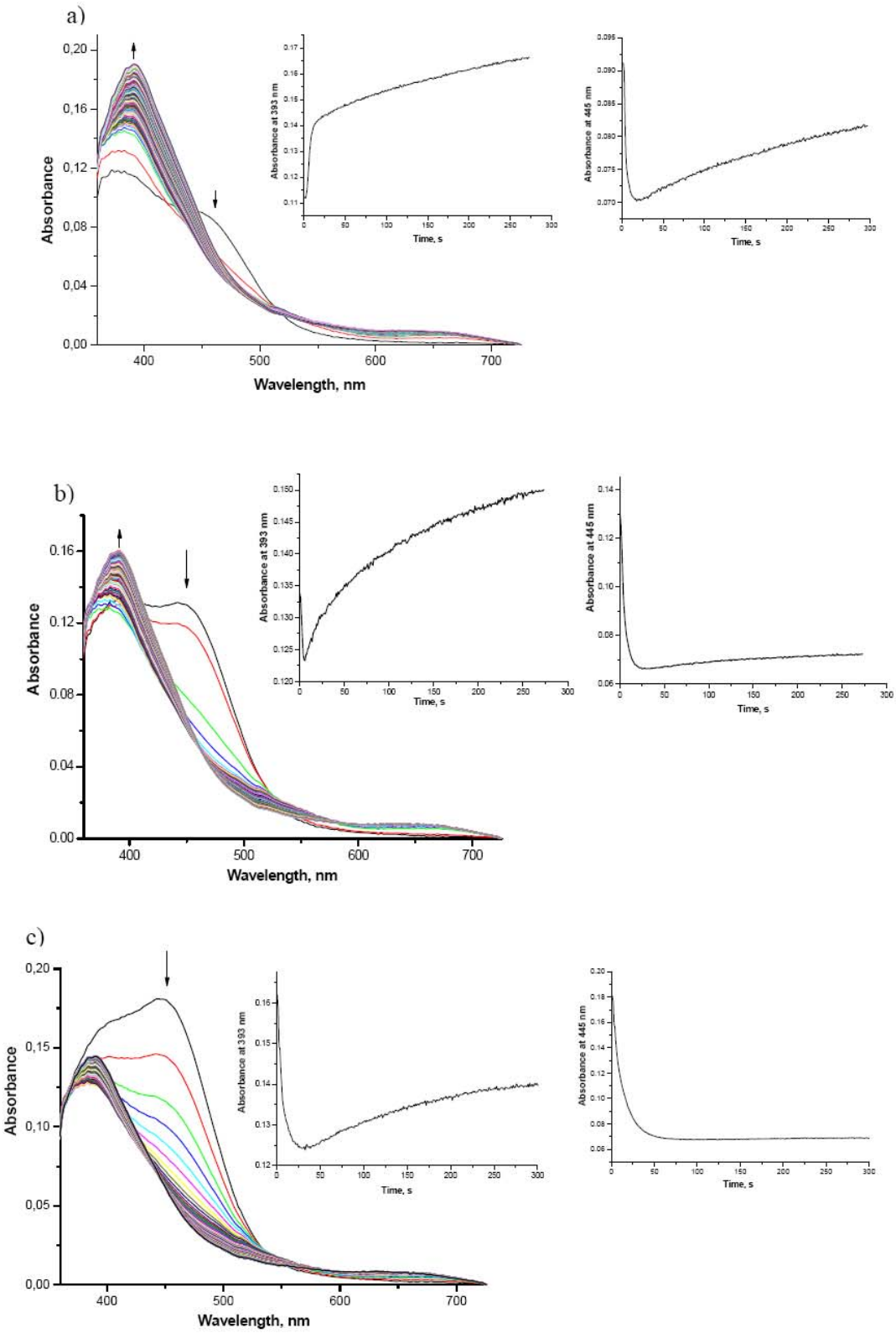


Figure S6. Summary of ESI-MS data: a) Spectrum recorded for the solution of 1 x 10^{-4} M $[Ru^{III}(edta)H_2O]^-$ in 1mM acetate buffer at pH = 5; b) Spectrum recorded after addition of 5 x 10^{-4} M NaN_3 to the solution of a); c) Spectrum recorded after addition of 3.5 x 10^{-3} M H_2O_2 to the solution of b); d) Reference spectrum of 1 x 10^{-4} M $[Ru^{III}(edta)NO]^-$ in 1mM acetate buffer at pH = 5.



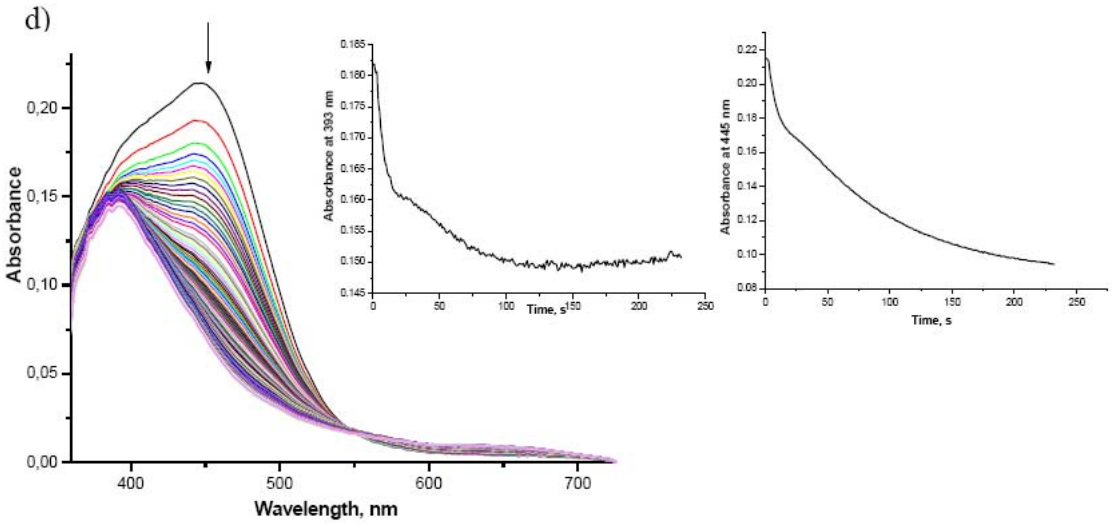


Figure S7. UV-Vis spectral changes and kinetic traces (at 393 and 445 nm) recorded after addition of 0.02 M H_2O_2 to a solution of 2 x 10^{-4} M $Ru^{III}(edta)(H_2O)^-$ containing a) 2 x 10^{-4} M; b) 4 x 10^{-4} M; c) 1 x 10^{-3} M and d) 4 x 10^{-3} M NaN_3 in 10 mM acetate buffer at pH 5.0 and 25 °C.

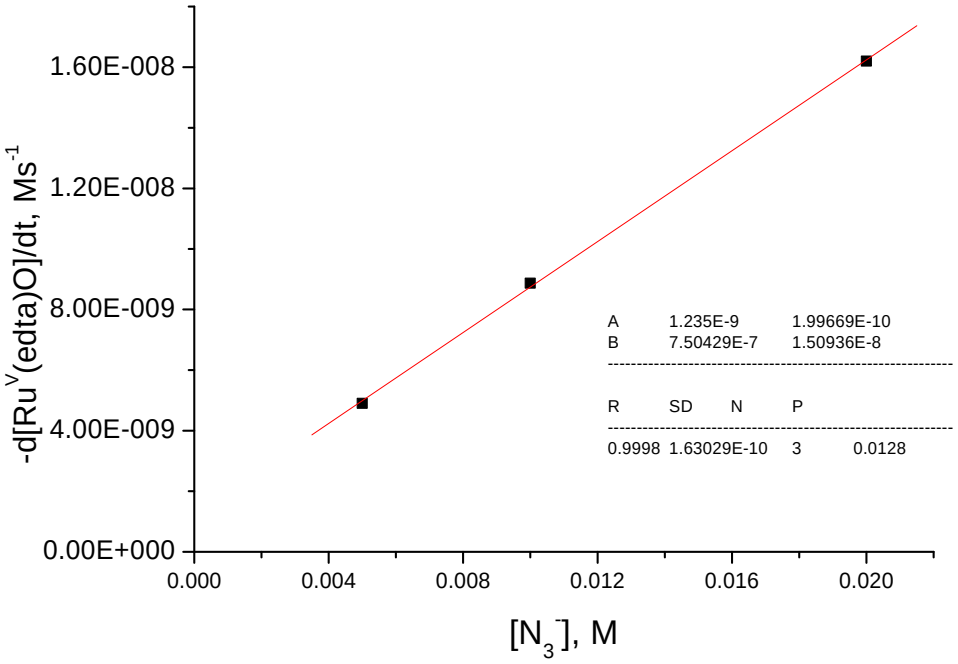


Figure S8. Effect of azide concentration on the rate of reduction of the $[Ru^{V}(edta)O]^{-}$ complex (determined from the maximum slope of the plots in Fig. 6b). The value of k_2 derived from the slope (7.5×10^{-7} s^{-1}) is 7.5×10^{-3} M^{-1} s^{-1}.

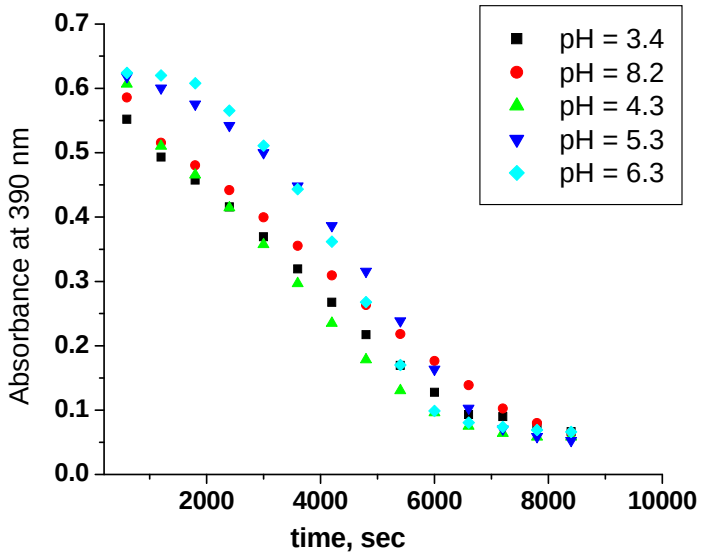


Figure S9. Effect of pH on the absorbance versus time traces (at 390 nm) for the oxidation of azide by $[Ru^{V}(edta)O]^{-}$ preformed by reacting $[Ru^{III}(edta)(H_2O)]^{-}$ (1 x 10^{-4} M) with H_2O_2 (5 x 10^{-4} M). T = 25 °C and $[N_3^{-}]$ = 2 x 10^{-3} M.