

Structure, solution chemistry, antiproliferative actions and protein binding properties of non-conventional platinum(II) compounds with sulfur and phosphorus donors

SUPPORTING INFORMATION

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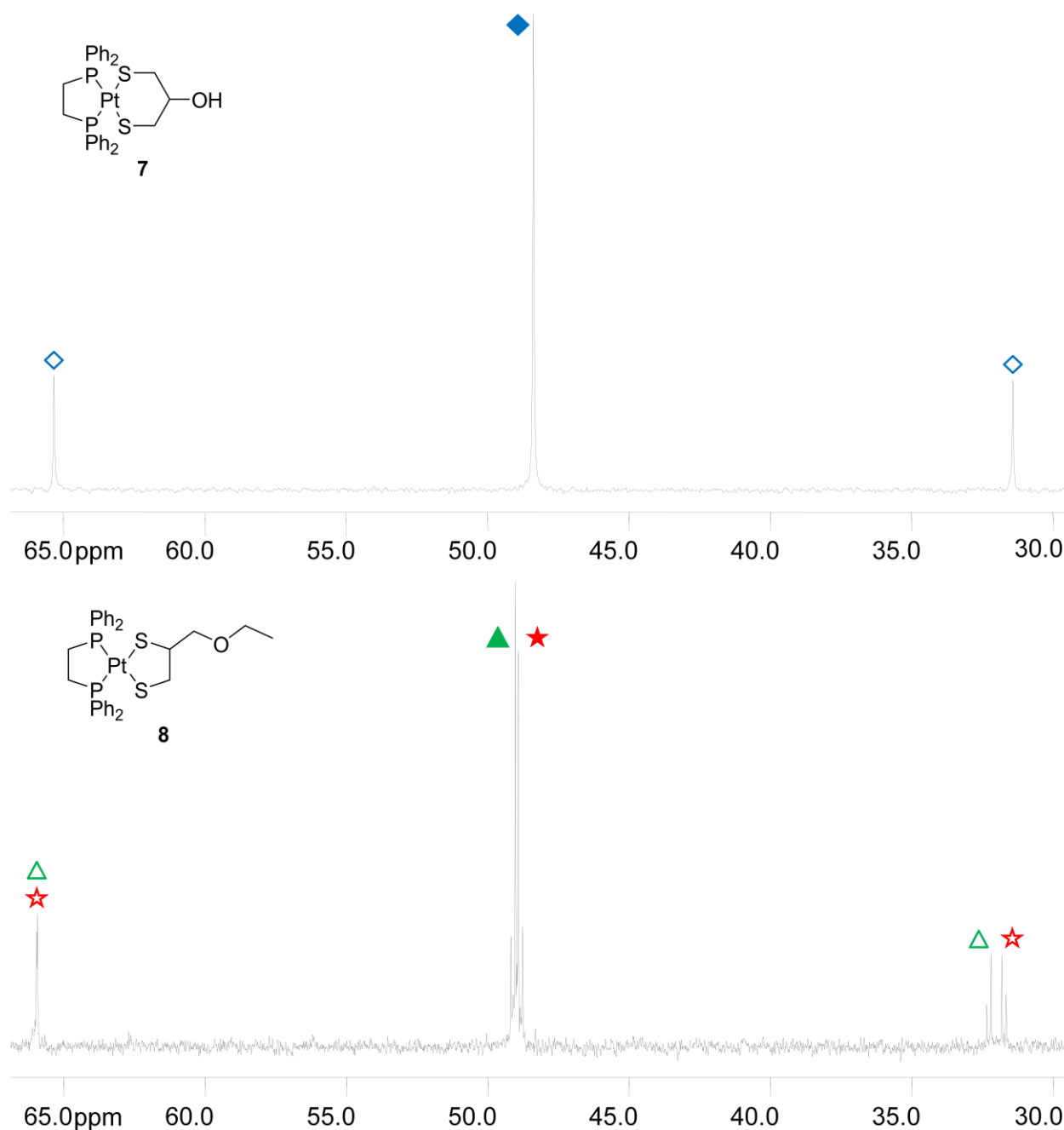


Figure S1. ³¹P{¹H} NMR spectra (81 MHz, CDCl₃) of **7** (top) and **8** (bottom), showing the structural differences of both compounds. **7** is a symmetric complex leading to one singlet at $\delta = 48.4$ ppm (◆) with platinum satellites ($^1J_{\text{PPt}}$ 2748 Hz). **8**, bearing two different P atoms, gives a set of two doublets, each showing Pt satellites in an AB spin system. $\delta = 49.1$ ppm (▲, $^1J_{\text{PPt}}$ 2720 Hz, $^2J_{\text{PP}}$ 12 Hz), 48.8 ppm (★, $^1J_{\text{PPt}}$ 2778 Hz, $^2J_{\text{PP}}$ 12 Hz). Due to a strong roof effect, the satellite signals at 65.9 ppm appear merged to a pseudo-singlet.

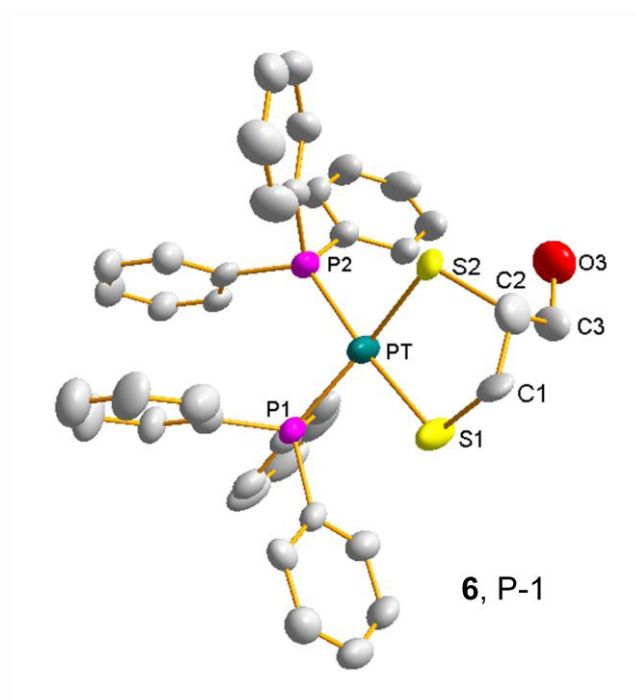


Figure S2. Molecular Structure of **6**. Disorders at the dithiolato moiety have been omitted for clarity. Thermal ellipsoids are given at the 50 % propability level.

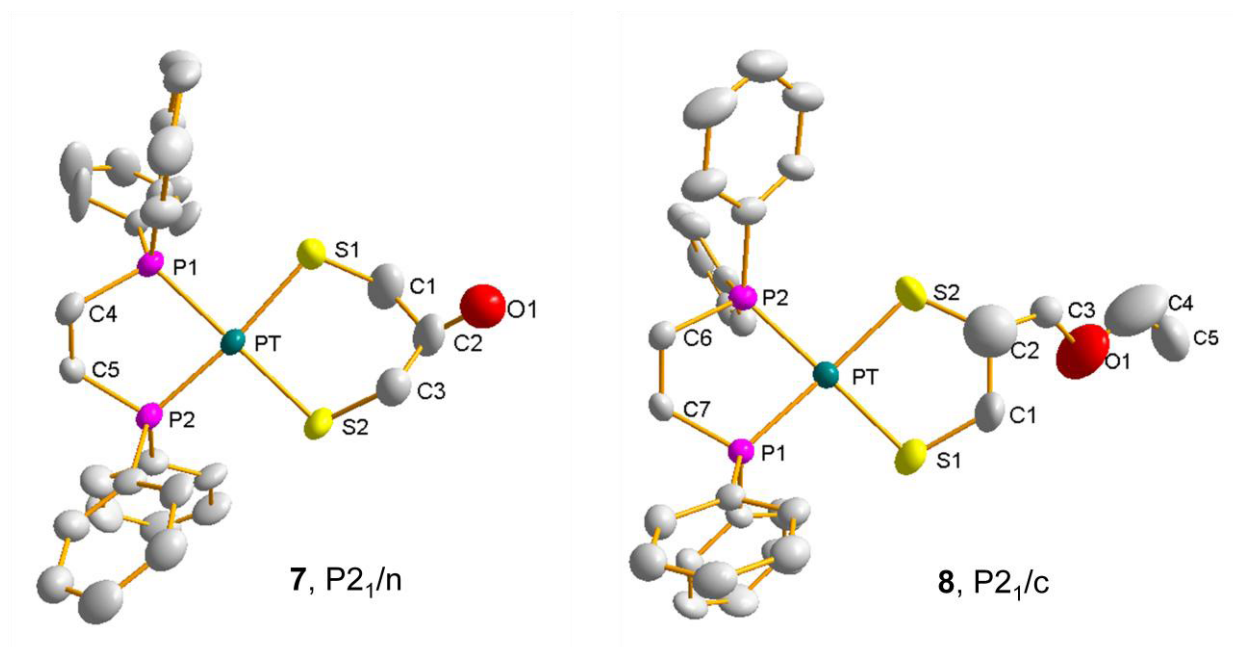


Figure S3. Molecular Structures of **7** and **8**. Disorders at the dithiolato moiety have been omitted for clarity. Thermal ellipsoids are given at the 50 % propability level.

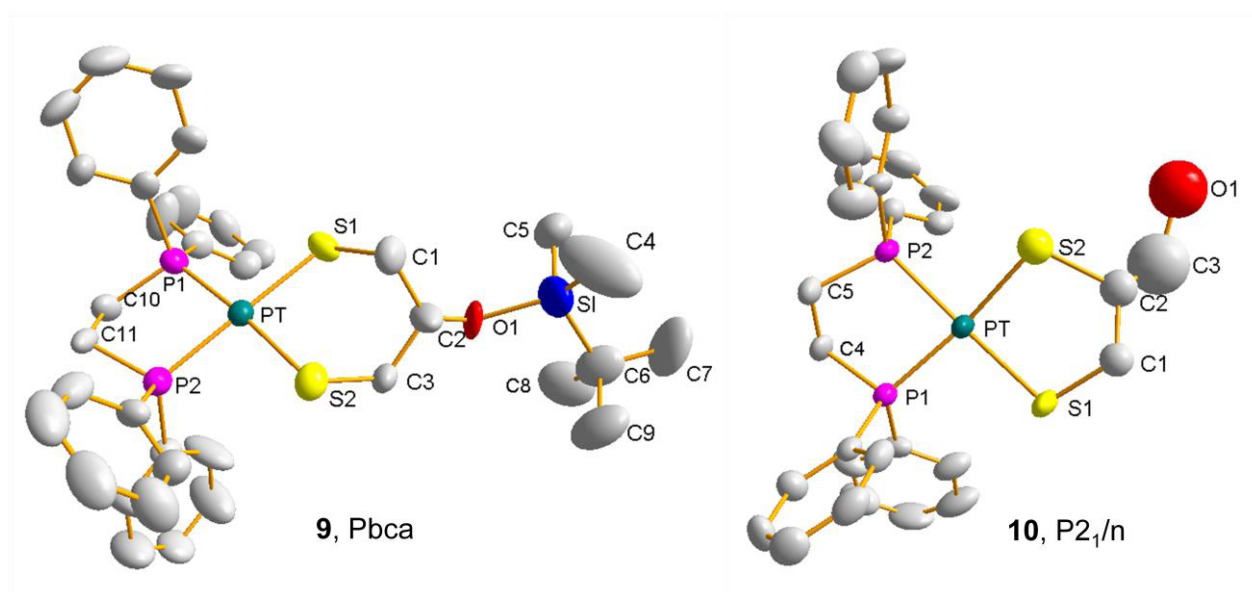


Figure S4. Molecular Structures of **9** and **10**. Disorders at the dithiolato moiety have been omitted for clarity. Thermal ellipsoids are given at the 50 % propability level.

Table S1. Crystal data and refinement details for the X-ray structure determinations of **6**, **7**, **8**, **9**, and **10**.

Compound	6	7	8	9	10
formula	C ₃₉ H ₃₆ OP ₂ PtS ₂ , CHCl ₃	C ₂₉ H ₃₀ OP ₂ PtS ₂ , 0.5 CH ₄ O, H ₂ O	C ₃₁ H ₃₄ OP ₂ PtS ₂	C ₃₅ H ₄₄ OP ₂ PtS ₂ Si	C ₂₉ H ₃₀ OP ₂ PtS ₂
fw (g·mol⁻¹)	961.20	749.72	743.73	829.94	715.68
T/°C	-90(2)	-90(2)	-90(2)	-90(2)	-90(2)
crystal system	triclinic	monoclinic	monoclinic	orthorhombic	monoclinic
space group	P $\bar{1}$	P 2 ₁ /n	P 2 ₁ /c	P bca	P 2 ₁ /n
a/ Å	11.6368(13)	9.0685(3)	15.6013(6)	17.8444(14)	9.1382(3)
b/ Å	12.5618(13)	28.1277(9)	18.2591(7)	13.7455(11)	25.8648(9)
c/ Å	14.784(2)	12.3952(3)	10.9863(4)	28.9636(18)	12.1756(4)
a/°	87.969(8)	90	90	90	90
β/°	78.924(7)	103.898(2)	104.966(2)	90	106.278(2)
γ/°	64.993(4)	90	90	90	90
V/Å³	1919.4(4)	3069.16(16)	3023.5(2)	7104.2(9)	2762.43(16)
Z	2	4	4	8	4
ρ (g·cm⁻³)	1.663	1.623	1.634	1.552	1.721
μ (cm⁻¹)	40.88	48.39	49.08	42.18	53.68
measured data	12394	18527	20310	19282	15833
data with I > 2σ(I)	4729	4638	5116	3924	4081
unique data (R_{int})	8227/0.0557	6922/0.0698	6808/0.0591	6757/0.1662	6188/0.0636
wR₂ (all data, on F²)^{a)}	0.1753	0.1845	0.0979	0.2660	0.1598
R₁ (I > 2σ(I))^{a)}	0.0894	0.0638	0.0386	0.0876	0.0569
S^{b)}	1.126	1.014	1.007	1.018	1.023
Res. dens./e·Å⁻³	1.446/-1.670	2.860/-2.192	1.396/-1.953	2.655/-2.228	1.946/-1.788
absorpt method	NONE	NONE	NONE	NONE	NONE
CCDC No.	776102	776103	776104	776105	776106

^{a)} Definition of the *R* indices: $R_1 = (\sum ||F_o| - F_c||) / \sum |F_o|$; $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \square^2(F_o^2) + (aP)^2 + bP$;
 $P = [2F_c^2 + \text{Max}(F_o^2)/3]$; ^{b)} $S = \{\sum [w(F_o^2 - F_c^2)^2] / (N_o - N_p)\}^{1/2}$.

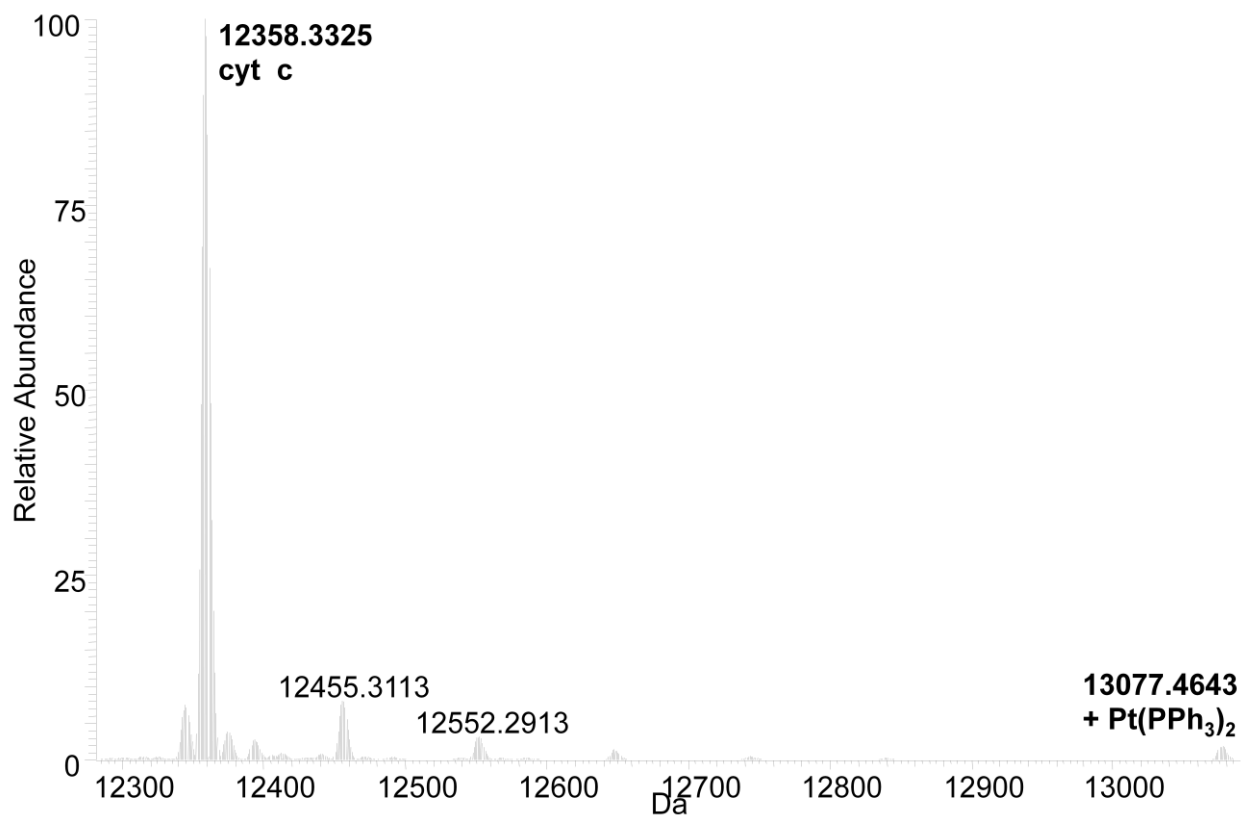


Figure S5. Deconvoluted ESI-MS spectrum of **1**, incubated with cyt c at a 1:3 ratio for 24 h at 37 °C.

A low-intensity signal (3 % r.i.) of a [cyt c + Pt(PPh₃)₂] fragment can be observed at 13077.46 Da.

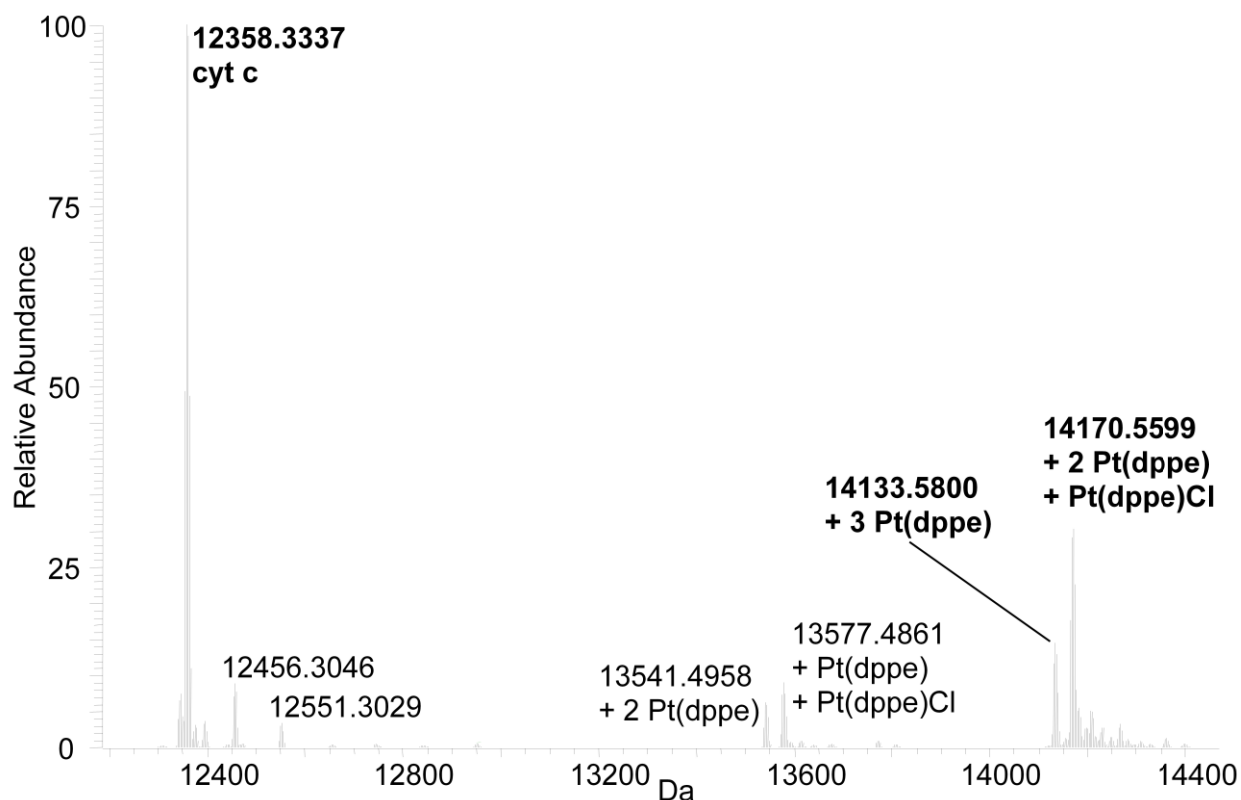


Figure S6. Deconvoluted ESI-MS spectrum of **2**, incubated with cyt c at a 3:1 ratio for 24 h at 37 °C. Weak signals corresponding to 2 Pt(dppe) units and Pt(dppe) + Pt(dppe)Cl bound to cyt c are observed in the 13500-13600 Da range. The signal at 14233.6 Da, belonging to [cyt c + 3 Pt(dppe)] is weaker (15 % r.i.) than the one at 14170.6 Da ([cyt c + 2 Pt(dppe) + Pt(dppe)Cl], 30 % r.i.).

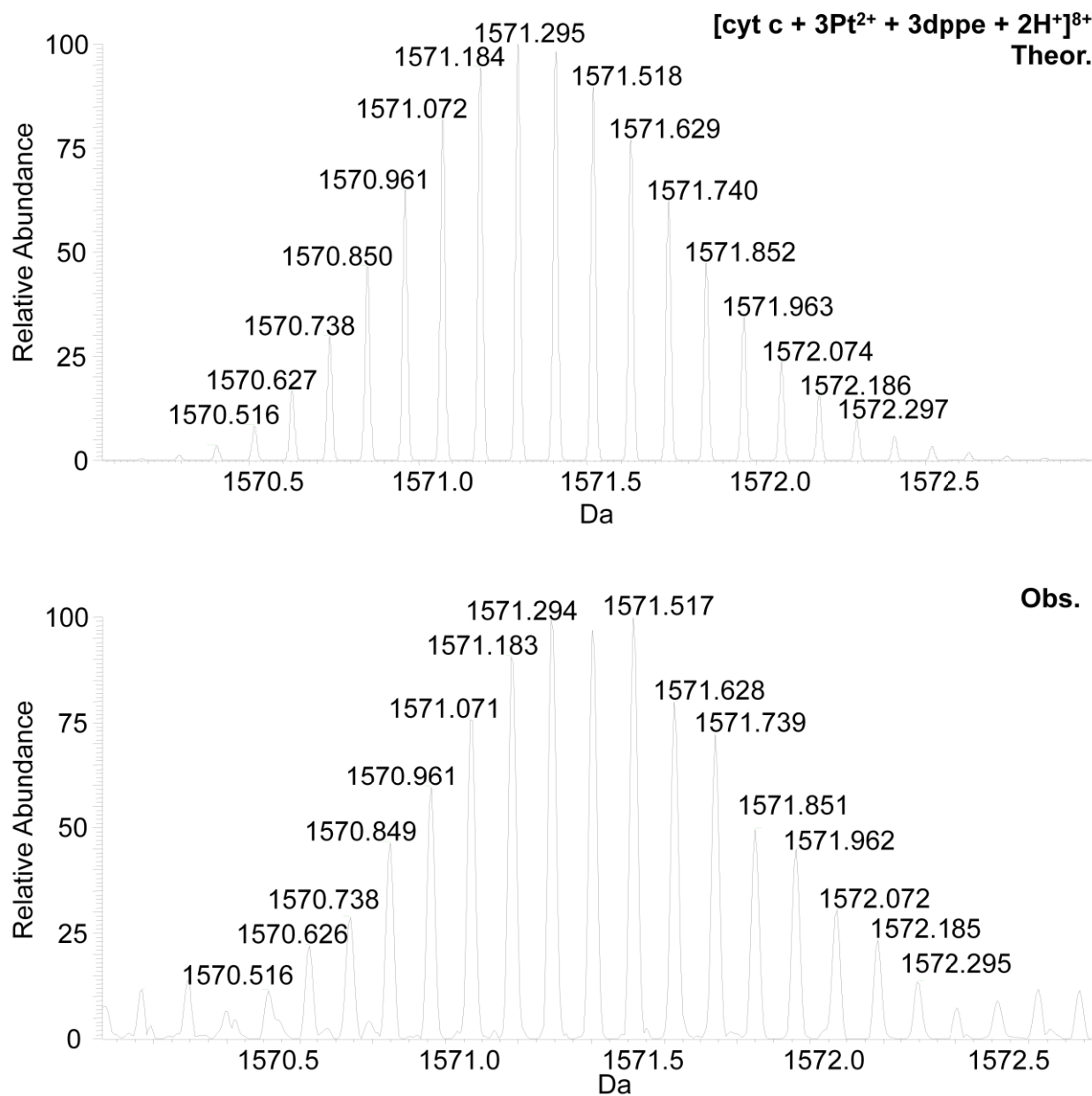


Figure S7. Isotope pattern of the ESI-MS peak of **2**, assigned to cyt c with 3 $[\text{Pt}(\text{dppe})]^{2+}$ fragments at $Z = +8$. Top, theoretical pattern; bottom, observed signal.

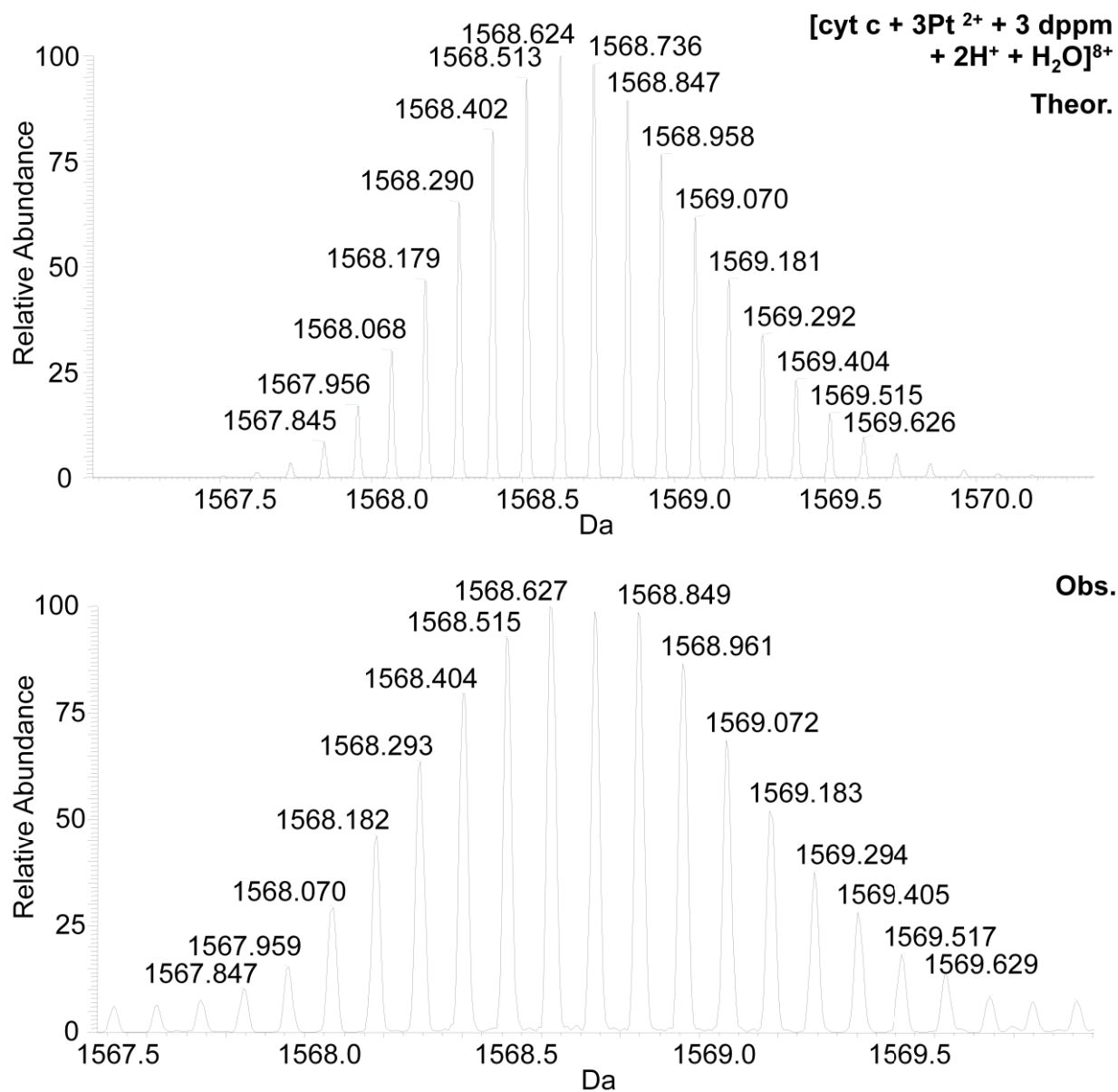


Figure S8. Isotope pattern of the ESI-MS peak of **3**, assigned to cyt c with 2 Pt(dppm) and 1 [Pt(dppm)H₂O]²⁺ bound fragments at Z = +8. Top, theoretical pattern; bottom, observed signal.

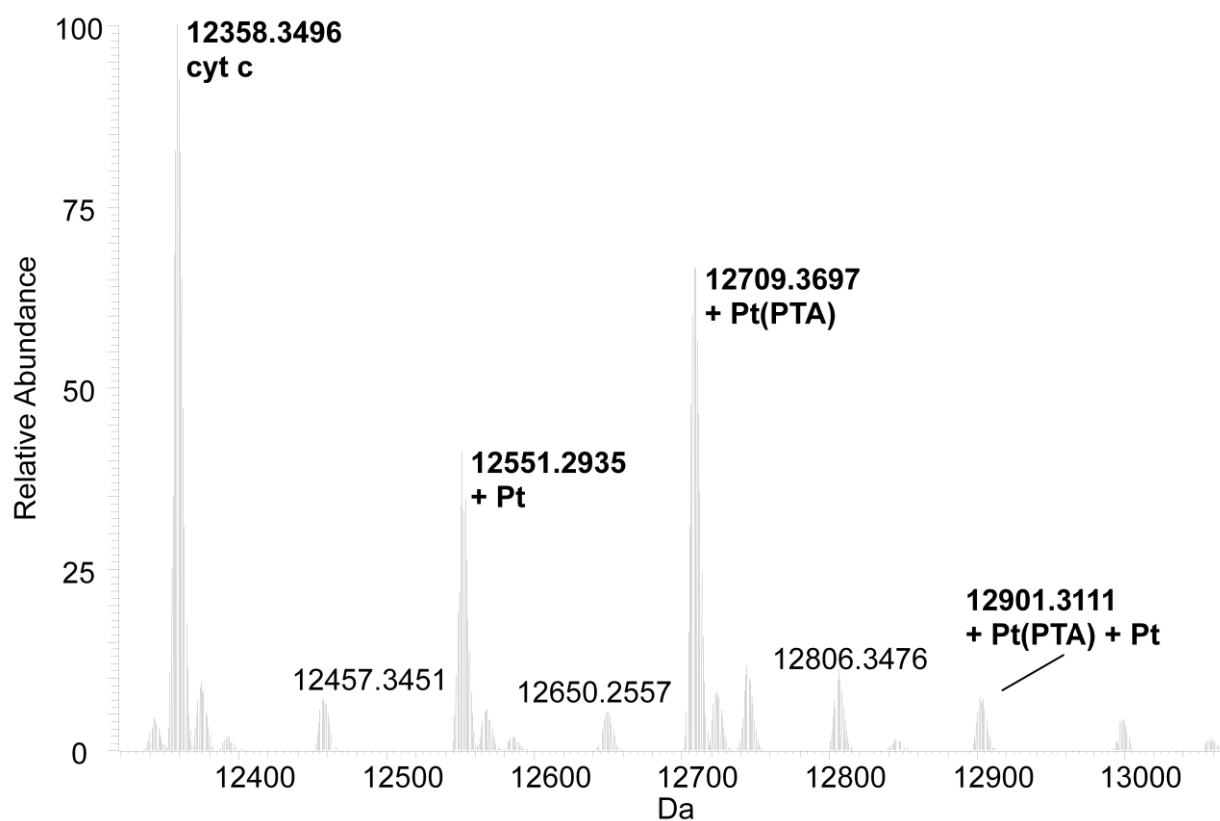


Figure S9. Deconvoluted ESI-MS spectrum of **4**, incubated with cyt c at a 1:1 ratio for 96 h at 37 °C.

Various adducts can be observed and progressive loss of the PTA ligands is indicated.