

Supplementary Material

Synthesis and Structures of Pincer-Type Rhodium(III) complex; Reactivity Toward Biomolecules

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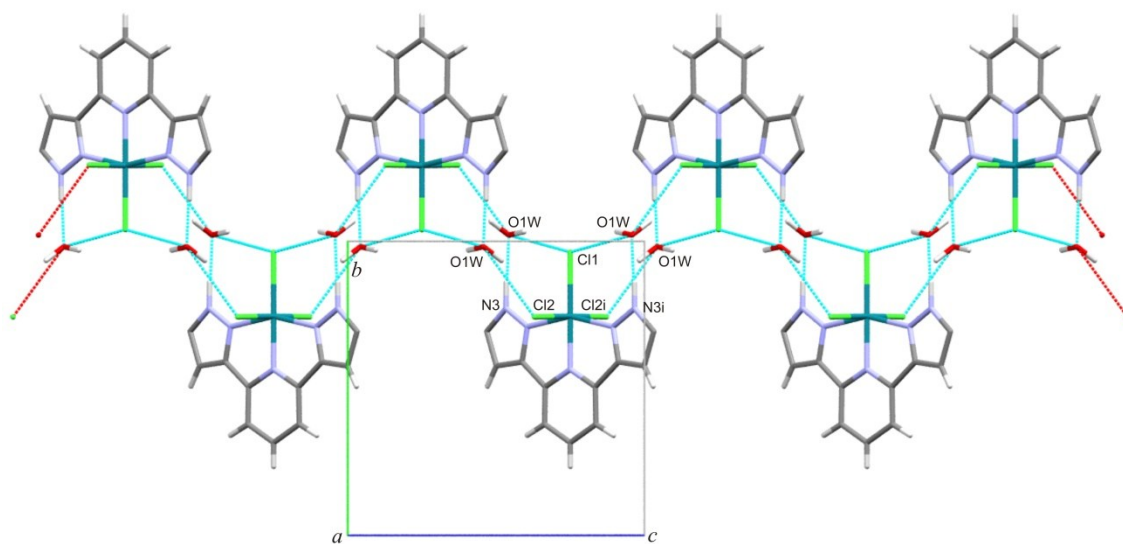


Figure S1. MERCURY¹¹ drawing showing the crystal packing of [Rh(LH₂^tBu)Cl₃] complex along the *a* axis. Hydrogen bonds are shown as light blue dashed lines.

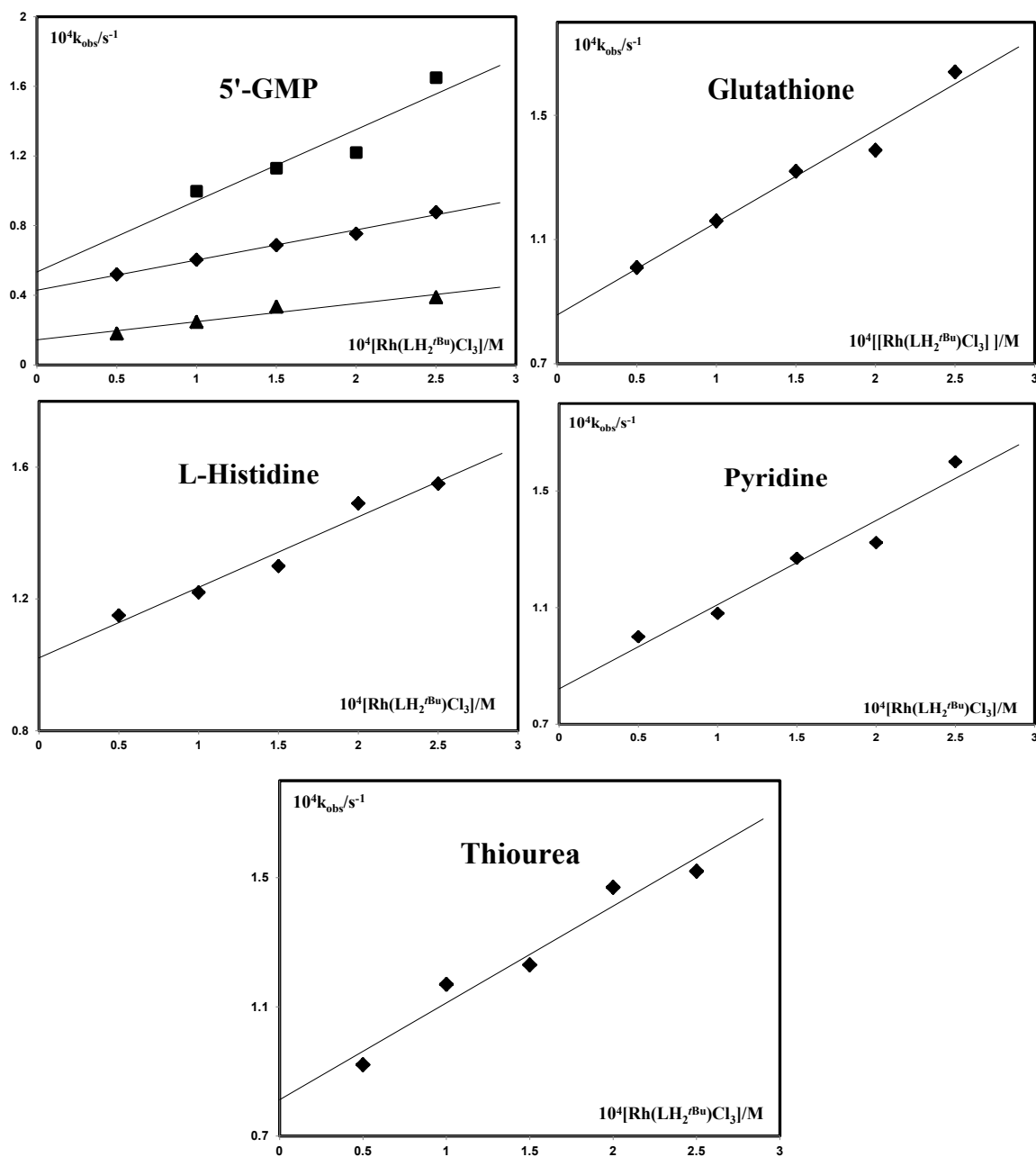


Figure S2. Pseudo-first order rate constants, k_{obs} , as a function of complex concentration and temperature for the substitution reactions between complex (1) and 5'-GMP (310, 298 and 288 K), GSH, Py and L-His at pH = 7.2 (25 mM HEPES buffer) in the presence of 50 mM NaCl at 310, 298 and 288 K.

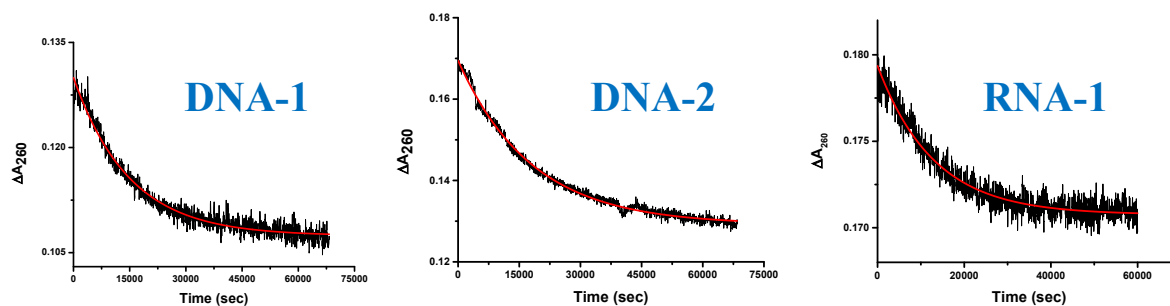


Figure S3. Absorbance change as a function of time after the addition of Rh^{III} complex to DNA-1, DNA-2 and RNA-1. All measurements were conducted with $(\mathbf{1}) = 50.0 \mu\text{M}$, $C_{\text{T}} = 3.0 \mu\text{M}$ and $T = 37 \text{ }^{\circ}\text{C}$ in PBS buffered solution; Phosphate buffer solution = 0.01 M, $C_{\text{NaCl}} = 0.137$, $C_{\text{KCl}} = 0.0027 \text{ M}$, pH 7.4). Fits of a single-exponential function to the experimental data are indicated with a solid line (red).

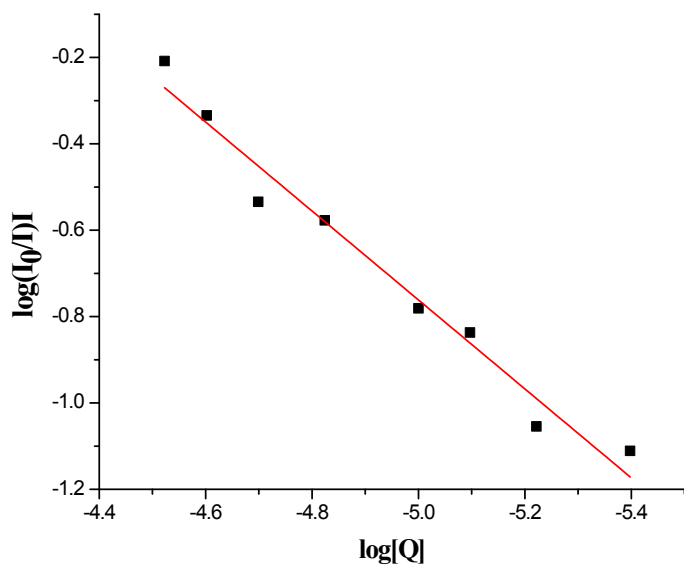


Figure S4. The linear plot shows $\log[(I_0/I)/I]$ vs. $\log[Q]$ for the interaction between (1) complex and CT-DNA; $Q = (1)$

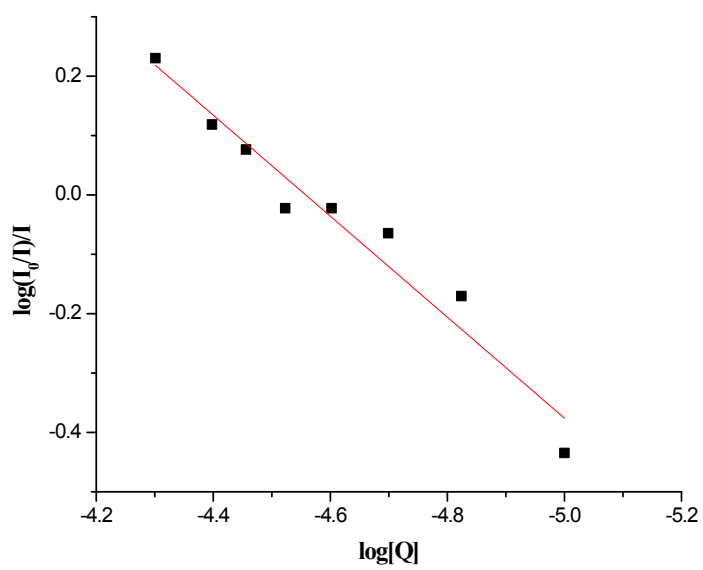


Figure S5. The linear plot shows $\log[(I_o/I)/I]$ vs. $\log[Q]$ for the interaction between (**1**) complex and BSA; $Q = (\mathbf{1})$.

Table S1. Hydrogen bond parameters for $[\text{Rh}^{\text{III}}(\text{H}_2\text{L}^{\text{tBu}})\text{Cl}_3]$ complex (\AA , $^\circ$)

<i>D-H...A</i>	<i>D-H</i>	<i>H...A</i>	<i>D...A</i>	<i>D-H...A</i>
O1W-H1W...Cl1 ¹	0.89(4)	2.35(4)	3.153(4)	151(4)
O1W-H2W...Cl2 ²	0.88(4)	2.43(4)	3.215(3)	149(4)
N3-H3...O1W ³	0.95(3)	1.76(3)	2.712(4)	177(3)

Symmetry codes: **1**: -x,1-y,-z; **2**: -x,y,1/2-z; **3**: x,1-y,-1/2+z

Table S2. Observed *pseudo*-first order rate constants as a function of complex concentration and temperature for the reaction between complex (**1**) and L-Met at pH = 7.2 (25 mM Hepes buffer) in the presence of 50 mM NaCl at 310, 298 and 288 K.

T(K)	$10^4 C_{(1)}/M$	$10^4 k_{\text{obsd}}/s^{-1}$
288.0	2.5	0.54(3) ^a
	2.0	0.51(3)
	1.5	0.40(3)
	1.0	0.32(3)
	0.5	0.22(3)
298.0	2.5	0.82(2)
	2.0	0.70(3)
	1.5	0.60(3)
	1.0	0.51(3)
	0.5	0.48(3)
310.0	2.5	1.10(4)
	2.0	0.98(3)
	1.5	0.84(3)
	1.0	0.73(3)
	0.5	0.64(4)

^aNumber of runs in parenthesis

Table S3. Observed *pseudo*-first order rate constants as a function of complex concentration and temperature for the reaction between complex (**1**) and 5'-GMP at pH = 7.2 (25 mM Hepes buffer) in the presence of 50 mM NaCl at 310, 298 and 288 K.

T(K)	$10^4 C_{(1)}/M$	$10^4 k_{\text{obsd}}/s^{-1}$
288.0	2.5	0.39(3)
	2.0	/
	1.5	0.33(3)
	1.0	0.25(3)
	0.5	0.18(3)
298.0	2.5	0.88(2)
	2.0	0.75(3)
	1.5	0.69(3)
	1.0	0.60(3)
	0.5	0.52(3)
310.0	2.5	1.65(4)
	2.0	1.22(3)
	1.5	1.13(3)
	1.0	1.00(3)
	0.5	/

Table S4. Observed *pseudo*-first order rate constants as a function of complex concentration and temperature for the reaction between complex (1) and GSH at pH = 7.2 (25 mM Hepes buffer) in the presence of 50 mM NaCl at 310, 298 and 288 K.

T(K)	$10^4 C_{(1)}/M$	$10^4 k_{\text{obsd}}/s^{-1}$
310.0	2.5	1.64(3)
	2.0	1.39(3)
	1.5	1.32(3)
	1.0	1.16(3)
	0.5	1.01(3)

Table S5. Observed *pseudo*-first order rate constants as a function of complex concentration and temperature for the reaction between complex (1) and L-His at pH = 7.2 (25 mM Hepes buffer) in the presence of 50 mM NaCl at 310, 298 and 288 K.

T(K)	$10^4 C_{(1)}/M$	$10^4 k_{\text{obsd}}/s^{-1}$
310.0	2.5	1.55(3)

2.0	1.49(3)
1.5	1.30(3)
1.0	1.22(3)
0.5	1.15(3)

Table S6. Observed *pseudo*-first order rate constants as a function of complex concentration for the reaction between (1) and DNA-1 in PBS buffer.

T(K)	$10^5 C_{(1)}/M$	$10^5 k_{\text{obsd}}/s^{-1}$
310.0	0.5	1.88(3) ^a
	1.5	3.24(3)
	3.0	5.81(3)
	5.0	6.73(3)

^aNumber of runs in parenthesis

Table S7. Observed *pseudo*-first order rate constants as a function of complex concentration for the reaction between (1) and DNA-2 in PBS buffer.

T(K)	$10^5 C_{(1)}/M$	$10^5 k_{\text{obsd}}/s^{-1}$
310	0.5	2.36(3)
	1.5	4.32(3)

3.0	5.42(3)
5.0	6.55(3)

Table S8. Observed *pseudo*-first order rate constants as a function of complex concentration for the reaction between (1) and DNA-3 in PBS buffer.

T(K)	$10^5 C_{(1)}/M$	$10^5 k_{\text{obsd}}/s^{-1}$
310	0.5	1.83(3)
	1.5	2.77(3)
	3.0	3.05(3)
	5.0	3.92(3)

Table S9. Observed *pseudo*-first order rate constants as a function of complex concentration for the reaction between (1) and RNA-1 in PBS buffer.

T(K)	$10^5 C_{(1)}/M$	$10^5 k_{\text{obsd}}/s^{-1}$
310	0.5	2.21(3)
	1.5	3.87(3)
	3.0	7.72(3)
	5.0	9.52(3)

