Supporting Information

Substitution behaviour of novel dinuclear Pt(II) complexes with bio-relevant nucleophiles

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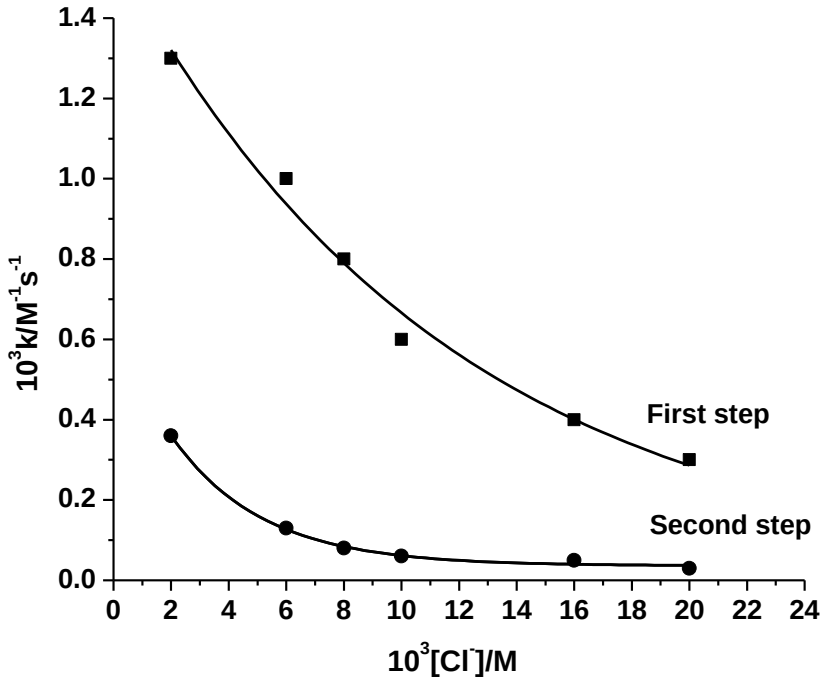

Figure S1. Effect of chloride concentration on the first and the second reaction steps of the dichloro **Pt3** complex (0.2 mM) with 5'- GMP (10 mM).

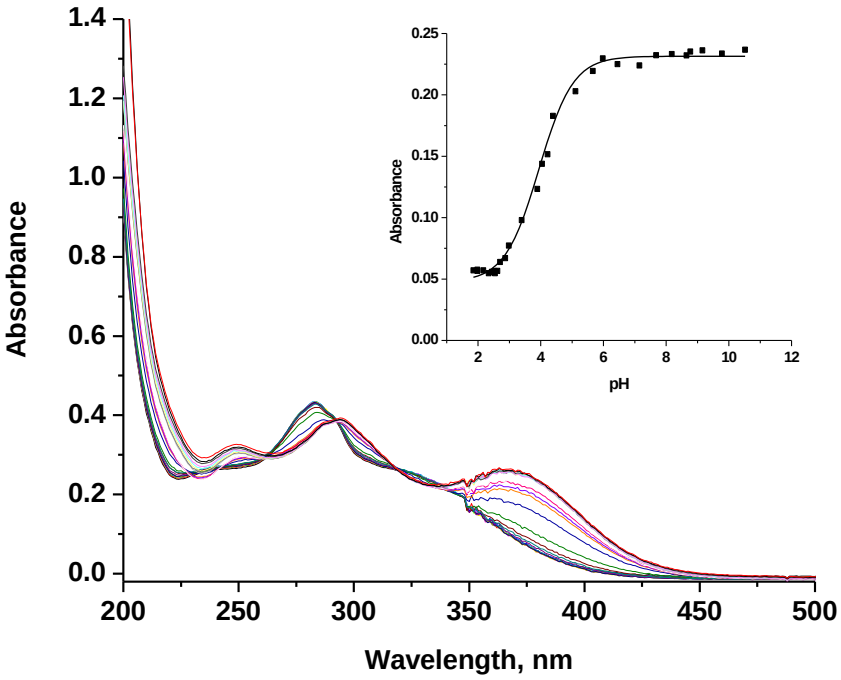

Figure S2. UV-Vis spectra of the diaqua **Pt1** complex recorded as a function of pH in the range 2 to 10 at I = 0.01 M ($NaClO_4$) and 25 ^{o}C. Inset: titration curve at 380 nm.

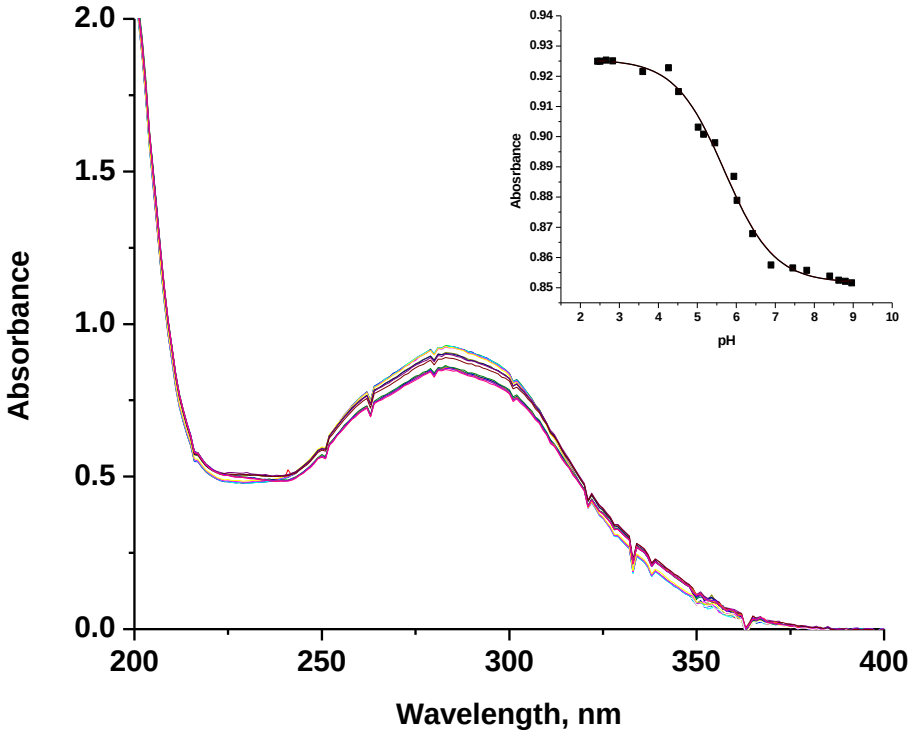

Figure S3. UV-Vis spectra of the diaqua **Pt2** complex recorded as a function of pH in the range 2 to 10 at I = 0.01 M ($NaClO_4$) and 25 ^{o}C. Inset: titration curve at 285 nm.

Table S1. Rate constants for the first and second reaction steps of the dichloro **Pt3** complex (0.2 mM) complex with 5'- GMP (10 mM) in the presence of different concentrations of NaCl in 25 mM Hepes buffer (pH = 7.2) at 37 ^{o}C.

[NaCl]/M	$10^3 k/M^{-1} s^{-1}$ (first step)	$10^4 k/M^{-1} s^{-1}$ (second step)
0.002	1.30 ± 0.10	3.60 ± 0.20
0.006	1.10 ± 0.10	1.30 ± 0.20
0.008	0.79 ± 0.20	0.80 ± 0.10
0.010	0.60 ± 0.10	0.60 ± 0.10
0.016	0.50 ± 0.10	0.50 ± 0.10
0.020	0.29 ± 0.10	0.34 ± 0.10

Table S2. Observed *pseudo-first*-order rate constants as a function of nucleophile concentration for the substitution reactions of the diaqua **Pt1** complex in 0.01 M $NaClO_4$ (pH = 2.5) at 37 ^{o}C.

LIGANDS	λ/nm	10^3C_L/M	$10^3k_{obsd1}/s^{-1}$	$10^4k_{obsd2}/s^{-1}$
Tu	330	1	870(3)[a]	-
		2	1630(3)	-
		3	2250(3)	-
		4	3168(3)	-
		5	4000(3)	-
GSH	260	1	358(4)	170(4)
		2	712(3)	340(4)
		3	1049(3)	559(4)
		4	1460(3)	710(3)
		5	1763(3)	860(3)
5'- GMP	330	1	202(4)	120(4)
		2	330(4)	240(4)
		3	500(3)	350(3)
		4	715(3)	440(3)
			873(3)	590(3)
		5	316(3)[b]	320(4)[b]
			1025(3)[c]	950(3)[c]

[a]Number of runs in parenthesis.
[b] Observed *pseudo-first* order rate constants at 25 ^{o}C.
[c] Observed *pseudo-first* order rate constants at 45 ^{o}C.

Table S3. Observed *pseudo-first*-order rate constants as a function of nucleophile concentration for the substitution reactions of the diaqua **Pt2** complex in 0.01 M $NaClO_4$ (pH = 2.5) at 37 ^{o}C.

LIGANDS	λ/nm	10^3C_L/M	$10^3k_{obsd1}/s^{-1}$	$10^4k_{obsd2}/s^{-1}$
Tu	300	1	6.00(4)[a]	-
		2	10.70(3)	-
		3	15.70(3)	-
		4	22.00(3)	-
		5	27.00(3)	-
GSH	240	1	3.30(4)	1.60(5)
		2	5.60(4)	2.80(5)
		3	9.80(3)	4.10(4)
		4	13.20(3)	5.30(4)
		5	15.00(3)	6.70(4)
5'- GMP	315	1	0.88(5)	1.02(5)
		2	2.20(5)	2.48(5)
		3	2.91(5)	3.30(4)
		4	3.80(4)	4.57(4)
			4.76(4)	5.10(4)
		5	1.17(4)[b]	1.69(4)[b]
			7.90(3)[c]	23.90(3)[c]

[a]Number of runs in parenthesis.
[b] Observed *pseudo-first* order rate constants at 25 ^{o}C.
[c] Observed *pseudo-first* order rate constants at 45 ^{o}C.

Table S4. Observed *pseudo-first*-order rate constants as a function of nucleophile concentration for the substitution reactions of the diaqua **Pt3** complex in 0.01 M $NaClO_4$ (pH = 2.5) at 37 ^{o}C.

LIGANDS	λ/nm	10^3C_L/M	$10^3k_{obsd1}/s^{-1}$	$10^4k_{obsd2}/s^{-1}$
Tu	325	1	2.60(4)[a]	-
		2	5.51(3)	-
		3	7.41(3)	-
		4	10.63(3)	-
		5	13.00(3)	-
GSH	250	1	1.10(5)	1.22(5)
		2	2.00(5)	1.92(5)
		3	3.12(4)	3.05(4)
		4	4.08(4)	3.51(4)
		5	5.00(4)	4.95(4)
5'- GMP	330	1	0.39(5)	0.69(5)
		2	0.65(5)	1.45(5)
		3	1.02(4)	1.95(4)
		4	1.32(4)	2.60(4)
			1.64(4)	3.31(4)
		5	0.53(4)[b]	1.51(4)[b]
			2.63(3)[c]	5.97(3)[c]

[a]Number of runs in parenthesis.
[b] Observed *pseudo-first* order rate constants at 25 ^{o}C.
[c] Observed *pseudo-first* order rate constants at 45 ^{o}C.

Table S5. Observed *pseudo-first*-order rate constants as a function of nucleophile concentration for the substitution reactions of the dichloro **Pt1** complex in 25 mM Hepes buffer (pH = 7.2) in the presence of 20 mM NaCl at 37 ^{o}C.

LIGANDS	λ/nm	10^3C_L/M	$10^3k_{obsd1}/s^{-1}$	$10^4k_{obsd2}/s^{-1}$
Tu	300	1	1.80(5)[a]	-
		2	3.60(4)	-
		3	4.80(3)	-
		4	6.80(3)	-
		5	8.00(3)	-
GSH	250	1	1.10(5)	1.80(4)
		2	2.00(5)	3.80(3)
		3	3.30(4)	5.20(3)
		4	4.10(3)	6.80(3)
		5	5.00(3)	8.70(3)
5'- GMP	315	1	0.13(5)	0.30(5)
		2	0.20(5)	0.43(5)
		3	0.32(5)	0.56(4)
		4	0.41(4)	0.74(4)
			0.46(4)	0.83(4)
		5	0.21(4)[b]	0.77(4)[b]
			1.22(4)[c]	4.20(3)[c]

[a]Number of runs in parenthesis.
[b] Observed *pseudo-first* order rate constants at 25 ^{o}C.
[c] Observed *pseudo-first* order rate constants at 45 ^{o}C.

Table S6. Observed *pseudo-first*-order rate constants as a function of nucleophile concentration for the substitution reactions of the dichloro **Pt2** complex in 25 mM Hepes buffer (pH = 7.2) in the presence of 20 mM NaCl at 37 ^{o}C.

LIGANDS	λ/nm	10^3C_L/M	$10^3k_{obsd1}/s^{-1}$	$10^4k_{obsd2}/s^{-1}$
Tu	300	1	1.50(4)[a]	-
		2	2.50(4)	-
		3	3.80(3)	-
		4	5.50(3)	-
		5	6.50(3)	-
GSH	245	1	0.78(4)	1.20(4)
		2	1.67(4)	2.16(4)
		3	2.39(3)	2.80(4)
		4	3.30(3)	3.30(3)
		5	3.90(3)	4.50(3)
5'- GMP	315	1	0.10(5)	0.20(5)
		2	0.14(5)	0.29(5)
		3	0.20(4)	0.47(4)
		4	0.27(4)	0.50(4)
			0.34(4)	0.70(4)
		5	0.16(4)[b]	0.58(4)[b]
			0.87(4)[c]	3.10(3)[c]

[a]Number of runs in parenthesis.
[b] Observed *pseudo-first* order rate constants at 25 ^{o}C.
[c] Observed *pseudo-first* order rate constants at 45 ^{o}C.

Table S7. Observed *pseudo-first* order rate constants as a function of nucleophile concentration for the substitution reactions of the dichloro **Pt3** complex in 25 mM Hepes buffer (pH = 7.2) in the presence of 20 mM NaCl at 37 ^{o}C.

LIGANDS	λ/nm	10^3C_L/M	$10^3k_{obsd1}/s^{-1}$	$10^4k_{obsd2}/s^{-1}$
Tu	310	1	1.10(4)[a]	-
		2	1.90(4)	-
		3	2.70(3)	-
		4	3.70(3)	-
		5	4.20(3)	-
GSH	260	1	0.74(5)	0.46(5)
		2	1.02(4)	0.85(5)
		3	1.43(4)	1.07(4)
		4	1.72(3)	1.42(3)
		5	2.20(4)	1.80(3)
5'- GMP	315	1	0.09(5)	0.08(5)
		2	0.13(5)	0.15(5)
		3	0.19(4)	0.23(4)
		4	0.22(4)	0.26(4)
			0.29(3)	0.34(4)
		5	0.08(4)[b]	0.28(4)[b]
			0.70(3)[c]	2.38(3)[c]

[a]Number of runs in parenthesis.
[b] Observed *pseudo-first* order rate constants at 25 ^{o}C.
[c] Observed *pseudo-first* order rate constants at 45 ^{o}C.

Table S8. ^{1}H NMR data for the calculation of the second-order rate constant for the reaction of the dichloro **Pt2** complex (10 mM) with 2 equivalents of 5'-GMP at pD = 6.7 and 22 °C. I_{free} is area of the signal for free 5'-GMP; $I_{coord.1^{st}\ react.}$ is area of the signal for the first coordinated 5'-GMP.

I_{free}	$I_{coord.1st\ react.}$	t(s)	$(0.01 * I_{coord.1^{st}\ react.}) / (I_{free}+I_{coord.1^{st}\ react.})$	$(1/(a_0-b_0))*\ln[(b_0*(a_0-x))/(a_0*(b_0-x))]$
1.048	-	1610	-	-
0.877	-	3790	-	-
0.969	-	5970	-	-
0.918	-	8150	-	-
0.903	0.296	10330	0.00247	79.43875
0.904	0.346	12510	0.00277	96.49408
0.915	0.382	14690	0.00295	108.0805
0.879	0.402	16870	0.00314	122.2537
0.897	0.438	19050	0.00328	134.0011
0.887	0.461	21230	0.00342	146.6811
0.888	0.501	23410	0.00361	166.1094
0.885	0.515	25590	0.00368	174.4169
0.943	0.590	27770	0.00385	195.5196
0.945	0.609	29950	0.00392	206.8148
0.916	0.635	32130	0.00409	236.3323
0.885	0.619	34310	0.00412	240.4183
0.902	0.698	36490	0.00436	-
0.830	0.649	39570	0.00439	-
0.873	0.727	42650	0.00454	-
0.924	0.768	47530	0.00455	-
0.886	0.771	52410	0.00465	-