Electronic Supplementary Information (ESI)

Kinetic and mechanistic studies on reactions of diruthenium(II,III) with biologically relevant reducing agents

Rodrigo Luis Silva Ribeiro Santos[a,b,c]; Rudi van Eldik[b,*]; Denise de Oliveira Silva[a,*]

[a] Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes, 748, CEP 05508-000, São Paulo, SP, Brazil.

[b] Inorganic Chemistry, Department of Chemistry and Pharmacy, University of Erlangen-Nuremberg, Egerlandstr. 1, 91058 Erlangen, Germany

[c] Present address: Departamento de Ciências Exatas e Tecnológicas, Universidade Estadual de Santa Cruz, Rod Jorge Amado, km 16, Ilheus BA, Brazil

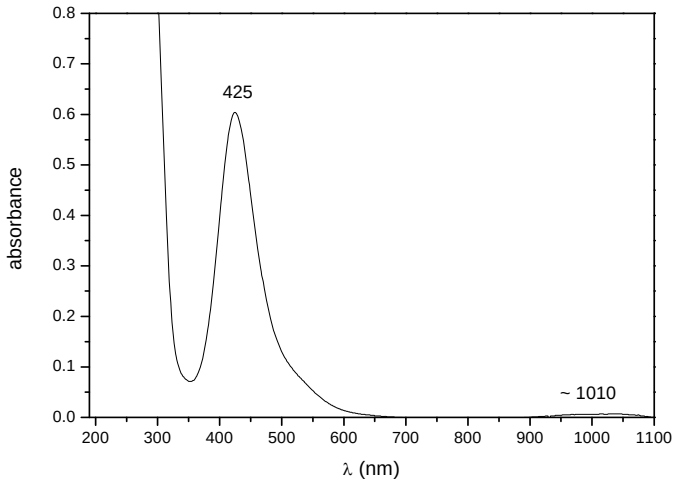

Fig. S1 – Typical electronic spectrum of the diaqua-Ru_2 complex. $[Ru_2(CH_3COO)_4Cl]$ (8.4×10^{-4} mol L^{-1}) dissolved in acetate buffer pH 5.0 (2.0×10^{-2} mol L^{-1})

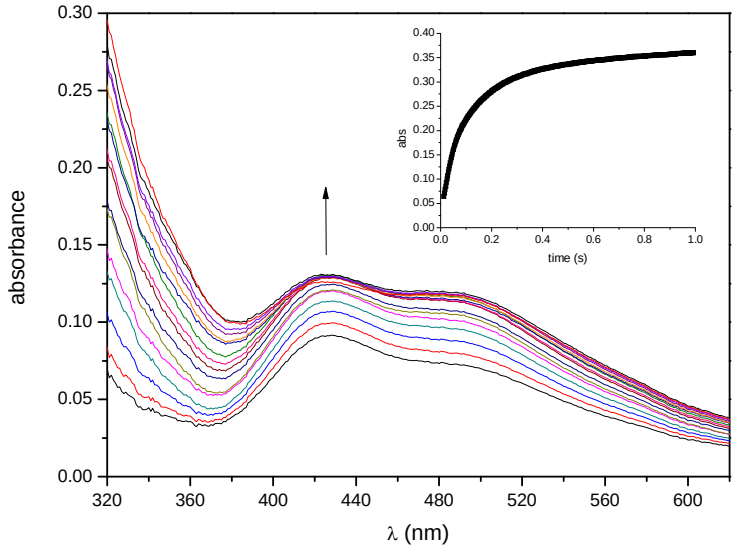

Fig. S2 – UV-Vis spectra recorded after addition of a 10 fold excess of glutathione to $[Ru_2(CH_3COO)_4(H_2O)_2]^+$ during the reaction up to 0.06 s. $[Ru_2(CH_3COO)_4(H_2O)_2]^+$ = 1.0×10^{-4} mol L^{-1}, [GSH] = 1.0×10^{-3} mol L^{-1}, 10 ^oC, pH 5.0. Inset: kinetic trace (0 – 1 s) fitted to a double exponential function (λ = 350 nm)

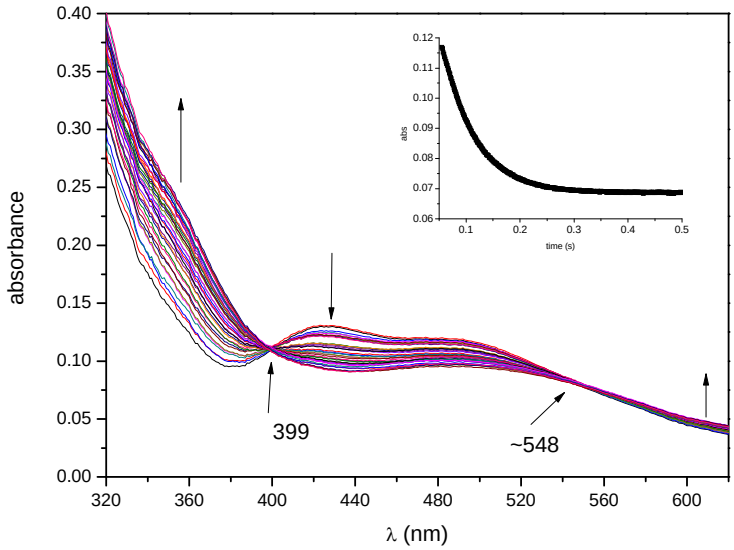

Fig. S3 – UV-Vis spectra recorded after addition of a 10 fold excess of glutathione to $[Ru_2(CH_3COO)_4(H_2O)_2]^+$ during the reaction between 0.06 and 0.2 s. $[Ru_2(CH_3COO)_4(H_2O)_2]^+ = 1.0 \times 10^{-4}$ mol L^{-1}, [GSH] = 1.0×10^{-3} mol L^{-1}, 10 ^oC, pH 5.0 Inset: kinetic trace (0.06 – 0.5 s) fitted to a single exponential function (λ = 425 nm)

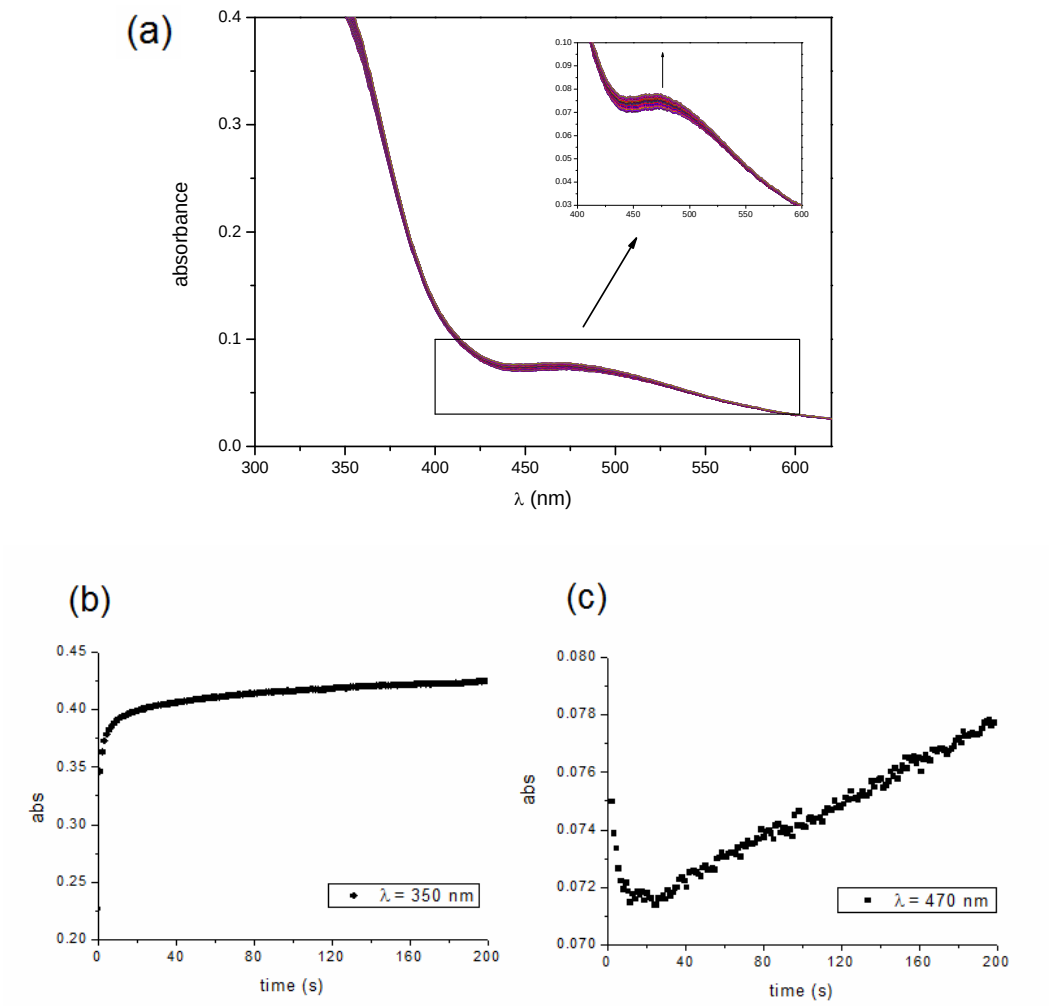

Fig. S4 – UV-Vis spectra recorded after addition of a 10 fold excess of glutathione to $[Ru_2(CH_3COO)_4(H_2O)_2]^+$ during the reaction between 25 and 200 s (a); kinetic trace recorded between the range 2 – 200 s at 350 nm (b); at 470 nm (c) ($[Ru_2(CH_3COO)_4(H_2O)_2]^+ = 1.0 \times 10^{-4}$ mol L^{-1}, [GSH] = 1.0×10^{-3} mol^{-1}, 10 ^oC, pH 5.0)

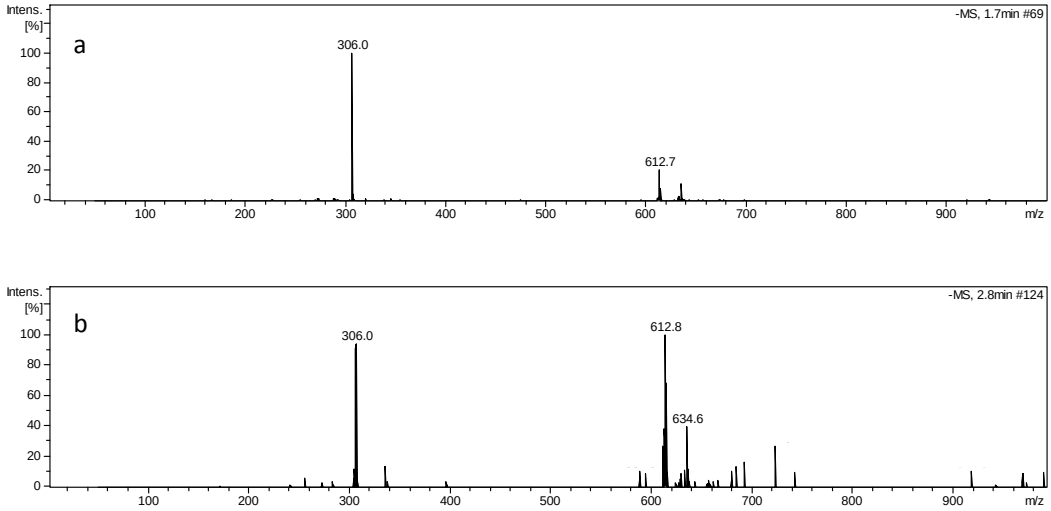

Fig. S5 – ESI-MS data (negative mode) obtained for GSH (a) and GSH with diaqua-Ru_2 complex immediately after mixing the solutions (b)

Table S1 – Observed rate constants (k_{obs}) obtained from the kinetic traces (at 350 nm) for the first step of the reaction of the diaqua-Ru_2 complex (0.2 mmol L^{-1}) with glutathione at different concentrations (10 °C and acetate buffer 20 mmol L^{-1} pH 5.0).

GSH (mol L^{-1})	k_{obs} (s^{-1})
2.0×10^{-3}	42.7
3.0×10^{-3}	64.0
4.0×10^{-3}	91.1
5.0×10^{-3}	111
6.0×10^{-3}	140
7.0×10^{-3}	162
8.0×10^{-3}	187
9.0×10^{-3}	208
1.0×10^{-2}	236
1.5×10^{-2}	345
2.0×10^{-2}	449

Table S2 – Observed rate constants (k_{obs}) obtained from the kinetic traces (at 425 nm) for the second step of the reaction of the diaqua-Ru_2 complex (0.1 mmol L^{-1}) with glutathione at different concentrations (10 °C and acetate buffer 20 mmol L^{-1} pH 5.0).

GSH (mol L^{-1})	k_{obs} (s^{-1})
1.0×10^{-3}	10.4
2.0×10^{-3}	18.6
3.0×10^{-3}	23.7
4.0×10^{-3}	27.0
5.0×10^{-3}	29.0
6.0×10^{-3}	31.4
7.0×10^{-3}	34.2
8.0×10^{-3}	36.5
2.5×10^{-2}	50.2
5.0×10^{-2}	57.3
7.5×10^{-2}	59.6

Table S3 – Observed rate constants (k_{obs}) obtained from the kinetic traces (at 350 nm) for the first step of the reaction of the diaqua-Ru_2 complex (0.2 mmol L^{-1}) with glutathione (10 mmol L^{-1}) at different temperatures (acetate buffer 20 mmol L^{-1} pH 5.0).

Temperature (°C)	k_{obs} (s^{-1})
5.0	140
10.6	266
15.5	413
21.0	658
25.4	917

Table S4 – Observed rate constants (k_{obs}) obtained from the kinetic traces (at 425 nm) for the first and second steps of the reaction of the diaqua-Ru_2 complex (0.6 mmol L^{-1}) with different concentrations of ascorbic acid (pH 5.0, 10 °C).

H_2A (mol L^{-1})	k_{obs} (s^{-1})	
	first step	second step
6.0×10^{-3}	3.22	0.739
9.0×10^{-3}	4.46	1.10
1.2×10^{-2}	5.45	1.36
1.5×10^{-2}	7.17	2.04
1.8×10^{-2}	8.11	2.34
2.1×10^{-2}	8.94	2.66
2.4×10^{-2}	10.3	3.19
2.7×10^{-2}	11.2	3.48
3.0×10^{-2}	12.7	4.14
4.5×10^{-2}	18.6	6.19
6.0×10^{-2}	23.9	7.96

Table S5 – Observed rate constants (k_{obs}) obtained from the kinetic traces (at 425 nm) for the first and second steps of the reaction of the diaqua-Ru_2 complex (0.6 mmol L^{-1}, pH 5.0) with ascorbic acid at different temperatures (H_2A = 30 mmol L^{-1}) and pressures (H_2A = 18 mmol L^{-1}).

Temperature (°C)	Pressure (MPa)	k_{obs} (s^{-1})	
		first step	second step
4.5	10.13	3.86	1.02
4.5	50.66	3.40	0.89
4.5	91.18	3.05	0.75
4.5	131.7	2.72	0.66
5.0	ambient	8.79	2.67
10.7	ambient	18.1	5.85
15.1	ambient	27.7	9.09
20.1	ambient	52.7	20.2
25.1	ambient	101	37.5
29.7	ambient	160	54.7
34.4	ambient	260	86.4

Table S6 – Observed rate constants (k_{obs}) obtained from the kinetic traces (at 425 nm) for the first and second steps of the reaction of the diaqua-Ru_2 complex (0.6 mmol L^{-1}) with ascorbic acid (18 mmol L^{-1}) in different chloride concentrations (pH 5.0, 10 °C).

NaCl (mol L^{-1})	k_{obs} (s^{-1})	
	first step	second step
0	9.84	2.69
7.5×10^{-3}	8.60	2.33
3.0×10^{-2}	7.00	1.92
6.0×10^{-2}	5.26	1.24
9.0×10^{-2}	4.33	1.02
1.2×10^{-1}	3.85	0.93
1.5×10^{-1}	3.04	0.73
3.0×10^{-1}	1.91	0.40
6.0×10^{-1}	1.52	0.32