Supplementary Material for:

L-Selenomethionine reduces platinum(IV) anticancer model compounds with strikingly faster rates than does L-methionine

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The supplementary material contains 2 supporting tables (**Tables S1 and S2**) and 4 supporting figures (**Figures S1–S4**).

Table S1. Observed pseudo first-order rate constants as a function of [Cl^-] for the reduction of *trans*-[$PtCl_2(CN)_4$]$^{2-}$ by SeMet at 25.0 °C and 1.0 M ionic strength.[a]

[Cl^-]/mM	k_{obsd}/s^{-1}
1.0	23.8 ± 0.5
2.0	25.8 ± 0.6
5.0	25.4 ± 0.5
10	25.2 ± 0.6
20	25.4 ± 0.5
30	25.3 ± 0.6
40	25.6 ± 0.6
60	25.0 ± 0.6
80	25.6 ± 0.5
100	25.6 ± 0.6

[a] Reaction conditions are: [Pt(IV)] = 0.05 mM; [SeMet] = 2.00 mM; [$HClO_4$] = 0.10 M; 255 nm.

Table S2. Dependence of observed second-order rate constants k' on pH for reduction of *trans*-$[PtX_2(CN)_4]^{2-}$ by SeMet at 25.0 °C and 1.0 M ionic strength.

Pt(IV) Complex	pH	$k'/M^{-1}s^{-1}$
$[PtCl_2(CN)_4]^{2-}$	0.25	$(1.03 \pm 0.03) \times 10^4$
	0.50	$(1.21 \pm 0.03) \times 10^4$
	1.20	$(1.25 \pm 0.04) \times 10^4$
	1.35	$(1.27 \pm 0.04) \times 10^4$
	1.72	$(1.40 \pm 0.05) \times 10^4$
	2.20	$(1.53 \pm 0.05) \times 10^4$
	3.25	$(1.56 \pm 0.05) \times 10^4$
	3.61	$(1.68 \pm 0.05) \times 10^4$
	4.41	$(1.72 \pm 0.05) \times 10^4$
	4.52	$(1.86 \pm 0.05) \times 10^4$
	5.29	$(1.76 \pm 0.05) \times 10^4$
	6.21	$(1.76 \pm 0.06) \times 10^4$
	6.53	$(1.60 \pm 0.06) \times 10^4$
	7.38	$(1.57 \pm 0.06) \times 10^4$
	7.77	$(1.85 \pm 0.06) \times 10^4$
	8.24	$(4.07 \pm 0.09) \times 10^4$
	8.69	$(4.80 \pm 0.15) \times 10^4$
	8.97	$(5.53 \pm 0.15) \times 10^4$
	9.17	$(5.85 \pm 0.16) \times 10^4$
	9.44	$(6.13 \pm 0.16) \times 10^4$
	9.72	$(6.15 \pm 0.17) \times 10^4$
	10.03	$(6.52 \pm 0.18) \times 10^4$
	10.32	$(6.44 \pm 0.18) \times 10^4$
	10.52	$(6.33 \pm 0.19) \times 10^4$
$[PtBr_2(CN)_4]^{2-}$	0.25	$(8.85 \pm 0.14) \times 10^5$

0.50	$(8.57 \pm 0.15) \times 10^5$
1.20	$(1.30 \pm 0.05) \times 10^6$
1.90	$(1.16 \pm 0.05) \times 10^6$
2.20	$(1.30 \pm 0.06) \times 10^6$
3.21	$(2.04 \pm 0.06) \times 10^6$
4.47	$(2.20 \pm 0.06) \times 10^6$
5.15	$(2.14 \pm 0.07) \times 10^6$
6.21	$(2.00 \pm 0.06) \times 10^6$
7.23	$(2.06 \pm 0.07) \times 10^6$

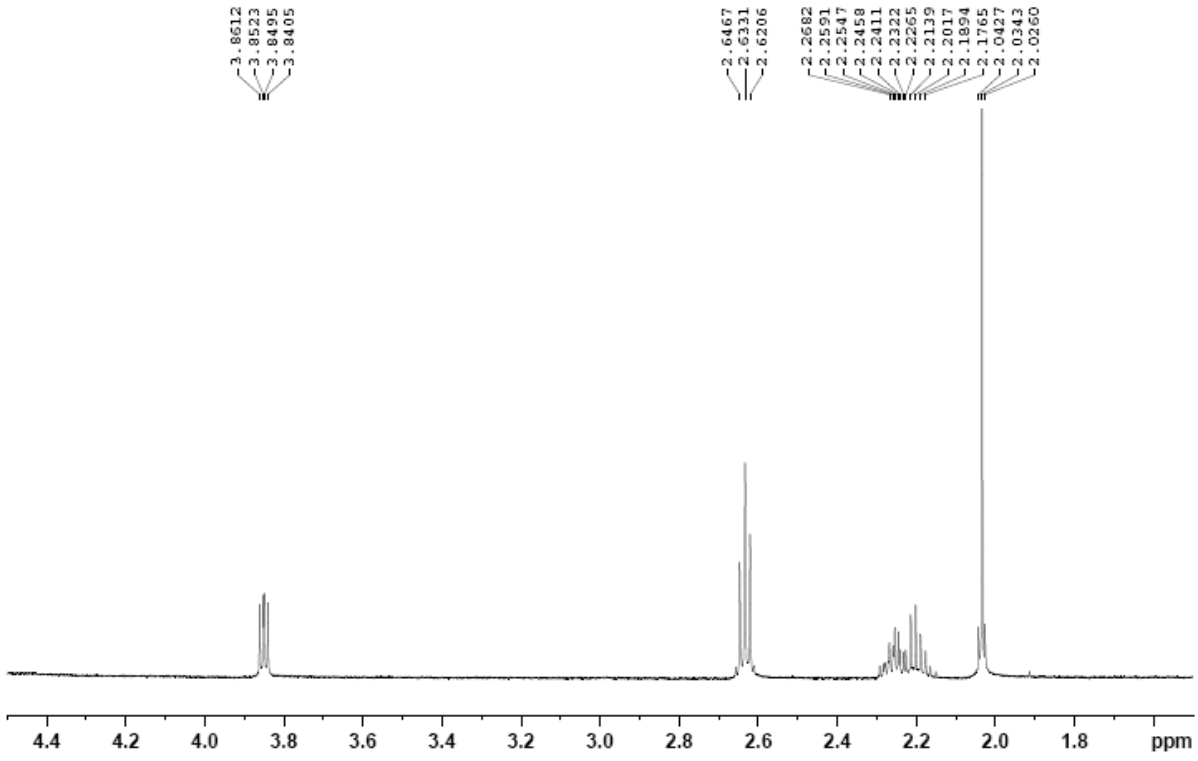

Figure S1. ^{1}H NMR spectrum for a sample of the purchased SeMet in aqueous solution. Sample preparation: 5 mM SeMet in D_2O at pD = 7.4 adjusted with DCl and NaOD. TSP was added to the sample as the reference. An Advance III 600 MHz digital NMR spectrometer (Bruker, Switzerland) was used for recording the spectrum.

Peak assignments for: $CH_3Se\text{-}CH_2\text{-}CH_2\text{-}CH(NH_3^+)\text{-}COO^-$:

CH_3Se- at 2.03 ppm, s; $Se\text{-}CH_2$- at 2.63 ppm, t; $\text{-}CH_2$- at 2.17-2.27 ppm, m;

$\text{-}CH(NH_3^+)$- at 3.85 ppm, t.

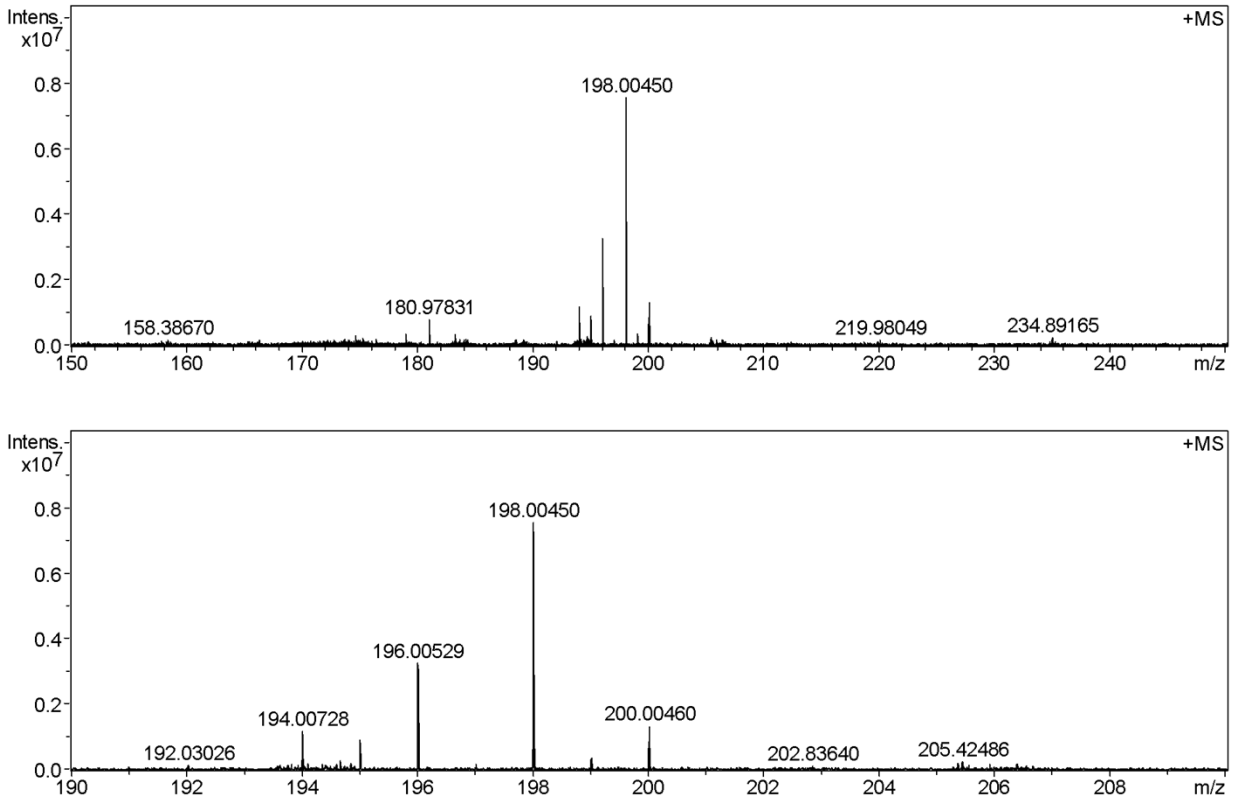

Figure S2. (**Top**): High resolution ESI-mass spectrum for a sample of the purchased SeMet in aqueous solution. Sample preparation: 2 mM SeMet in 10 mM HCl flushed by nitrogen gas. (**Bottom**): An expended range between *m/z* 190 and 210 shows the isotopic pattern around *m/z* 198.

Peak assignments: (**Top**) *m/z* around 198 *from* SeMet▪H^+;

m/z around 181 *from* (SeMet – NH_3)▪H^+.

Calculated isotopic patterns *versus* the measured ones for SeMet▪H^+:

Calculated value	Measured value (**Bottom spectrum**)
194.00602 (18.1%)	194.00728
195.00672 (15.3%)	195.00735
196.00411 (47.4%)	196.00529
198.00835 (100%)	198.00450
200.00352 (19%)	200.00460

Theoretical calculations for the high resolution mass peaks of (SeMet – NH_3)▪H^+ are:

180.97679 (100%) *versus* 180.97831 (found on the **top spectrum**).

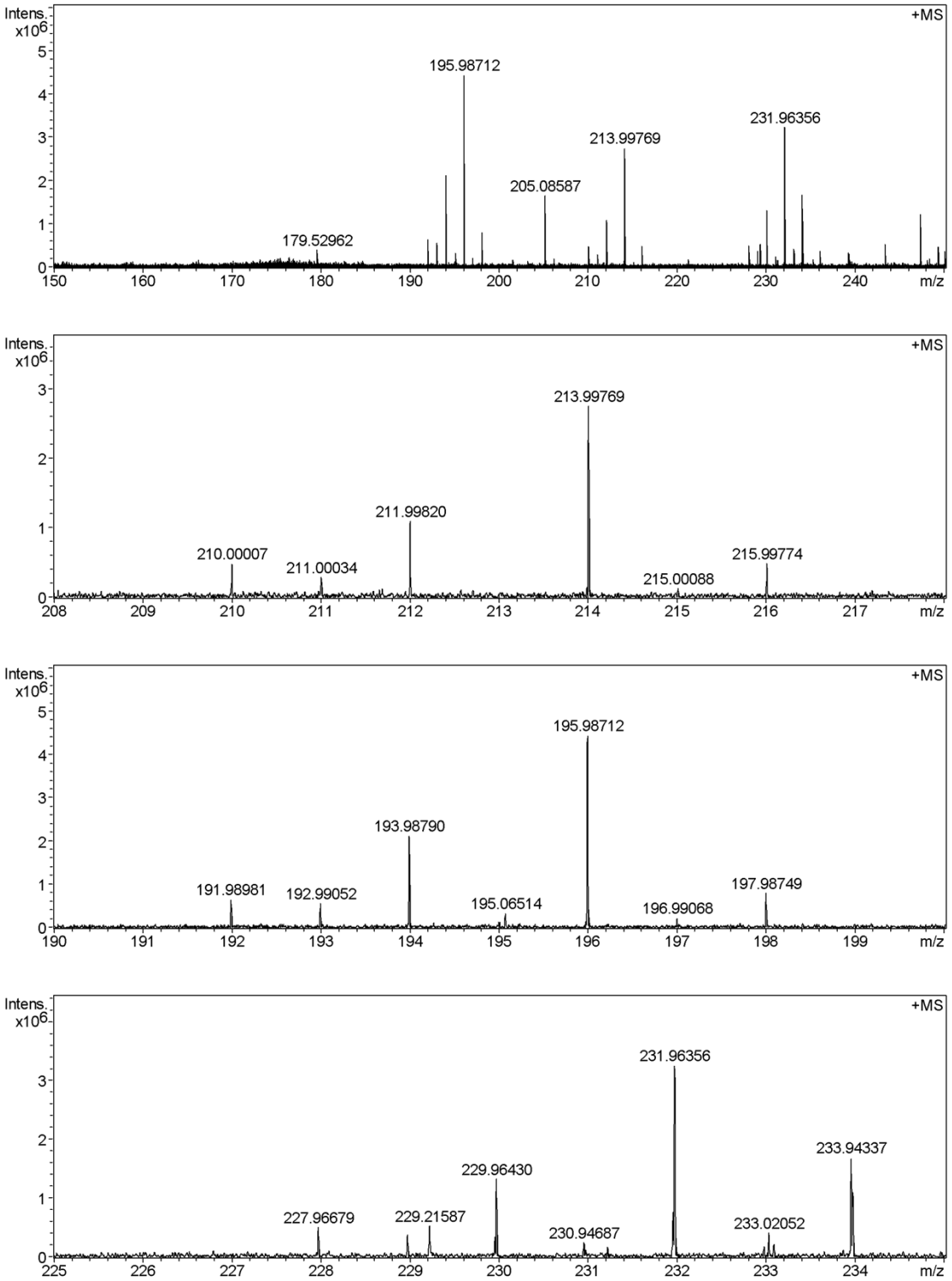

Figure S3. (**Top**): High resolution ESI-mass spectrum for a reaction mixture of 1.0 mM SeMet and 1.2 mM $[PtCl_2(CN)_4]^{2-}$ in 10 mM HCl. The **bottom three spectra** are the expanded ranges

for the 3 major peaks around *m/z* 214, 196 and 232 to show the isotopic patterns.

Peak assignments: *m/z* around 214 *from* L-selenomethionine selenoxide O=SeMet▪H^+;

m/z around 196 *from* (O=SeMet – H_2O)▪H^+;

m/z around 232 *from* L-selenomethionine hydrated selenoxide $(HO)_2$SeMet▪H^+.

Calculated isotopic patterns *versus* the measured ones for O=SeMet▪H^+:

Calculated value	Measured value
210.00094 (18.1%)	210.00007
211.00164 (15.3%)	211.00034
211.99903 (47.4%)	211.99820
213.99825 (100%)	213.99769
215.00161 (5.4%)	215.99774

Calculated isotopic patterns *versus* the measured ones for (O=SeMet – H_2O)▪H^+ are:

Calculated value	Measured value
191.99307 (18.1%)	191.98981
192.99107 (15.3%)	192.99052
193.98846 (47.4%)	193.98790
194.99182 (2.6%)	195.06514
195.98768 (100%)	195.98712
196.99104 (5.4%)	196.99068
197.98787 (19 %)	197.98749

Calculated isotopic patterns *versus* the measured ones for $(HO)_2$SeMet▪H^+ are:

Calculated value	Measured value
228.01151 (18.1%)	227.96679
229.01291 (15.3%)	229.21587
230.00960 (47.4%)	229.96430
232.00882 (100%)	231.96356
233.01218 (5.4%)	233.02052
234.00901 (19%)	233.94337

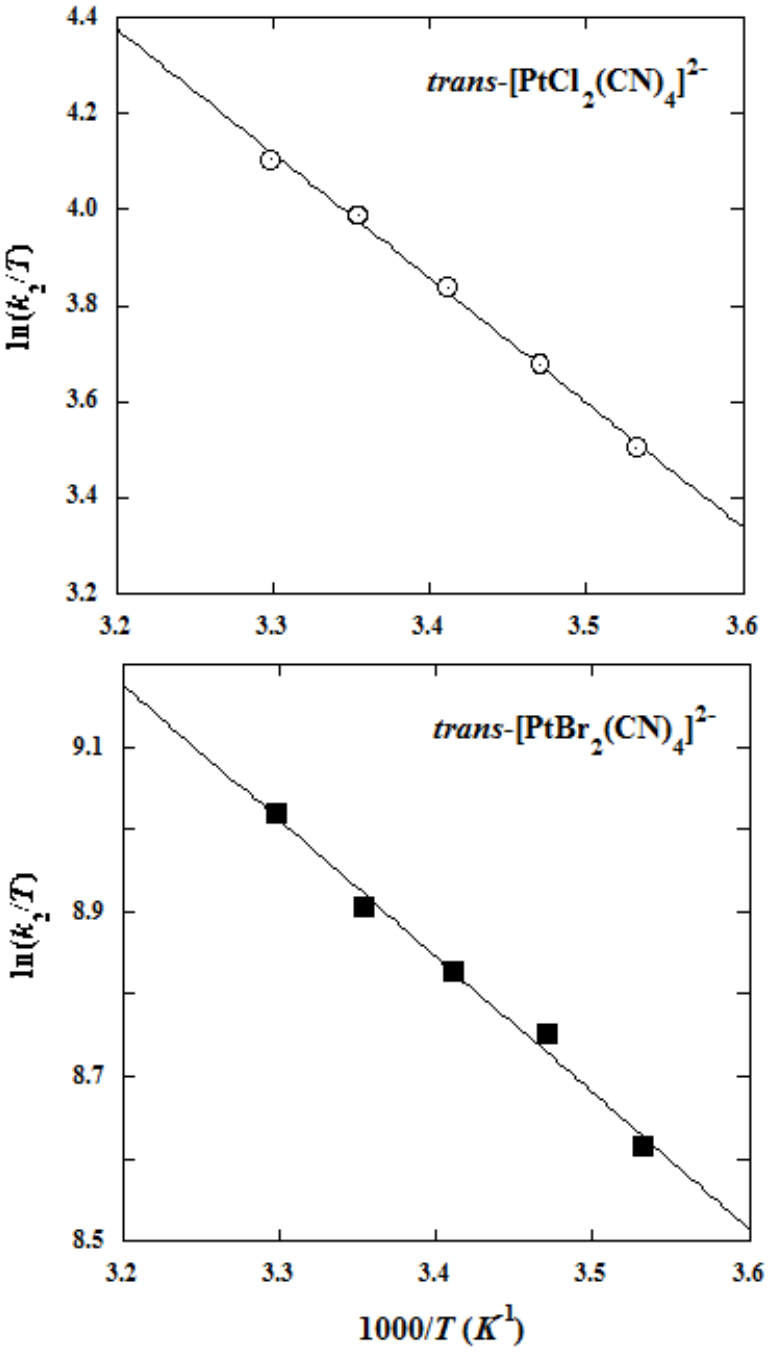

Figure S4. Eyring plots for the second-order rate constants k_2 in Scheme 1.