Electronic Supplementary Information

Reduction of some Pt(IV) complexes with biologically important sulfur-donor ligands

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Table S1. Observed *pseudo*-first order rate constants as a function of ligand concentration for the reactions of the $[PtCl_4(bipy)]$ complex at pH 2.0 (0.01 M $HClO_4$) with addition of 0.2 M NaCl at 310 K.

Reducing agent	λ/nm	10^3[L]/M	k_{obsd}/s^{-1}
GSH	280	10	2.20(5)
		15	3.36(6)
		20	4.13(6)
		25	4.90(7)
		30	6.60(5)
L- Cys	280	10	1.32(6)
		15	1.70(5)
		20	2.40(5)
		25	3.05(6)
		30	3.60(6)
L- Met	280	10	0.50(5)
		15	0.82(6)
		20	0.96(6)
		25	1.20(5)
		30	1.56(7)

Table S2. Observed *pseudo*-first order rate constants as a function of ligand concentration for the reactions of the $[PtCl_4(dach)]$ complex at pH 2.0 (0.01 M $HClO_4$) with addition of 0.2 M NaCl at 310 K.

Reducing agent	λ/nm	10^3[L]/M	k_{obsd}/s^{-1}
GSH	260	10	0.69(5)
		15	0.96(6)
		20	1.30(6)
		25	1.54(7)
		30	1.96(5)
L- Cys	260	10	0.62(6)
		15	0.85(5)
		20	1.10(5)
		25	1.45(6)
		30	1.74(6)
L- Met	250	10	0.37(5)
		15	0.62(6)
		20	0.78(6)
		25	0.91(5)
		30	1.19(7)

Table S3. Observed *pseudo*-first order rate constants as a function of ligand concentration for the reactions of the $[PtCl_4(en)]$ complex at pH 2.0 (0.01 M $HClO_4$) with addition of 0.2 M NaCl at 310 K.

Reducing agent	λ/nm	10^3[L]/M	k_{obsd}/s^{-1}
GSH	260	10	0.33(6)
		15	0.45(5)
		20	0.66(6)
		25	0.78(7)
		30	0.93(5)
L- Cys	260	10	0.21(7)
		15	0.31(5)
		20	0.40(5)
		25	0.48(6)
		30	0.62(6)
L- Met	260	10	0.15(5)
		15	0.21(6)
		20	0.28(6)
		25	0.33(5)
		30	0.44(7)

Table S4. Observed *pseudo*-first order rate constants as a function of ligand concentration for the reactions of the $[PtCl_4(bipy)]$ complex at pH 2.0 (0.01 M $HClO_4$) and 310 K.

Reducing agent	λ/nm	10^3[L]/M	k_{obsd}/s^{-1}
GSH	280	10	2.05(5)
		15	3.00(6)
		20	3.89(6)
		25	4.56(7)
		30	6.00(5)
L- Cys	280	10	1.10(6)
		15	1.66(5)
		20	2.20(5)
		25	2.60(6)
		30	3.30(6)
L- Met	280	10	0.49(5)
		15	0.79(6)
		20	0.97(6)
		25	1.10(5)
		30	1.55(7)

Table S5. Observed *pseudo*-first order rate constants as a function of ligand concentration for the reactions of the $[PtCl_4(dach)]$ complex at pH 2.0 (0.01 M $HClO_4$) and 310 K.

Reducing agent	λ/nm	10^3[L]/M	k_{obsd}/s^{-1}
GSH	260	10	0.66(7)
		15	0.94(6)
		20	1.20(6)
		25	1.49(7)
		30	1.89(5)
L- Cys	260	10	0.59(6)
		15	0.84(5)
		20	1.10(5)
		25	1.38(6)
		30	1.67(6)
L- Met	250	10	0.37(7)
		15	0.60(7)
		20	0.77(6)
		25	0.90(5)
		30	1.10(5)

Table S6. Observed *pseudo*-first order rate constants as a function of ligand concentration for the reactions of the $[PtCl_4(en)]$ complex at pH 2.0 (0.01 M $HClO_4$) and 310 K.

Reducing agent	λ/nm	10^3[L]/M	k_{obsd}/s^{-1}
GSH	260	10	0.31(7)
		15	0.44(5)
		20	0.67(6)
		25	0.77(7)
		30	0.90(7)
L- Cys	260	10	0.20(7)
		15	0.27(5)
		20	0.41(7)
		25	0.43(5)
		30	0.59(6)
L- Met	260	10	0.13(7)
		15	0.23(6)
		20	0.27(6)
		25	0.33(5)
		30	0.41(7)

Table S7. Observed *pseudo*-first order rate constants as a function of ligand concentration for the reactions of the $[PtCl_4(bipy)]$ complex at pH 7.2 in 25 mM Hepes buffer with addition of 0.2 M NaCl at 310 K.

Reducing agent	λ/nm	10^3[L]/M	k_{obsd}/s^{-1}
GSH	320	10	52.00(5)
			51.46(5)[a]
		15	58.00(6)
		20	63.00(6)
		25	67.00(7)
		30	72.00(5)
			72.36(5)[b]
L- Cys	280	10	20.52(6)
		15	23.90(5)
		20	25.00(5)
		25	26.30(6)
		30	28.07(6)
L- Met	280	10	5.70(5)
		15	6.10(6)
		20	6.90(6)
		25	7.46(5)
		30	8.69(7)

[a] 1×10^{-3} M $[PtCl_4(bipy)]$ and 1×10^{-2} M GSH with addition of 0.5 mM EDTA
[b] 1×10^{-3} M $[PtCl_4(bipy)]$ and 3×10^{-2} M GSH with addition of 0.5 mM EDTA

Table S8. Observed *pseudo*-first order rate constants as a function of ligand concentration for the reactions of the $[PtCl_4(dach)]$ complex at pH 7.2 in 25 mM Hepes buffer with addition of 0.2 M NaCl at 310 K.

Reducing agent	λ/nm	10^3[L]/M	k_{obsd}/s^{-1}
GSH	260	10	45.00(6)
		15	49.00(5)
		20	53.00(7)
		25	57.00(5)
		30	64.00(6)
L- Cys	260	10	12.10(7)
		15	15.00(6)
		20	16.50(5)
		25	17.40(6)
		30	19.50(5)
L- Met	280	10	3.10(7)
		15	3.90(6)
		20	4.40(5)
		25	5.20(6)
		30	5.80(7)

Table S9. Observed *pseudo*-first order rate constants as a function of ligand concentration for the reactions of the $[PtCl_4(en)]$ complex at pH 7.2 in 25 mM Hepes buffer with addition of 0.2 M NaCl at 310 K.

Reducing agent	λ/nm	10^3[L]/M	k_{obsd}/s^{-1}
GSH	260	10	35.48(6)
		15	40.10(5)
		20	45.90(7)
		25	47.00(5)
		30	53.88(6)
L- Cys	260	10	8.50(7)
		15	10.01(6)
		20	11.48(5)
		25	12.56(6)
		30	15.63(5)
L- Met	270	10	2.12(7)
		15	2.66(6)
		20	3.06(5)
		25	4.20(6)
		30	4.50(7)

Table S10. Observed *pseudo*-first order rate constants as a function of glutathione concentrations for the reactions of the $[PtCl_4(bipy)]$ complex at different chloride concentrations (pH 7.2, 310 K).

$[Cl^-]$/M	10^3[L]/M	k_{obsd}/s^{-1}
In the absence of NaCl	10	0.59(6)
	15	0.67(5)
	20	0.72(7)
	25	0.76(6)
	30	0.79(6)
With 0.02	10	5.90(5)
	15	6.78(6)
	20	7.30(6)
	25	7.70(7)
	30	8.30(5)
With 0.05	10	11.86(5)
	15	14.09(6)
	20	15.50(6)
	25	15.98(7)
	30	16.73(5)
With 0.10	10	22.30(6)
	15	24.50(5)
	20	26.70(7)
	25	28.50(7)
	30	31.50(6)
With 0.15	10	32.00(5)
	15	37.00(6)
	20	42.00(7)
	25	43.00(6)
	30	48.00(6)
With 0.20	10	52.00(5)
	15	58.00(6)
	20	63.00(6)
	25	67.00(6)
	30	72.00(5)

Table S11. Observed *pseudo*-first order rate constants as a function of glutathione concentrations for the reactions of the $[PtCl_4(dach)]$ complex at different chloride concentrations (pH 7.2, 310 K).

$[Cl^-]$/M	10^3[L]/M	k_{obsd}/s^{-1}
In the absence of NaCl	10	0.050(6)
	15	0.065(5)
	20	0.073(7)
	25	0.078(6)
	30	0.082(6)
With 0.02	10	4.70(5)
	15	5.10(6)
	20	5.50(6)
	25	5.87(7)
	30	6.60(5)
With 0.20	10	45.00(6)
	15	49.00(5)
	20	53.00(7)
	25	57.00(5)
	30	64.00(6)

Table S12. Observed *pseudo*-first order rate constants as a function of glutathione concentrations for the reactions of the $[PtCl_4(en)]$ complex at different chloride concentrations (pH 7.2, 310 K).

$[Cl^-]$/M	10^3[L]/M	k_{obsd}/s^{-1}
In the absence of NaCl	10	0.015(6)
	15	0.019(6)
	20	0.024(7)
	25	0.033(5)
	30	0.036(6)
With 0.02	10	3.51(5)
	15	4.15(7)
	20	4.63(5)
	25	4.72(7)
	30	5.40(5)
With 0.20	10	35.48(6)
	15	40.10(5)
	20	45.90(7)
	25	47.00(5)
	30	53.88(6)

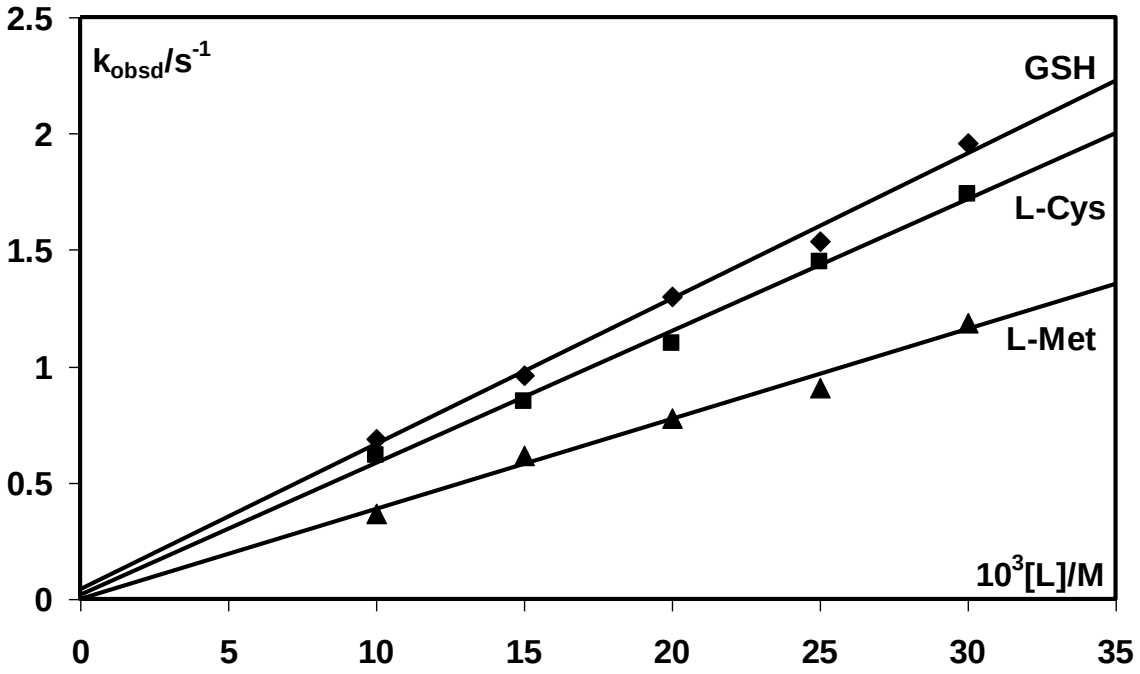


Fig. S1. *Pseudo*-first order rate constants plotted as a function of reducing agent (L) concentration for the reactions of the $[PtCl_4(dach)]$ complex at pH 2.0 (0.01 M $HClO_4$) in the presence of 0.2 M NaCl at 310 K.

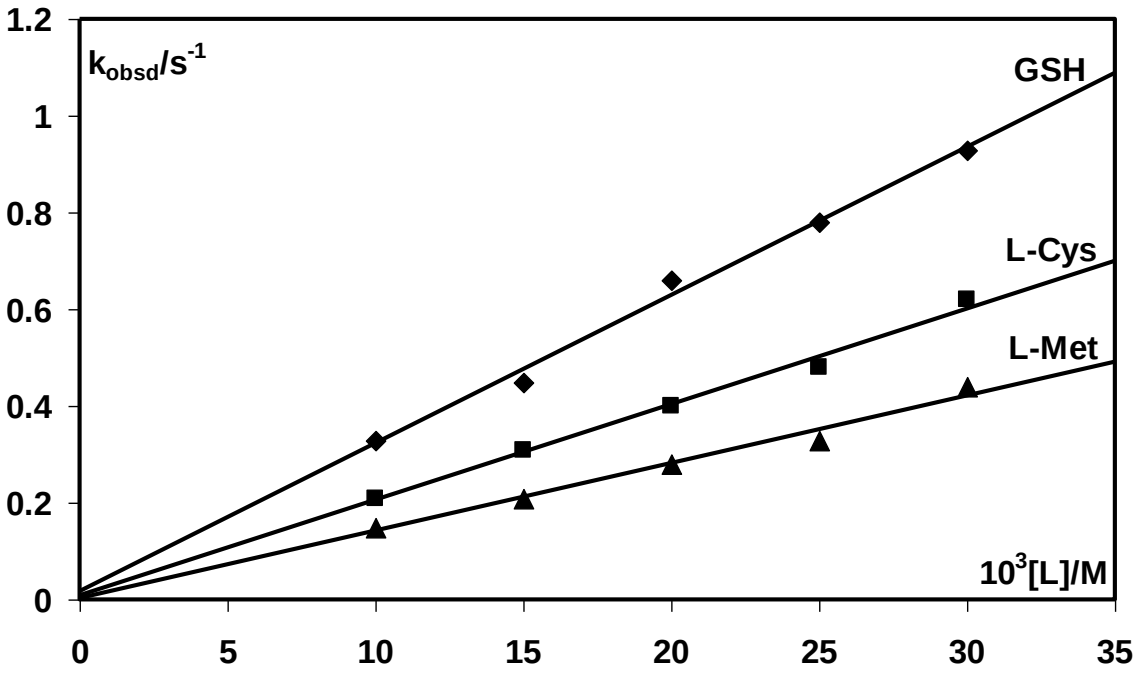


Fig. S2. *Pseudo*-first order rate constants plotted as a function of reducing agent (L) concentration for the reactions of the $[PtCl_4(en)]$ complex at pH 2.0 (0.01 M $HClO_4$) in the presence of 0.2 M NaCl at 310 K.

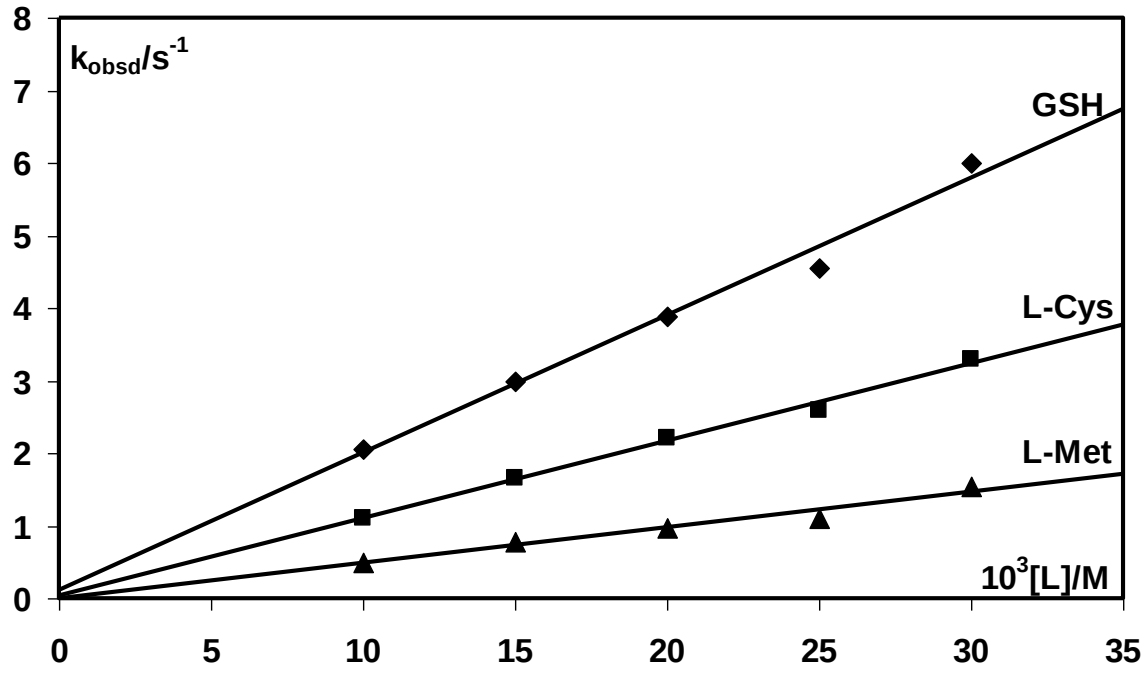


Fig. S3. *Pseudo*-first order rate constants plotted as a function of reducing agent (L) concentration for the reactions of the $[PtCl_4(bipy)]$ complex at 310 K and pH 2.0 (0.01 M $HClO_4$).

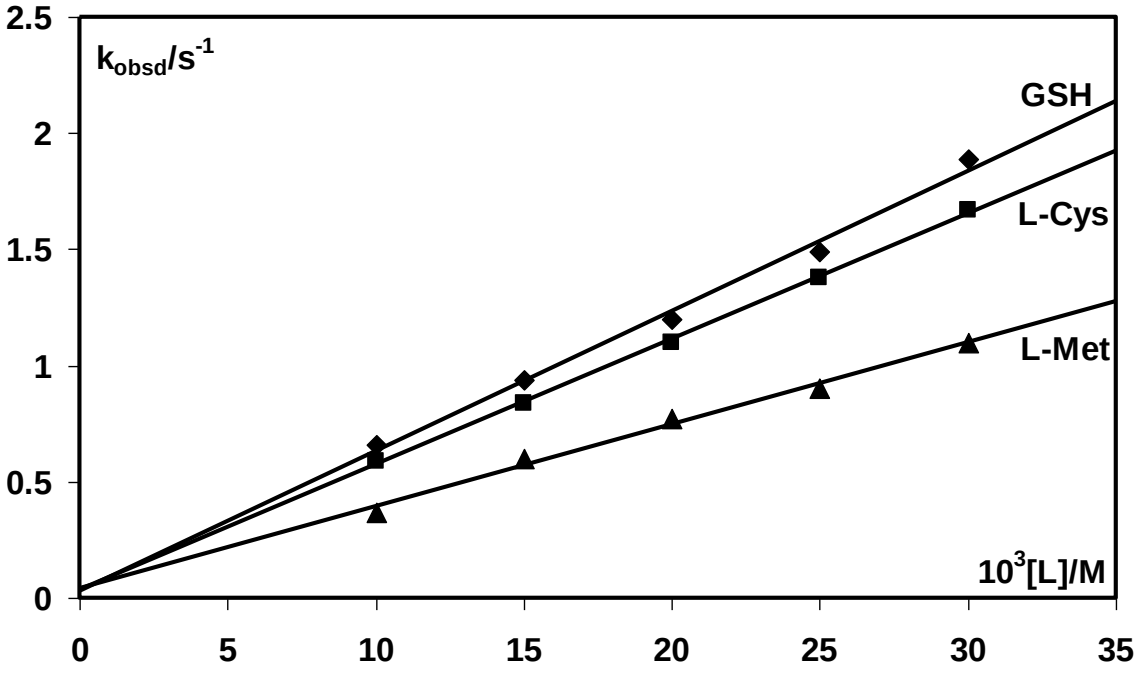


Fig. S4. *Pseudo*-first order rate constants plotted as a function of reducing agent (L) concentration for the reactions of the $[PtCl_4(dach)]$ complex at 310 K and pH 2.0 (0.01 M $HClO_4$).

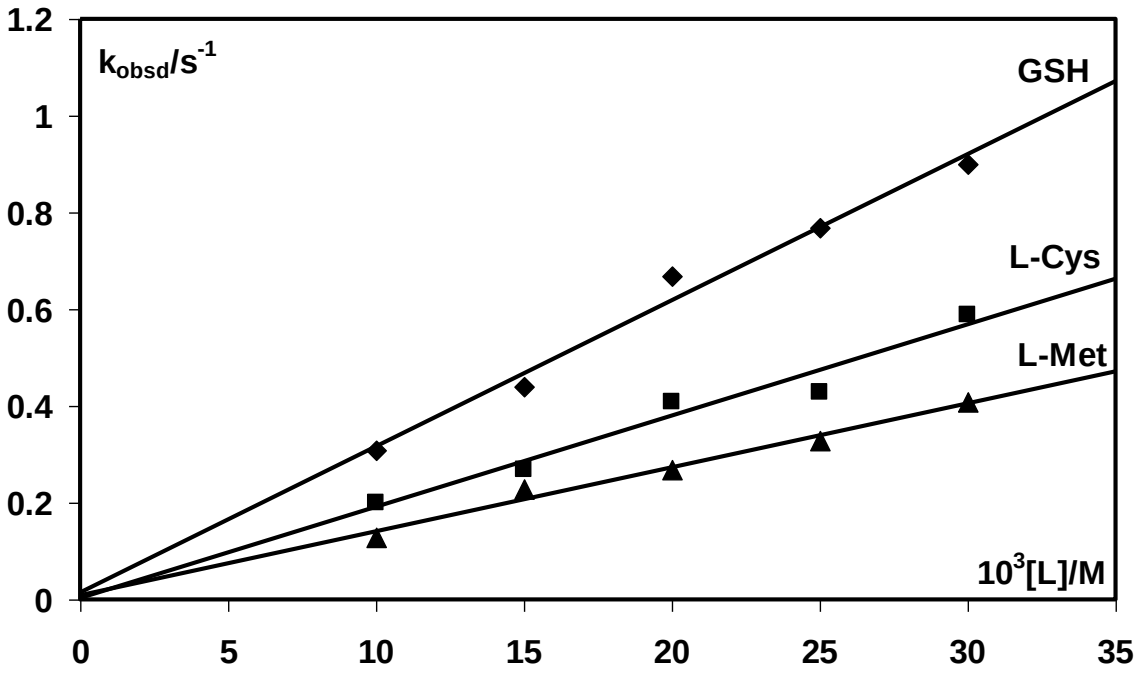


Fig. S5. *Pseudo*-first order rate constants plotted as a function of reducing agent (L) concentration for the reactions of the $[PtCl_4(en)]$ complex at 310 K and pH 2.0 (0.01 M $HClO_4$).

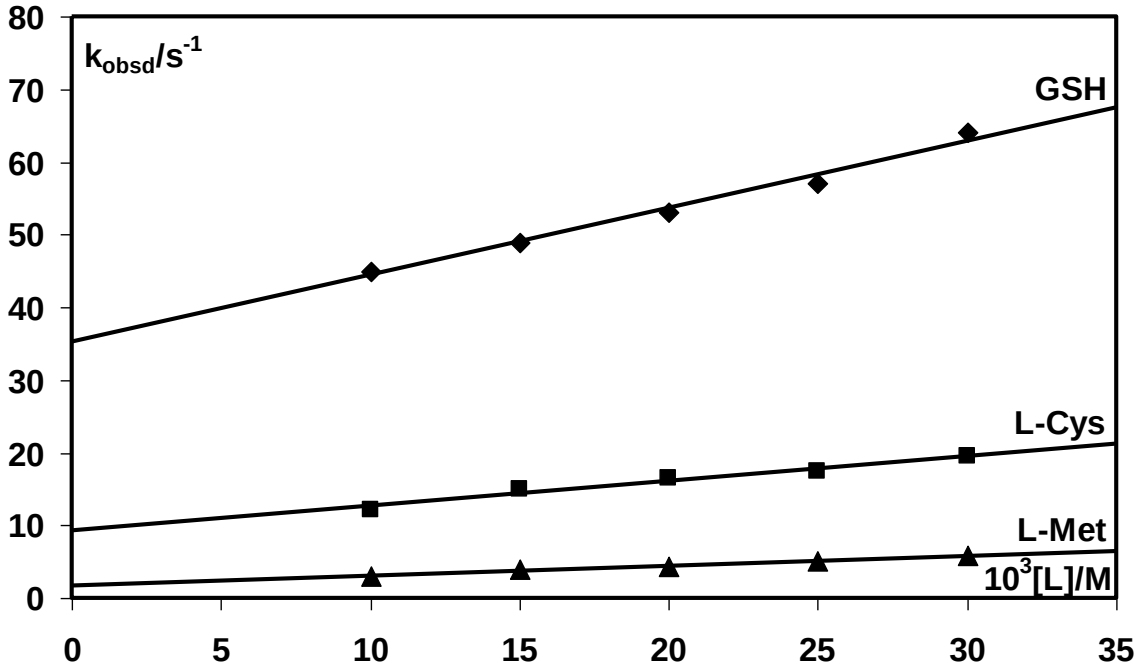


Fig. S6. *Pseudo*-first order rate constants plotted as a function reducing agent (L) concentration for the reactions of the $[PtCl_4(dach)]$ complex at pH 7.2 (25 mM Hepes buffer) in the presence of 0.2 M NaCl at 310 K.

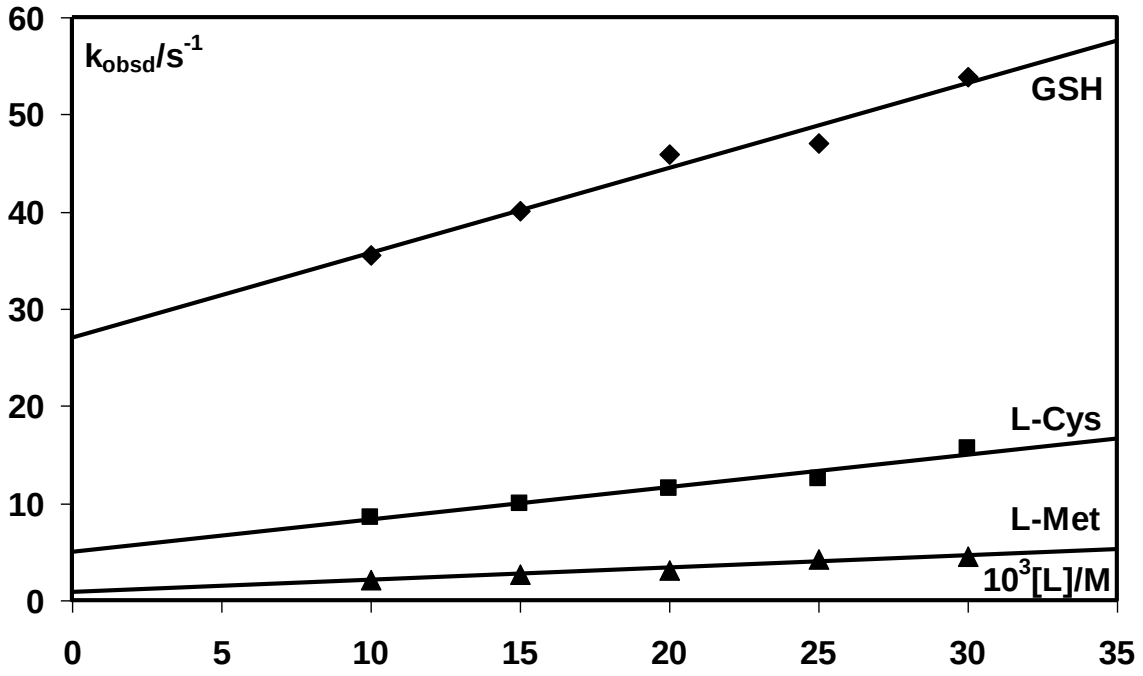


Fig. S7. *Pseudo*-first order rate constants plotted as a function of reducing agent (L) concentration for the reactions of the $[PtCl_4(en)]$ complex at pH 7.2 (25 mM Hepes buffer) in the presence of 0.2 M NaCl at 310 K.

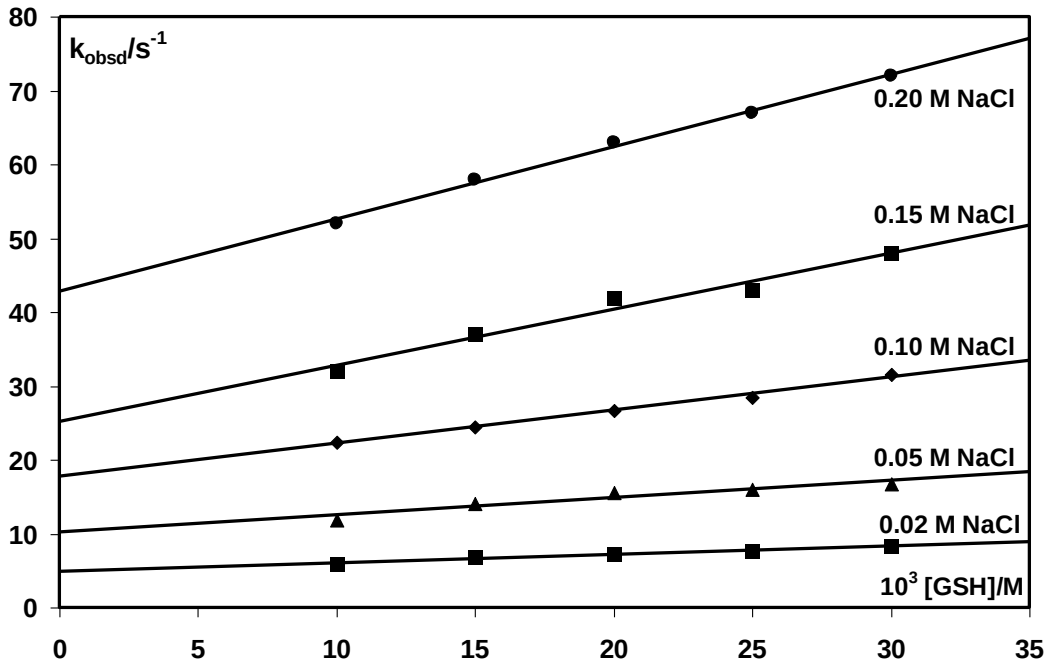


Fig. S8. *Pseudo*-first order rate constants plotted as a function of glutathione concentration for the reactions of the $[PtCl_4(bipy)]$ complex at pH 7.2 (25 mM Hepes buffer) in the presence of different chloride concentrations at 310 K.

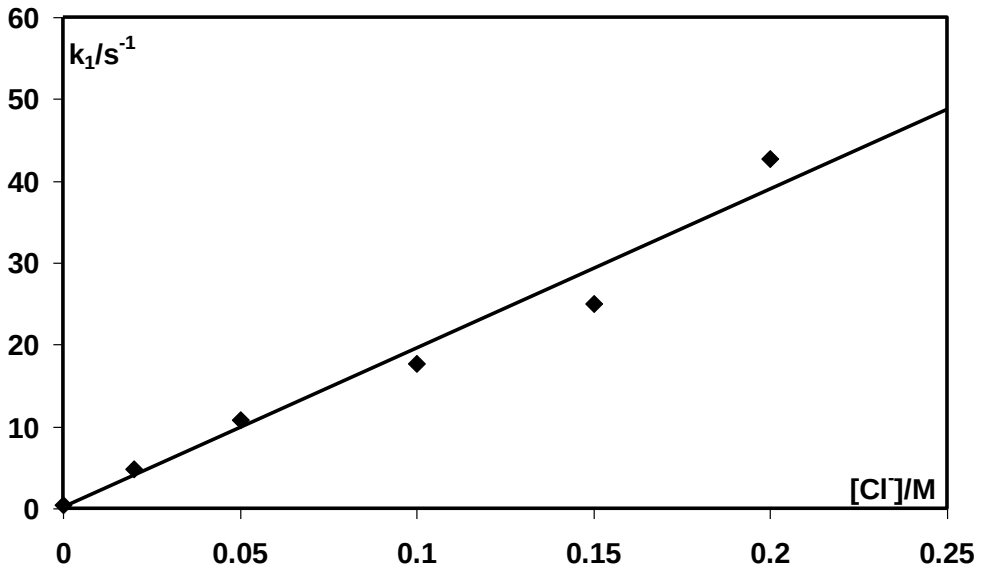


Fig. S9. The dependence of the rate constant k_1 as a function of chloride concentration for the reaction of the $[PtCl_4(bipy)]$ complex with glutathione at pH 7.2 and 310 K.

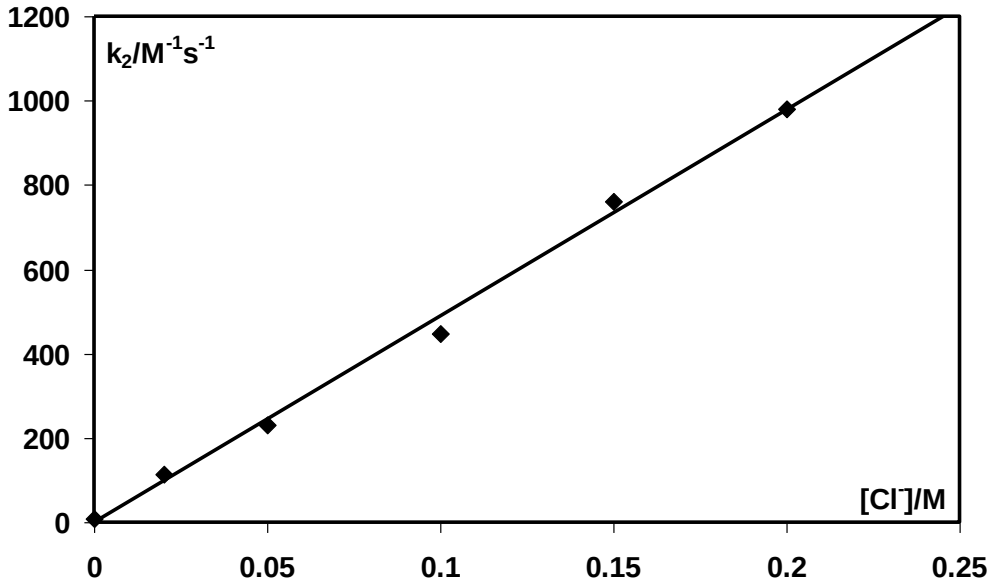


Fig. S10. The dependence of the rate constant k_2 as a function of chloride concentration for the reaction of the $[PtCl_4(bipy)]$ complex with glutathione at pH 7.2 and 310 K.

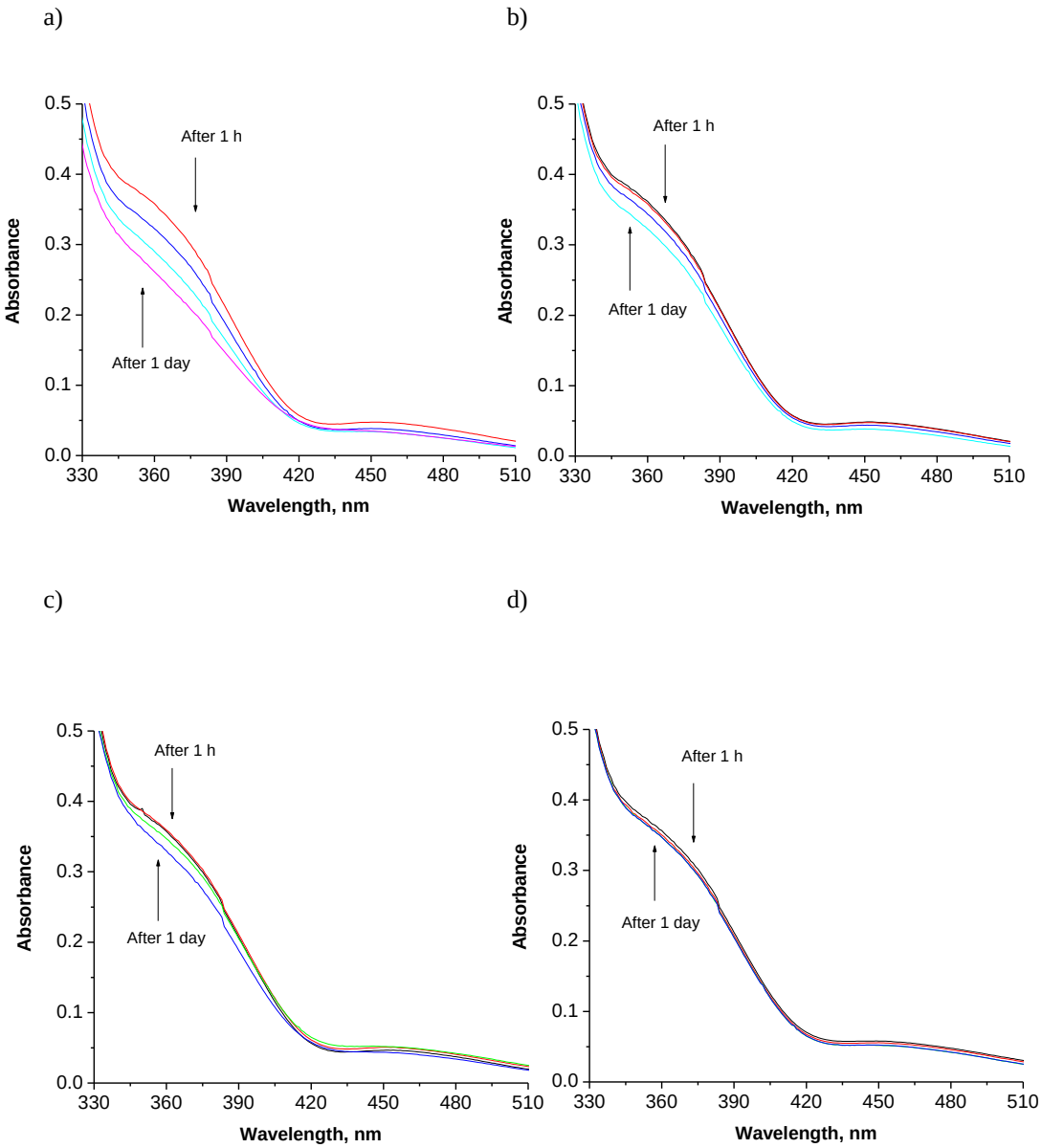


Fig. S11. The UV-Vis spectra of the complex of $[PtCl_4(en)]$ (1 x 10^{-3} M) at pH 7.2 (25 mM Hepes buffer) at 310 K and a) in the absence of NaCl after 1h, 3h, 4h, 1 day; b) in the presence of 0.05 M NaCl after 1h, 3h, 4h, 1 day; c) in the presence of 0.1 M NaCl after 1h, 3h, 4h, 1 day; d) in the presence of 0.2 M NaCl after 1h, 3h, 4h, 1 day.

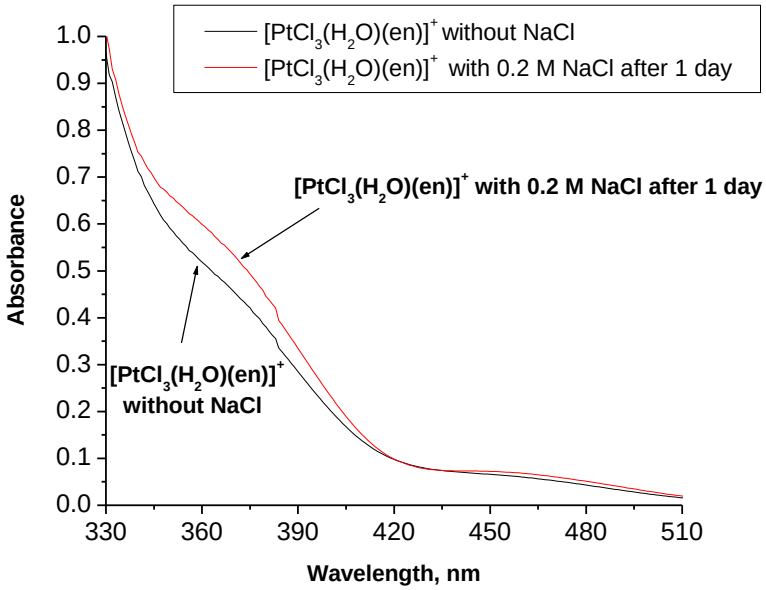


Fig. S12. The UV-Vis spectrum of the complex $[PtCl_3(H_2O)(en)]^+$ (2×10^{-3} M) at pH 3.0 and 310 K without NaCl is marked black and red is marked spectrum of the complex $[PtCl_3(H_2O)(en)]^+$ with 0.2 M NaCl recorded after 1 day.

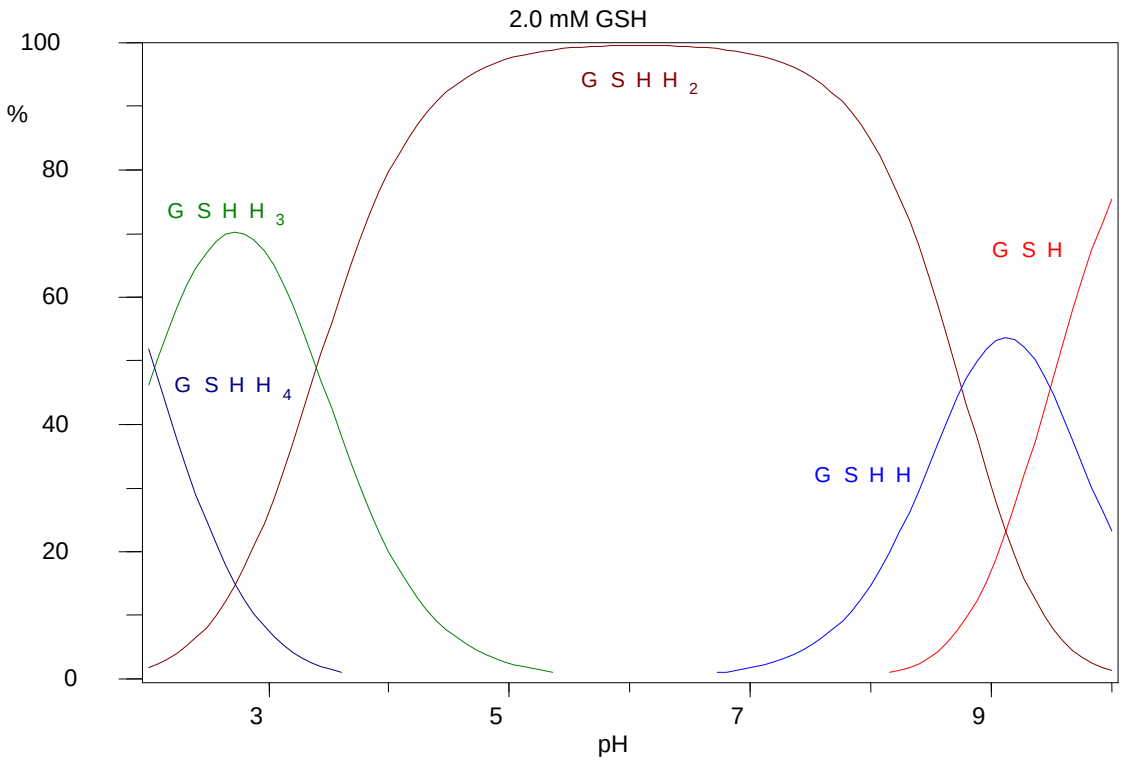


Fig. S13. Distribution diagram for glutathione as a function of pH.

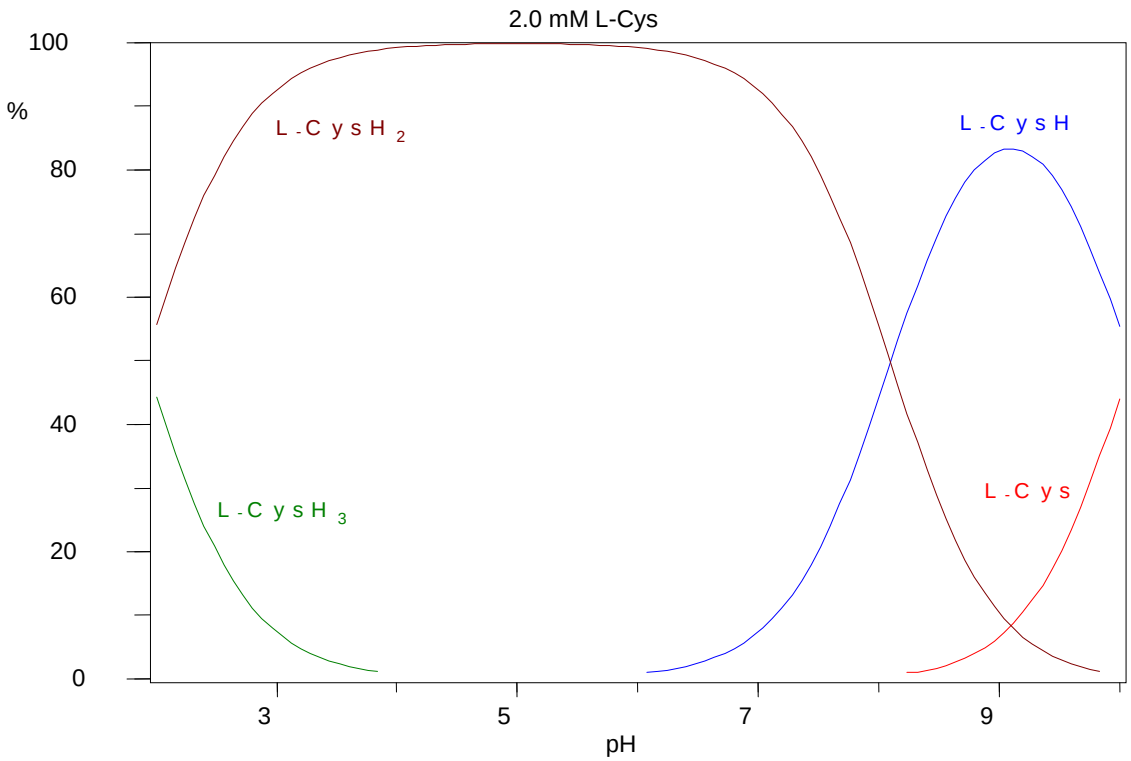


Fig. S14. Distribution diagram for L-cysteine as a function of pH.

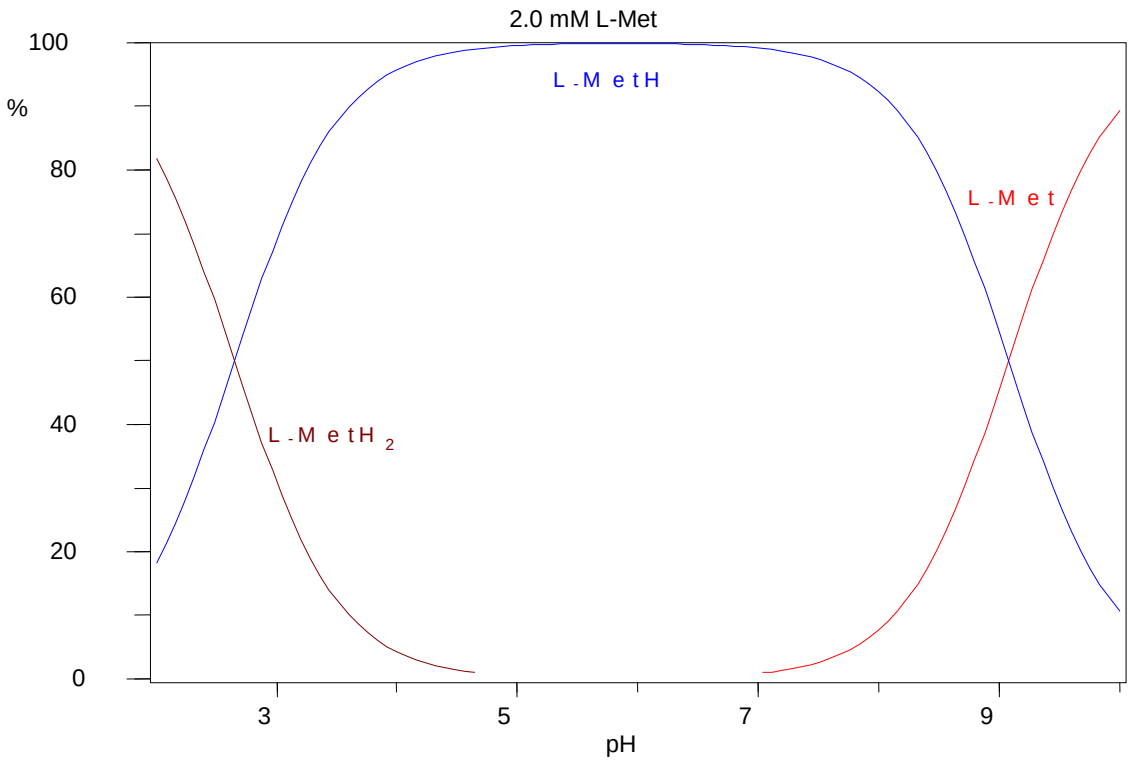
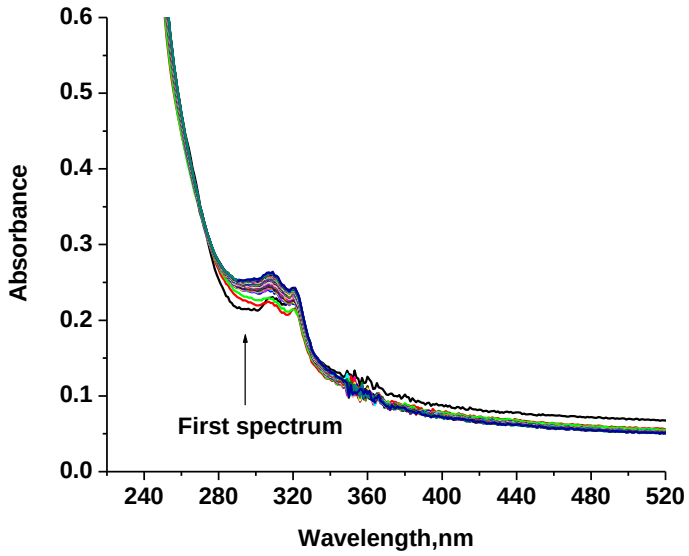


Fig. S15. Distribution diagram for L-methionine as a function of pH.

a)



b)

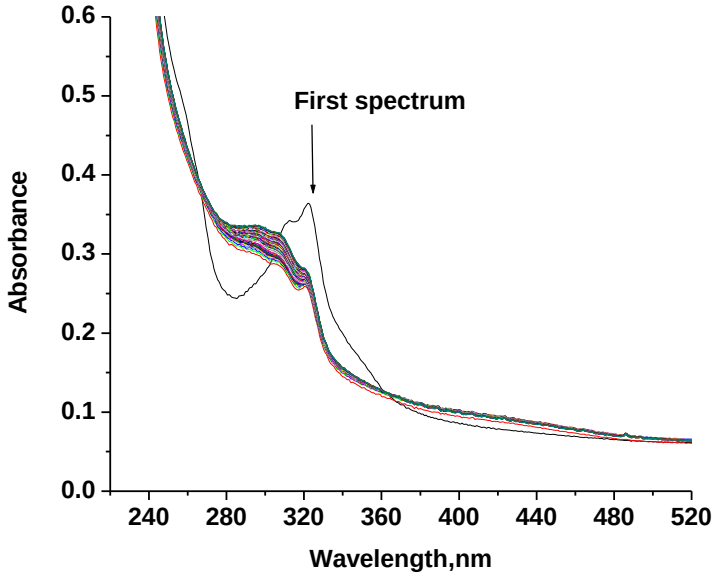


Fig. S16. UV-Vis spectra recorded for the reaction of $[PtCl_4(bipy)]$ (1 x 10^{-3} M) with a) 5 x 10^{-2} M GSH and b) 1 x 10^{-2} M GSH as a function of time at pH 7.2 (25 mM Hepes buffer) with addition of 0.2 M NaCl at 310 K.