

Supplementary Material

Kinetic and mechanistic study on the reactions of [Pd(dien)H₂O]²⁺ and [Pt(dien)H₂O]²⁺ with L-cysteine and S-methyl-L-cysteine.

Biljana V. Petrović and Živadin D. Bugarčić*

Table S1. Rate constants as a function of temperature for the reactions between $[\text{Pd}(\text{dien})\text{H}_2\text{O}]^{2+}$ and $[\text{Pt}(\text{dien})\text{H}_2\text{O}]^{2+}$ with L-cysteine and S-methyl L-cysteine in 0.1 M NaClO_4 at pH = 1.0.

| Complex | Ligand | T K | k_1 $\text{M}^{-1}\text{s}^{-1}$ | k_{-1} s^{-1} |
|---|----------------|--------|---------------------------------------|-------------------------------|
| $[\text{Pd}(\text{dien})\text{H}_2\text{O}]^{2+}$ | L-cysteine | 288.0 | $(5.08 \pm 0.08) \cdot 10^2$ | $(5.6 \pm 0.5) \cdot 10^{-1}$ |
| | | 293.0 | $(6.79 \pm 0.25) \cdot 10^2$ | $(6.7 \pm 2) \cdot 10^{-1}$ |
| | | 297.9 | $(9.11 \pm 0.1) \cdot 10^2$ | $(6.9 \pm 0.7) \cdot 10^{-1}$ |
| | | 303.0 | $(1.18 \pm 0.03) \cdot 10^3$ | $(8.9 \pm 2) \cdot 10^{-1}$ |
| | S-meth-L-cyst. | 293.0 | $(1.87 \pm 0.05) \cdot 10^3$ | $(0.9 \pm 0.3) \cdot 10^{-1}$ |
| | | 297.9 | $(2.60 \pm 0.1) \cdot 10^3$ | $(1.1 \pm 0.8) \cdot 10^{-1}$ |
| | | 302.9 | $(3.38 \pm 0.06) \cdot 10^3$ | $(1.2 \pm 0.3) \cdot 10^{-1}$ |
| | | 307.9 | $(4.54 \pm 0.1) \cdot 10^3$ | $(2.9 \pm 0.7) \cdot 10^{-1}$ |
| $[\text{Pt}(\text{dien})\text{H}_2\text{O}]^{2+}$ | L-cysteine | 288.2 | $(7.5 \pm 0.8) \cdot 10^{-3}$ | $(0.2 \pm 0.1) \cdot 10^{-4}$ |
| | | 298.1 | $(1.28 \pm 0.08) \cdot 10^{-2}$ | $(0.3 \pm 0.1) \cdot 10^{-4}$ |
| | | 307.4 | $(2.28 \pm 0.01) \cdot 10^{-2}$ | $(1.1 \pm 0.2) \cdot 10^{-4}$ |
| | S-meth-L-cyst. | 288.0 | $(2.2 \pm 0.1) \cdot 10^{-2}$ | $(0.4 \pm 0.1) \cdot 10^{-4}$ |
| | | 298.1 | $(3.87 \pm 0.02) \cdot 10^{-2}$ | $(0.6 \pm 0.1) \cdot 10^{-4}$ |
| | | 307.9 | $(6.81 \pm 0.06) \cdot 10^{-2}$ | $(6.0 \pm 2) \cdot 10^{-4}$ |

Table S2. Observed *pseudo*-first order rate constants as a function of ligand concentration at different temperature for the reactions between $[\text{Pd}(\text{dien})\text{H}_2\text{O}]^{2+}$ with L-cysteine and S-methyl L-cysteine at pH = 1.0, in 0.1 M NaClO_4 .

| L-cysteine | | | S-methyl-L-cysteine | | |
|------------|------------------------|---|---------------------|------------------------|---|
| T(K) | $10^{-3} C_L/\text{M}$ | $10^{-4} k_{\text{obsd}}/\text{s}^{-1}$ | T(K) | $10^{-3} C_L/\text{M}$ | $10^{-4} k_{\text{obsd}}/\text{s}^{-1}$ |
| 288.0 | 3.46 | 2.306(4)* | 288.0 | 2.29 | 4.52(5) |
| | 5.78 | 3.54(4) | | 4.77 | 8.779(4) |
| | 8.01 | 4.605(5) | | 6.68 | 12.835(6) |
| | 10.12 | 5.714(6) | | 9.54 | 17.551(6) |
| | | 11.78 | | 22.41(5) | |
| 293.1 | 3.46 | 2.995(5) | 292.9 | 2.29 | 6.08(5) |
| | 5.78 | 4.749(6) | | 4.77 | 12.21(5) |
| | 8.01 | 6.045(6) | | 6.68 | 17.46(6) |
| | 10.12 | 7.548(4) | | 9.54 | 26.02(4) |
| | | 11.78 | | 30.08(5) | |
| 297.9 | 1.47 | 2.011(5) | 297.9 | 2.29 | 7.65(5) |
| | 2.25 | 2.656(5) | | 3.52 | 12.2(6) |
| | 2.82 | 3.406(4) | | 4.77 | 16.02(5) |
| | 4.22 | 4.451(6) | | 6.68 | 23.14(5) |
| | 5.63 | 5.812(6) | | 9.54 | 32.11(4) |
| | 7.62 | 7.542(5) | | | |
| | 8.44 | 8.46(4) | | | |
| | 10.20 | 10.157(5) | | | |
| | 14.08 | 13.41(4) | | | |
| 303.0 | 3.46 | 4.869(5) | 302.9 | 2.29 | 11.0(6) |
| | 5.78 | 7.842(4) | | 4.77 | 21.25(4) |
| | 8.01 | 10.398(5) | | 6.68 | 31.0(4) |
| | 10.12 | 12.722(6) | | 9.54 | 43.61(5) |

*Number of runs with parenthesis.

Table S3. Observed *pseudo*-first order rate constants as a function of ligand concentration at different temperature for the reactions between $[\text{Pt}(\text{dien})\text{H}_2\text{O}]^{2+}$ with L-cysteine and S-methyl L-cysteine at pH = 1.0, in 0.1 M NaClO_4 .

| L-cysteine | | | S-methyl-L-cysteine | | |
|------------|------------------------|---|---------------------|------------------------|---|
| T(K) | $10^{-3} C_L/\text{M}$ | $10^{-4} k_{\text{obsd}}/\text{s}^{-1}$ | T(K) | $10^{-3} C_L/\text{M}$ | $10^{-4} k_{\text{obsd}}/\text{s}^{-1}$ |
| 288.2 | 5.28 | 0.48(5) | 288.0 | 4.17 | 1.0(5) |
| | 10.55 | 1.1(6) | | 10.0 | 2.7(6) |
| | 21.10 | 1.7(6) | | 20.0 | 4.1(6) |
| | 25.64 | 2.1(5) | | 25.4 | 6.1(5) |
| 298.1 | 2.67 | 0.6(5) | 298.1 | 2.67 | 1.8(5) |
| | 4.27 | 0.8(5) | | 5.17 | 2.8(4) |
| | 5.13 | 0.9(4) | | 10.34 | 4.2(4) |
| | 7.69 | 1.4(5) | | 16.03 | 6.9(5) |
| | 10.25 | 1.8(6) | | 20.29 | 7.9(6) |
| | 15.83 | 2.3(5) | | 25.63 | 11.0(5) |
| | 20.51 | 2.9(6) | | | |
| 307.8 | 2.67 | 0.5(5) | 307.9 | 2.67 | 7.0(4) |
| | 5.13 | 2.4(4) | | 5.34 | 10.0(4) |
| | 7.69 | 2.8(4) | | 10.68 | 13.0(5) |
| | 10.25 | 3.3(5) | | 16.02 | 17.0(4) |
| | 15.83 | 4.8(5) | | 21.36 | 20.0(5) |

Table S4. Observed *pseudo*-first order rate constants as a function of ligand concentration at different pH value for the reactions between $[\text{Pd}(\text{dien})\text{H}_2\text{O}]^{2+}$ with L-cysteine and S-methyl L-cysteine at 298 K, in 0.1 M NaClO_4 .

| L-cysteine | | | S-methyl-L-cysteine | | |
|------------|------------------------|---------------------------------|---------------------|------------------------|---------------------------------|
| pH | $10^{-3} C_L/\text{M}$ | $k_{\text{obsd}}/\text{s}^{-1}$ | pH | $10^{-3} C_L/\text{M}$ | $k_{\text{obsd}}/\text{s}^{-1}$ |
| 0.5 | 1.44 | 1.575(5) | 0.5 | 2.67 | 7.76(5) |
| | 2.05 | 1.979(6) | | 4.48 | 12.62(6) |
| | 3.46 | 3.174(6) | | 6.28 | 17.99(6) |
| | 4.50 | 3.854(5) | | 7.71 | 22.04(6) |
| | 5.78 | 4.902(5) | | 9.64 | 27.32(5) |
| | 7.18 | 5.866(5) | | 12.56 | 35.74(6) |
| | 8.09 | 6.458(6) | | | |
| | 8.62 | 6.799(5) | | | |
| | 10.12 | 7.784(5) | | | |
| | 11.06 | 8.546(6) | | | |
| | 12.96 | 10.24(6) | | | |
| 1.0 | 1.47 | 2.011(5) | 1.0 | 2.29 | 7.65(6) |
| | 2.25 | 2.656(4) | | 3.52 | 12.2(6) |
| | 2.82 | 3.406(5) | | 4.77 | 16.02(5) |
| | 4.22 | 4.451(5) | | 6.68 | 23.14(6) |
| | 5.63 | 5.812(6) | | 9.54 | 32.11(5) |
| | 7.62 | 7.542(5) | | | |
| | 8.44 | 8.460(4) | | | |
| | 10.20 | 10.157(5) | | | |
| | 14.08 | 13.410(4) | | | |
| | | | | | |
| 1.5 | 1.44 | 2.50(5) | 1.5 | 2.67 | 11.18(6) |
| | 3.09 | 4.40(4) | | 3.86 | 16.94(5) |
| | 4.31 | 6.044(4) | | 5.78 | 23.87(5) |
| | 5.76 | 7.45(5) | | 7.71 | 32.66(4) |
| | 7.18 | 8.904(4) | | 9.54 | 40.21(4) |
| | 10.06 | 12.612(5) | | | |
| | | | | | |

Table S5. Observed *pseudo*-first order rate constants as a function of ligand concentration at different pH value for the reactions between $[\text{Pt}(\text{dien})\text{H}_2\text{O}]^{2+}$ with L-cysteine and S-methyl L-cysteine at 298 K, in 0.1 M NaClO_4 .

| L-cysteine | | | S-methyl-L-cysteine | | |
|------------|------------------------|---|---------------------|------------------------|---|
| pH | $10^{-3} C_L/\text{M}$ | $10^{-4} k_{\text{obsd}}/\text{s}^{-1}$ | pH | $10^{-3} C_L/\text{M}$ | $10^{-4} k_{\text{obsd}}/\text{s}^{-1}$ |
| 0.5 | 2.64 | 0.4(5) | 0.5 | 2.63 | 1.1(6) |
| | 6.33 | 0.9(6) | | 6.31 | 1.7(6) |
| | 9.49 | 1.3(6) | | 9.46 | 2.0(6) |
| | 12.66 | 1.6(6) | | 12.62 | 3.0(5) |
| | 18.99 | 2.2(5) | | 18.93 | 4.1(5) |
| | 25.33 | 3.0(6) | | 25.24 | 5.6(6) |
| 1.0 | 2.67 | 0.6(5) | 1.0 | 2.67 | 1.8(5) |
| | 4.27 | 0.8(5) | | 5.17 | 2.8(4) |
| | 5.13 | 0.9(4) | | 10.34 | 4.2(4) |
| | 7.69 | 1.4(5) | | 16.03 | 6.9(5) |
| | 10.25 | 1.8(6) | | 20.29 | 7.9(6) |
| | 15.83 | 2.3(5) | | 25.63 | 11.0(5) |
| | 20.51 | 2.9(6) | | | |
| 1.5 | 2.64 | 0.9(5) | 1.5 | 4.10 | 13.0(5) |
| | 6.33 | 1.6(4) | | 6.25 | 16.0(5) |
| | 9.49 | 2.0(4) | | 12.5 | 21.0(4) |
| | 12.66 | 2.5(5) | | 18.7 | 26.0(4) |
| | 18.98 | 3.8(4) | | 25.0 | 33.0(5) |
| | 25.32 | 4.8(5) | | | |