New Journal of Chemistry

Platinum(II) complexes with hybrid amine-imidazolin-2-imine ligands and their reactivity toward bio-molecules

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[(DACH(Im^{Pr}H))(AuCl_{2})]:

$^1$H NMR (300 MHz; CDCl$_3$): $\delta$ = 5.65 (bs, 2H, NH), 4.98 (sept, 4H, $J_{HH}$ 7.0 Hz, $CHMe_2$), 3.40 (bs, 2H, $CH_2CH(NH)CH(NH)CH_2$), 2.22 (s, 12H, $CCH_3$), 1.79 - 1.60 (m, 6H, $CH_2$), 1.60 (d, 12H, $J_{HH}$ 7.0 Hz, $CH(CH_3)_2$), 1.52 (d, 12H, $J_{HH}$ 7.0 Hz, $CH(CH_3)_2$), 1.23 - 1.18 (m, 2H, $CH_2$) ppm.

$^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ = 147.5 ($N_2CNH$), 124.3 ($CMe$), 63.4 ($CH_2CH(NH)CH(NH)CH_2$), 50.4 ($CHMe_2$), 35.6 ($CH_2$), 25.5 ($CH_2$), 22.6 ($CH(CH_3)_2$), 20.8 ($CH(CH_3)_2$), 11.7 ($CCH_3$) ppm.
Figure S1. Mass spectrum of the [Pt(DPENIm^{Pr})Cl_2] complex.
Figure S2. UV-vis spectra recorded for 0.1 mM \([\text{Pt(DPENIm}^{\text{Pr}})(\text{H}_2\text{O})_2]^{2+}\) in the pH range 2 to 12 at 25 °C. Insert: Plot of absorbance vs pH at 262 nm.
Figure S3. The effect of different concentrations of chloride ions on the change in absorbance in the solution of the complex [Pt(DPENIm^Pr)Cl2] in 25 mM Hepes buffer (pH ≈ 7.2) at 245 nm.
Figure S4. *Pseudo-*first-order rate constants plotted as a function of nucleophile concentration for the first and second step of the substitution reactions of the [Pt(DMEAIm)\textsuperscript{Pr}Cl\textsubscript{2}] complexes with TU, L-Met, L-His and 5’-GMP at pH = 7.2 and 310 K in 25 mM Hepes buffer and 30 mM NaCl.
Figure S5. *Pseudo*-first-order rate constants plotted as a function of nucleophile concentration for the first and second step of the substitution reactions of the [Pt(DPENIm\(^{\text{Pr}}\))Cl\(_2\)] complexes with TU, L-Met, L-His and 5'-GMP at pH = 7.2 and 310 K in 25 mM Hepes buffer and 30 mM NaCl.
Figure S6. Pseudo-first-order rate constants plotted as a function of complex concentration for the first and second step of the substitution reactions of the [Pt(DMEAlm^Pr)Cl_2] and [Pd(DPENlm^Pr)Cl_2] complexes with L-Met at pH = 7.2 and 310 K in 25 mM Hepes buffer and 30 mM NaCl.
Table S1. Activation parameters for the first and the second reaction steps between investigated Pt(II) complexes and TU at pH = 7.2, 25 mM Hepes buffer and 30 mM NaCl.

<table>
<thead>
<tr>
<th></th>
<th>first step</th>
<th>second step</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta H_1^{\neq}$</td>
<td>$\Delta S_1^{\neq}$</td>
</tr>
<tr>
<td>[Pt(DMEAIm$i^\text{Pr})\text{Cl}_2]$</td>
<td>47 ± 1</td>
<td>-115 ± 4</td>
</tr>
<tr>
<td>[Pt(DPENIm$i^\text{Pr})\text{Cl}_2]$</td>
<td>38 ± 6</td>
<td>-149 ± 18</td>
</tr>
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</table>
Table S2. Observed *pseudo*-first order rate constants as a function of nucleophile concentration and temperature for the first and second reaction step between complex [Pt(DMEAIm$^{Pr}$)Cl$_2$] and TU at pH = 7.2 (25 mM Hepes buffer) in the presence of 30 mM NaCl at 310, 298 and 288 K.

<table>
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<tr>
<th>T(K)</th>
<th>$C_{\text{TU}}$/M</th>
<th>first step $k_{\text{obsd1}/s^{-1}}$</th>
<th>second step $k_{\text{obsd2}/s^{-1}}$</th>
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<tbody>
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<td>/</td>
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<td>310.0</td>
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<td>0.00009(4)</td>
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Table S3. Observed pseudo-first order rate constants as a function of nucleophile concentration and temperature for the reaction between complex [Pt(DMEAImPr)Cl₂] and L-Met at pH = 7.2 (25 mM Hepes buffer) in the presence of 30 mM NaCl at 310 K.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>C_{L-Met}/M</th>
<th>first step k_{obsd1}/s⁻¹</th>
<th>second step k_{obsd2}/s⁻¹</th>
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Table S4. Observed pseudo-first order rate constants as a function of nucleophile concentration and temperature for the reaction between complex [Pt(DMEAImPr)Cl₂] and L-His at pH = 7.2 (25 mM Hepes buffer) in the presence of 30 mM NaCl at 310 K.

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<th>T(K)</th>
<th>C_{L-His}/M</th>
<th>first step 10⁵ k_{obsd1}/s⁻¹</th>
<th>second step 10⁶ k_{obsd2}/s⁻¹</th>
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<td>1.18(3)</td>
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**Table S5.** Observed pseudo-first order rate constants as a function of nucleophile concentration and temperature for the reaction between complex [Pt(DMEAImPr)Cl₂] and 5’-GMP at pH = 7.2 (25 mM Hepes buffer) in the presence of 30 mM NaCl at 310 K.

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<th>T(K)</th>
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<th>first step $10^5 k_{obsd1}/s^{-1}$</th>
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Table S6. Observed *pseudo*-first order rate constants as a function of nucleophile concentration and temperature for the first and second reaction step between complex \([\text{Pt(DPENIm}^{\text{Pr}})\text{Cl}_2]\) and TU at pH = 7.2 (25 mM Hepes buffer) in the presence of 30 mM NaCl at 310, 298 and 288 K.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>C_{TU}/M</th>
<th>first step $k_{\text{obsd1}}$/s$^{-1}$</th>
<th>second step $k_{\text{obsd2}}$/s$^{-1}$</th>
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Table S7. Observed pseudo-first order rate constants as a function of nucleophile concentration and temperature for the reaction between complex [Pt(DPENIm\textsuperscript{Pr})Cl\textsubscript{2}] and L-Met at pH = 7.2 (25 mM Hepes buffer) in the presence of 30 mM NaCl at 310 K.

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<th>T(K)</th>
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<th>first step $k_{\text{obsd1}}$/s\textsuperscript{-1}</th>
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Table S8. Observed pseudo-first order rate constants as a function of nucleophile concentration and temperature for the reaction between complex [Pt(DPENIm\textsuperscript{Pr})Cl\textsubscript{2}] and L-His at pH = 7.2 (25 mM Hepes buffer) in the presence of 30 mM NaCl at 310 K.

<table>
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<tr>
<th>T(K)</th>
<th>C\textsubscript{L-His}/M</th>
<th>first step $10^5k_{\text{obsd1}}$/s\textsuperscript{-1}</th>
<th>second step $10^6k_{\text{obsd2}}$/s\textsuperscript{-1}</th>
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**Table S9.** Observed *pseudo*-first order rate constants as a function of nucleophile concentration and temperature for the reaction between complex [Pd(DPENImPr)Cl₂] and 5'-GMP at pH = 7.2 (25 mM Hepes buffer) in the presence of 30 mM NaCl at 310 K.

<table>
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<th>T(K)</th>
<th>C_Gly/M</th>
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Table S10. The rate constants for the back reactions of the first and the second reaction step of the substitution reactions of the Pt(II) complexes with TU, L-Met, L-His and 5’-GMP at pH = 7.2 (25 mM Hepes buffer) in the presence of 30 mM NaCl at 310 K.

<table>
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<tr>
<th></th>
<th>[Pt(DMEAIm\textsuperscript{Pr})Cl\textsubscript{2}]</th>
<th>[Pt(DPENIm\textsuperscript{Pr})Cl\textsubscript{2}]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>first step ( k_1 [\text{Cl}^-][\text{M}^{-1}\text{s}^{-1}] )</td>
<td>second step ( k_2 [\text{Cl}^-][\text{M}^{-1}\text{s}^{-1}] )</td>
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<td>((7.0 \pm 0.2) \times 10^{-5})</td>
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<tr>
<td>L-Met</td>
<td>((2.0 \pm 0.1) \times 10^{-4})</td>
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</tr>
<tr>
<td>L-His</td>
<td>((1.0 \pm 0.1) \times 10^{-5})</td>
<td>((1.1 \pm 0.1) \times 10^{-6})</td>
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<tr>
<td>5’-GMP</td>
<td>((3.7 \pm 0.2) \times 10^{-5})</td>
<td>((2.2 \pm 0.1) \times 10^{-6})</td>
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