Electronic Supplementary Information

Synthesis and structures of novel 1-methylcytosinato-bridged (ethylenediamine)platinum(II) and platinum(III) dinuclear complexes

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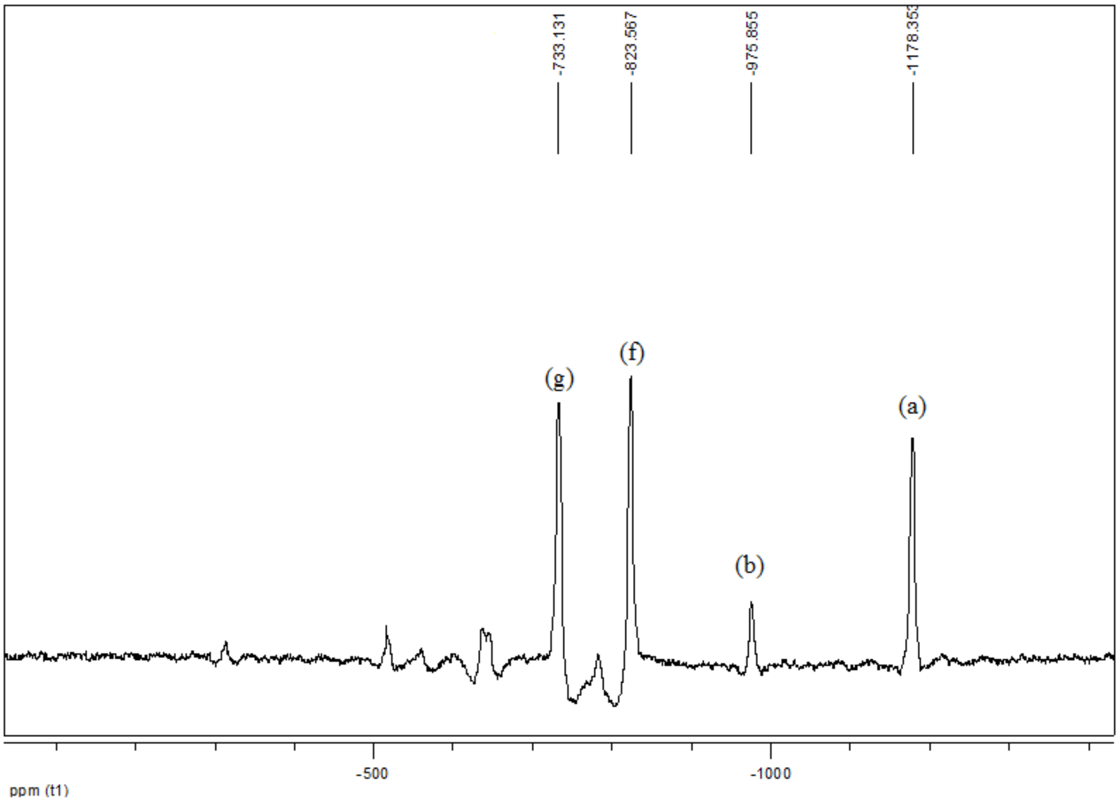

Figure S1. ^{195}Pt NMR (9:1 H_2O:D_2O) spectrum of the products obtained from the reaction of $[Pt(en)(H_2O)_2]^{2+}$ with 1 equiv of 1-MeCyt (as described in the Experimental Section) after 24 h at 40 °C. The pH of the solution was 3. The chemical shifts are referenced to $K_2[PtCl_4]$. The resonances are assigned as follows: (a) $[Pt(en)(MeCyt)_2]^{2+}$ (**3**), -1178 ppm; (b) $[Pt(en)(MetCyt)Cl]^{+}$ (**4**), -975 ppm; (f) ht-$[(en)Pt(MetCyt\text{-}H)_2Pt(en)]^{2+}$ (**1**), -823 ppm; (g) $[Pt(en)(MetCyt\text{-}H)(H_2O)]^{+}$, -733 ppm.

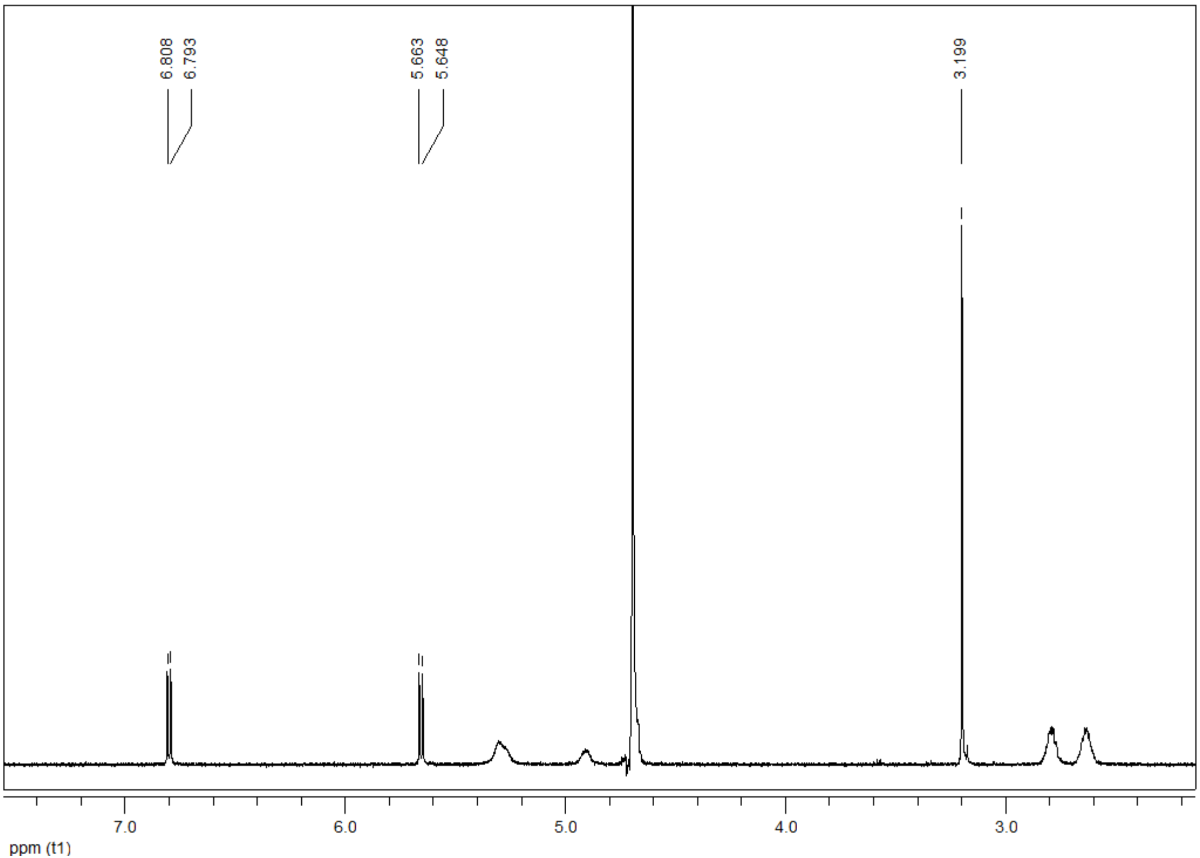

Figure S2. ^{1}H NMR spectrum (9:1 H_2O:D_2O) of ht-[(en)Pt(MetCyt-H)$_2$Pt(en)](NO_3)$_2$·H_2O (**1**).

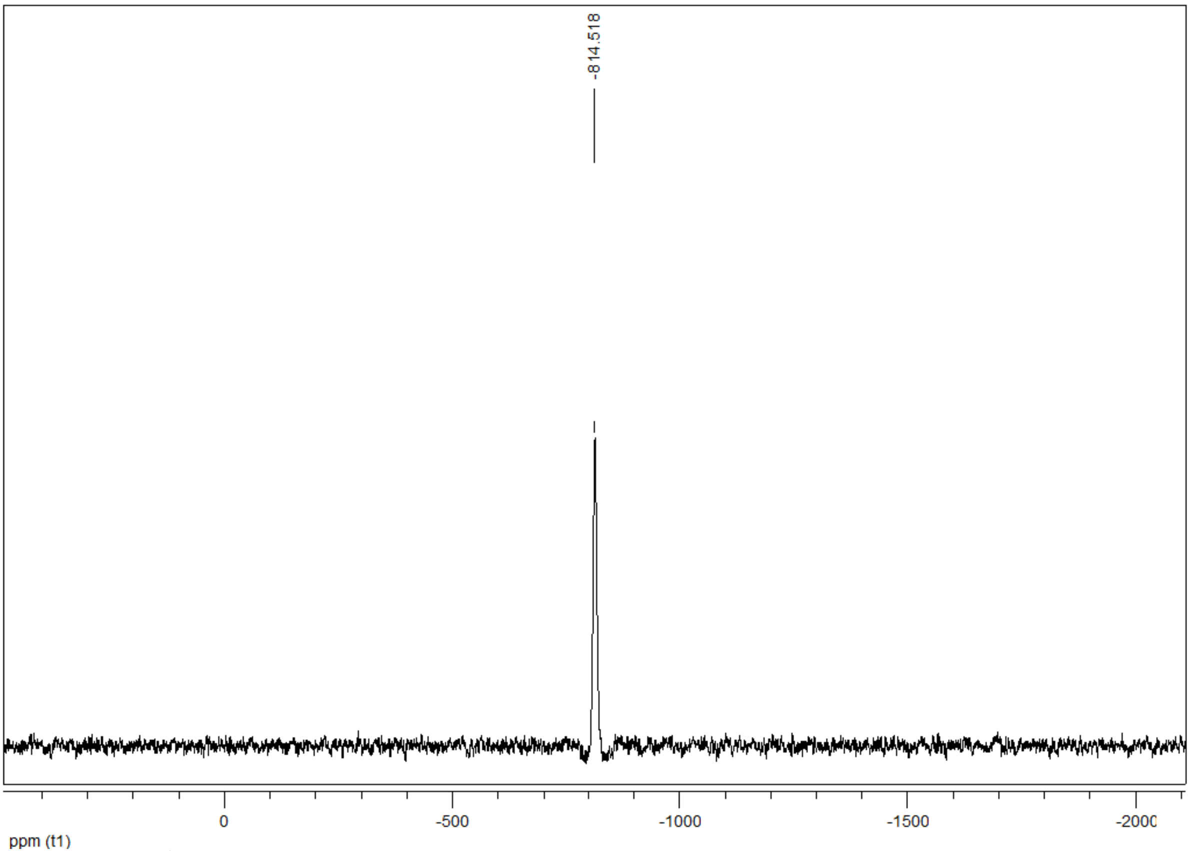

Figure S3. ^{195}Pt NMR (9:1 H_2O:D_2O) spectrum of ht-[(en)Pt(MetCyt-H)$_2$Pt(en)](NO_3)$_2$·H_2O(**1**).

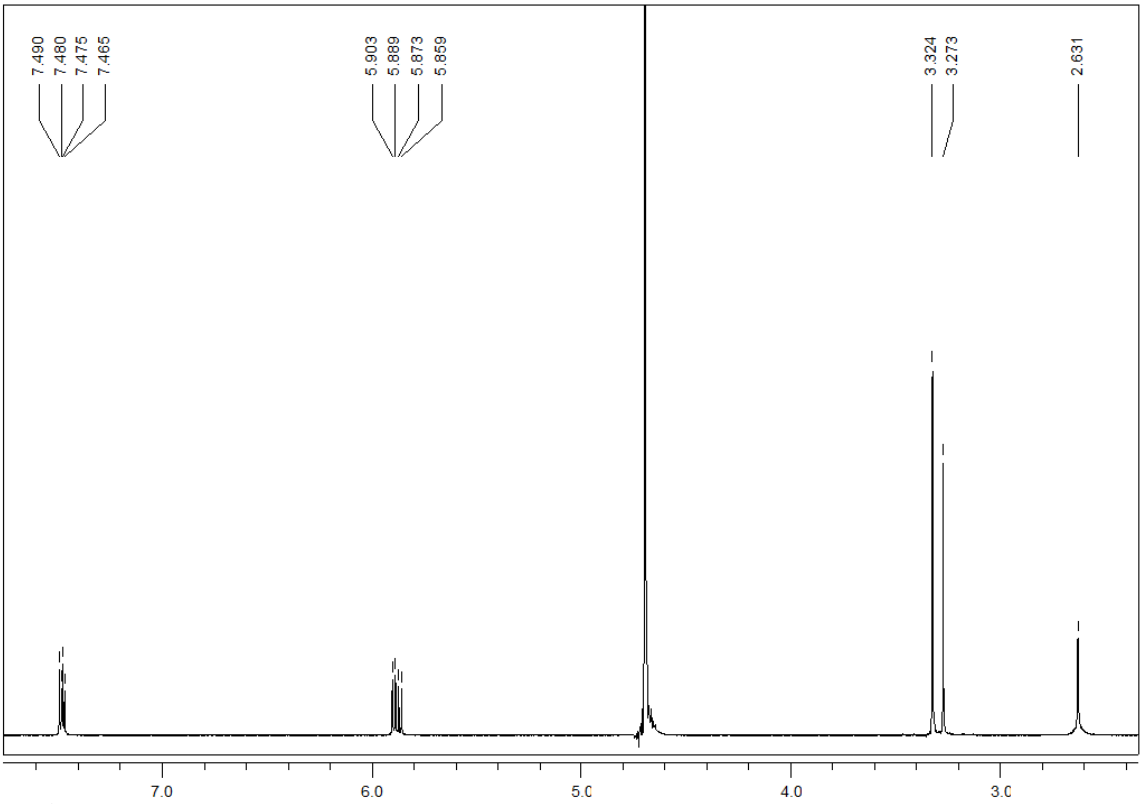

Figure S4. ^{1}H NMR spectrum (D$_2$O) of [Pt^{II}(en)(MetCyt)$_2$](NO$_3$)$_2$·MetCyt (**2**).

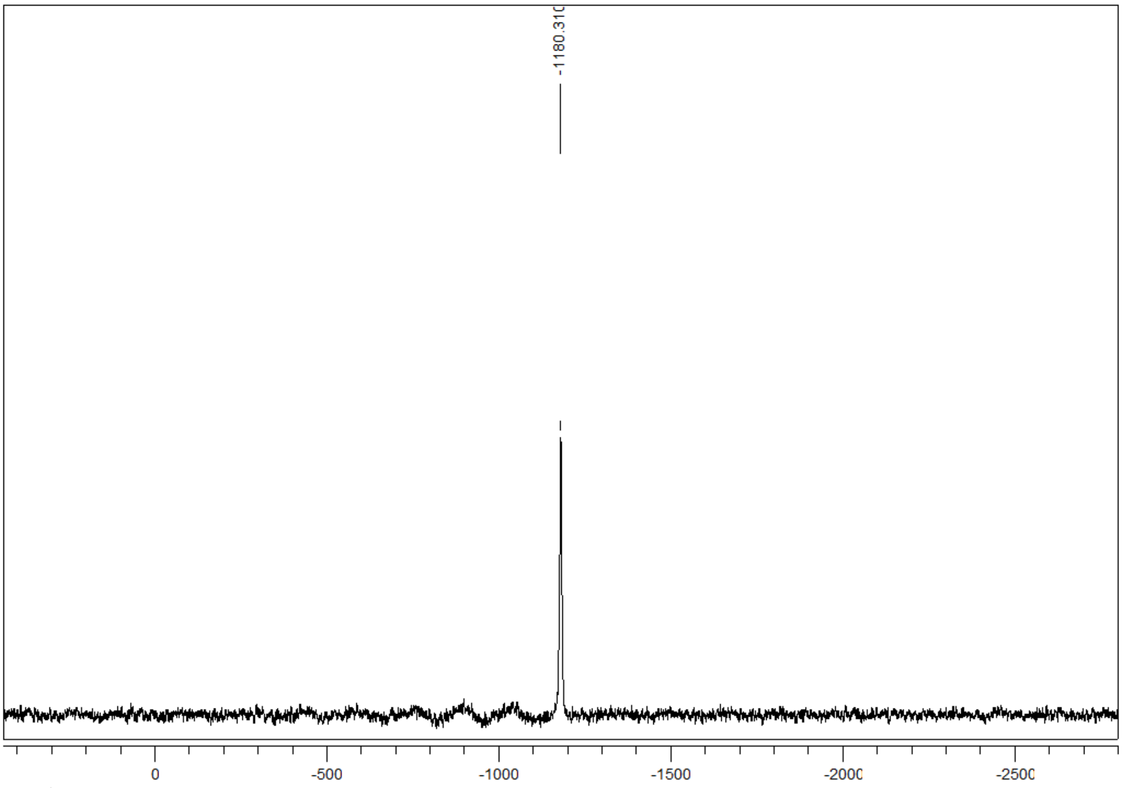

Figure S5. ^{195}Pt NMR spectrum (D$_2$O) of [Pt^{II}(en)(MetCyt)$_2$](NO$_3$)$_2$·MetCyt (**2**).

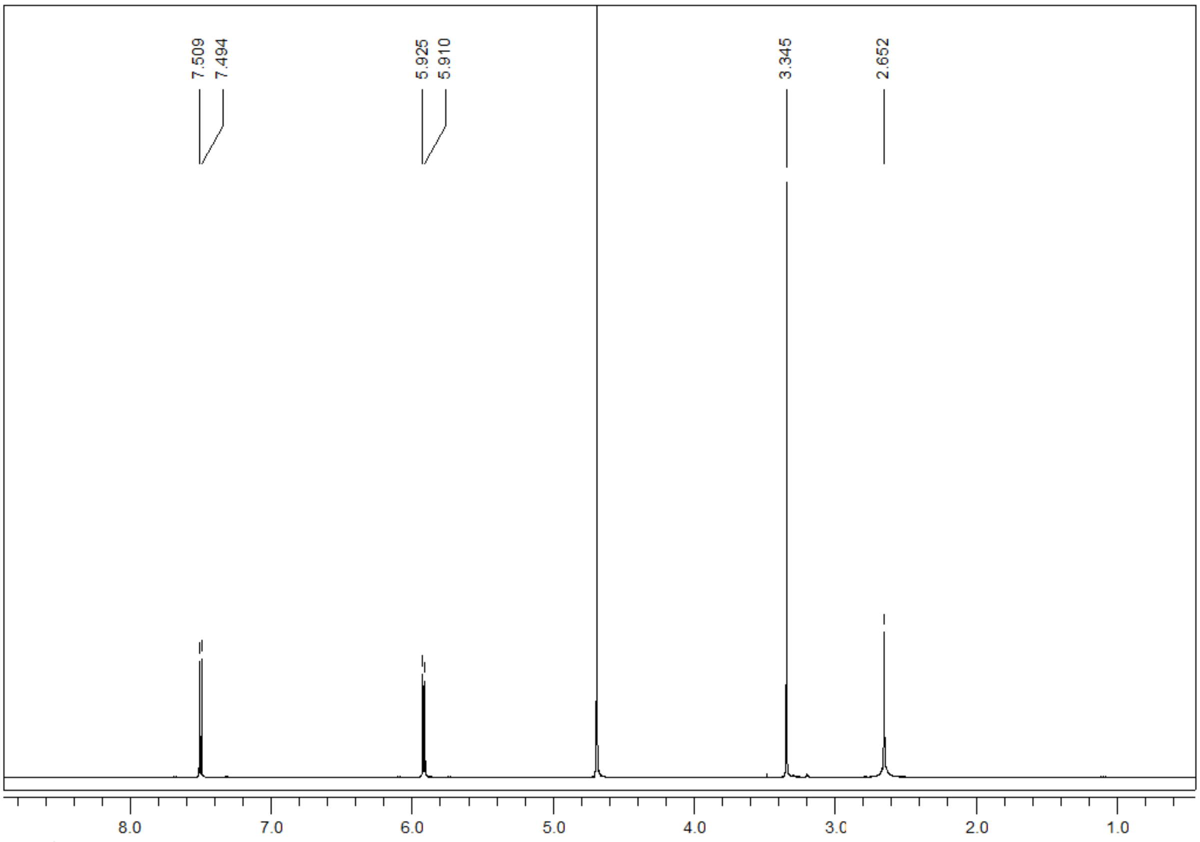

Figure S6. ^{1}H NMR spectrum (D$_2$O) of [Pt^{II}(en)(MetCyt)$_2$](NO$_3$)$_2$ (**3**).

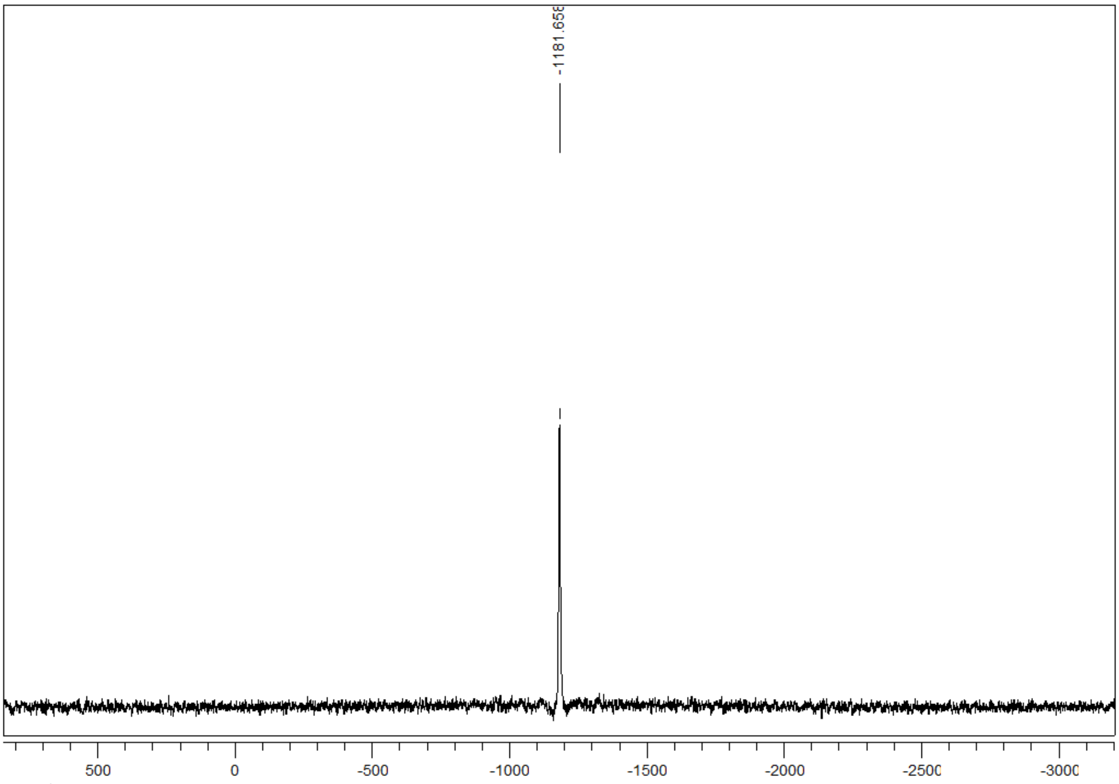

Figure S7. ^{195} Pt NMR spectrum (D$_2$O) of [Pt^{II}(en)(MetCyt)$_2$](NO$_3$)$_2$ (**3**).

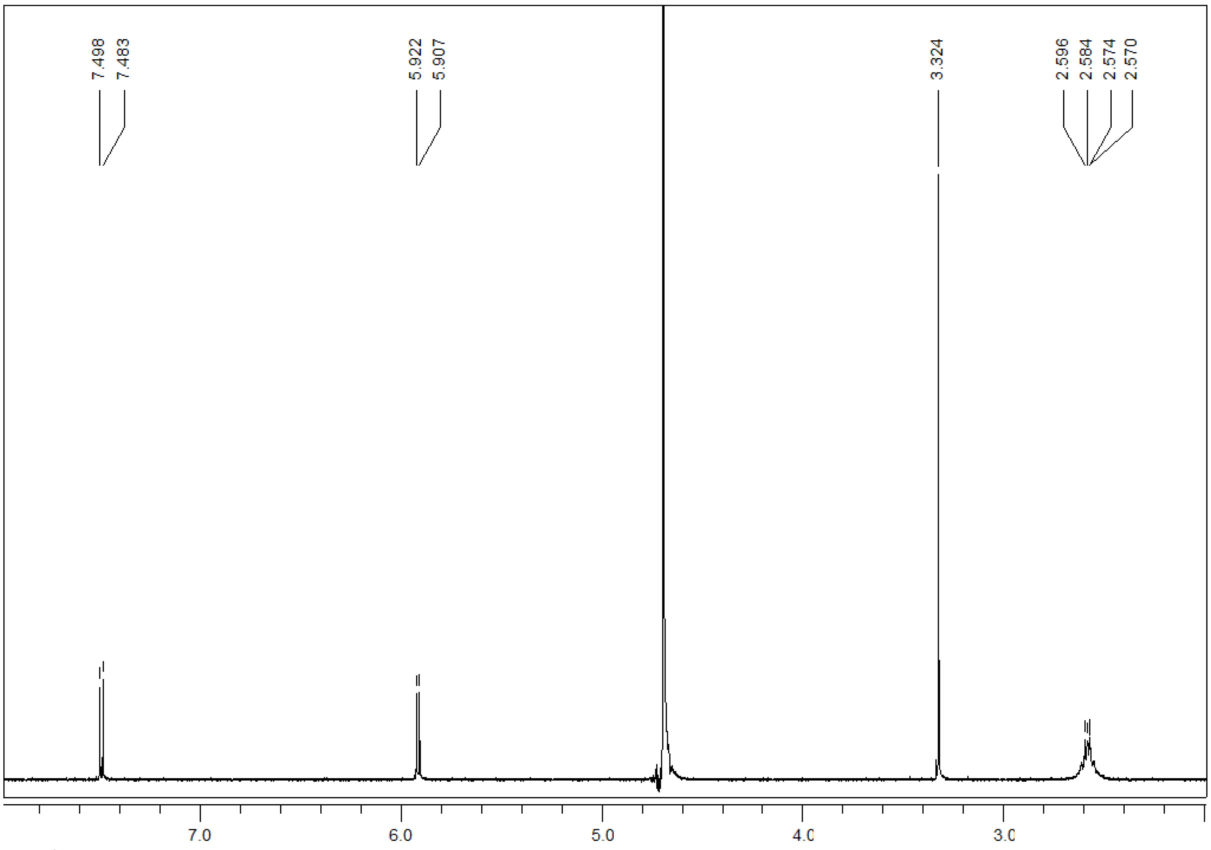

Figure S8. ^{1}H NMR spectrum (D_2O) of [Pt^{II}(en)(MetCyt)Cl]NO_3 (**4**).

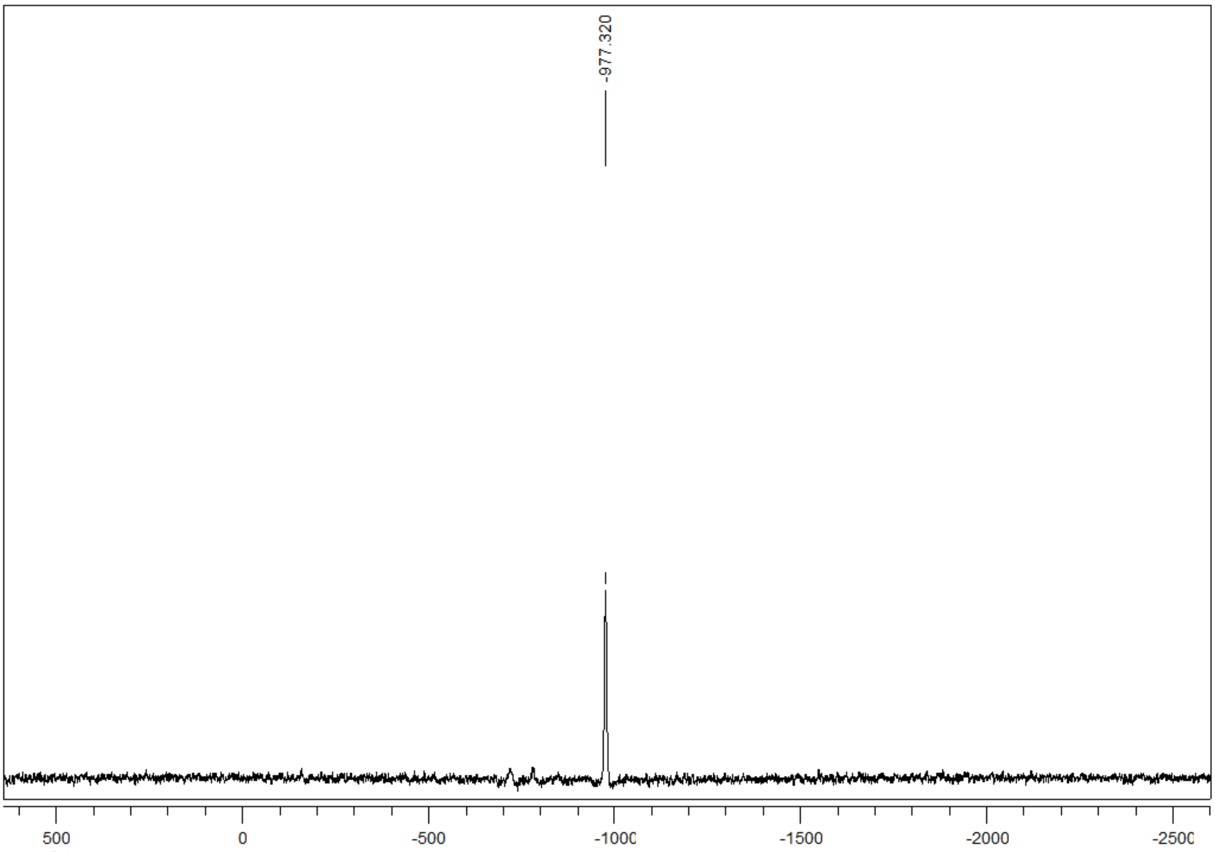

Figure S9. ^{195} Pt NMR spectrum (D_2O) of [Pt^{II}(en)(MetCyt)Cl]NO_3 (**4**).

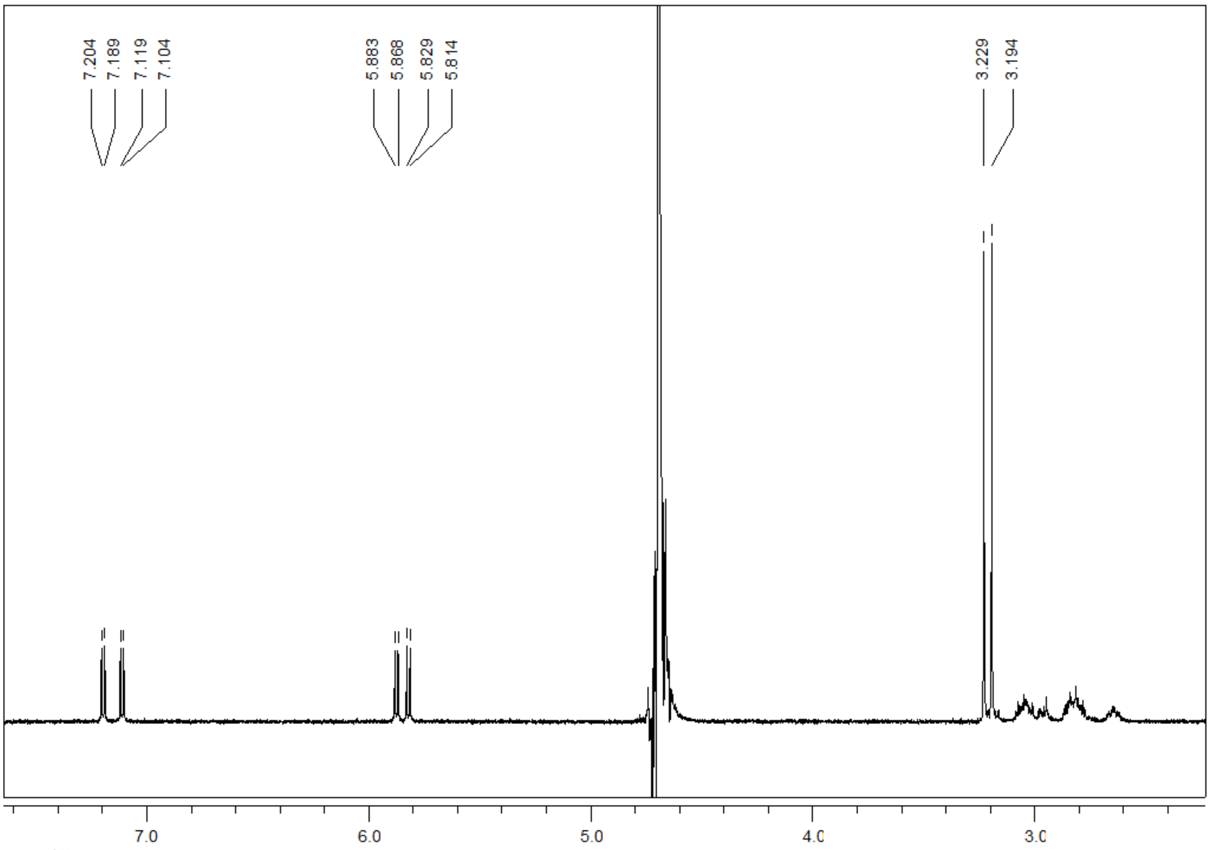

Figure S10. ^{1}H NMR spectrum (D_2O) of ht-[H_2O(en)Pt(MetCyt-H)$_2$Pt(en)OH](ClO_4)$_3$ (**6**).

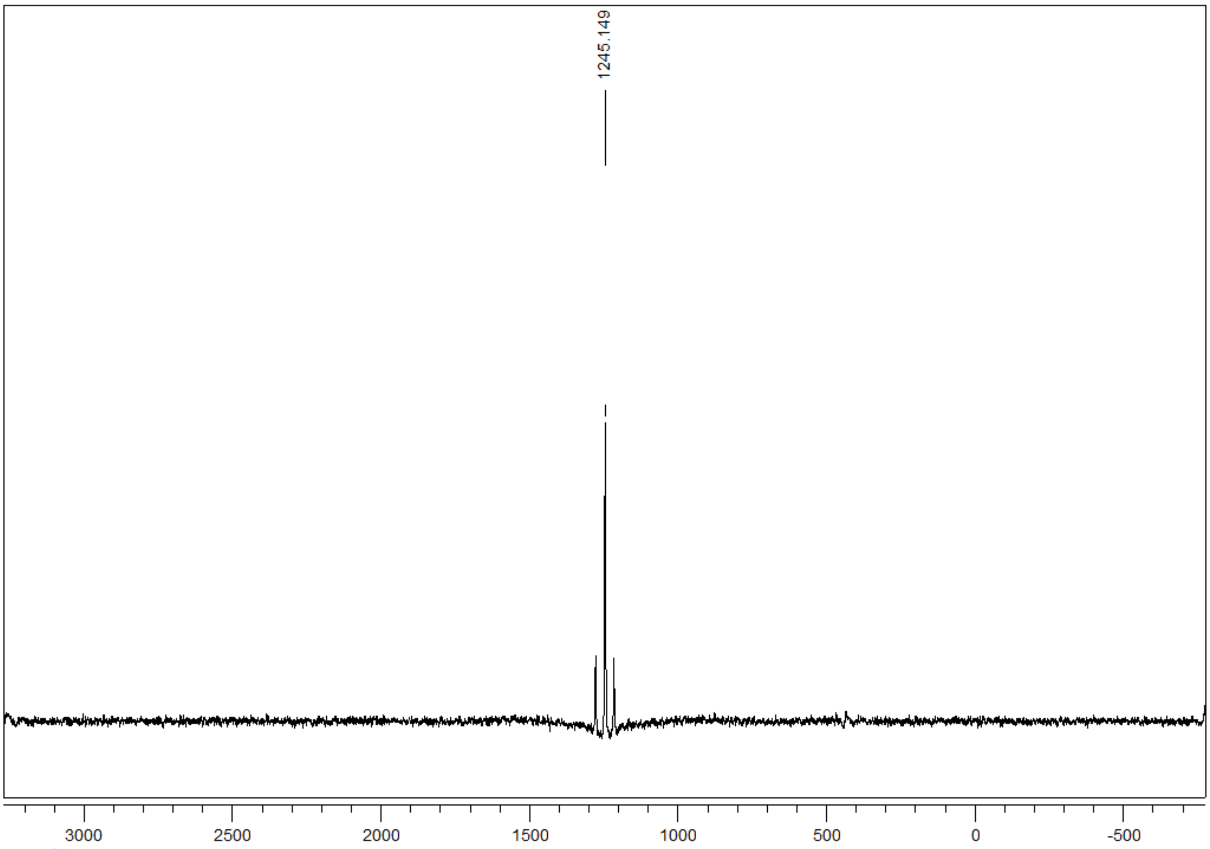

Figure S11. ^{195}Pt NMR spectrum (D_2O) of ht-[H_2O(en)Pt(MetCyt-H)$_2$Pt(en)OH](ClO_4)$_3$ (**6**).

Table S1. Comparison of Geometric Parameters of Head-to-Head α-Pyridonate and Head-to-Tail 1-Methylcytosinate-Bridged Platinum Dimers

Compound	Formal oxidation state	Pt-Pt Distance (Å)	τ(°)[a]	ω(°)[b]	Ref.
Head-Head α-Pyridonate Bridged Platinum Dimers					
$[Pt_2(en)_2(C_5H_4NO)_2]_2(NO_3)_4$ (**9**)	2	2.992(1)	39.6	24.9	33
$[Pt_2(en)_2(C_5H_4NO)_2(NO_2)(NO_3)]_2(NO_3)_5$ (**10**)	3	2.6382(6)	30.7	36.2	17
$[Pt_2(NH_3)_4(C_5H_4NO)_2]_2(NO_3)_4$ (**11**)	2	2.877(1)	30.0	20.3	33
$[Pt_2(NH_3)_4(C_5H_4NO)_2(H_2O)(NO_3)](NO_3)_3$ (**12**)	3	2.540(1)	20.0	23.2	33
Head-Tail 1-Methylcytosinate-Bridged Platinum Dimers					
$[Pt_2(en)_2(MetCyt\text{-}H)_2](NO_3)_2$ (**1**)	2	2.9816(3)	34.4	18.7	c
$[(SO_4)(en)Pt(MeCyt\text{-}H)_2Pt(en)(SO_4)]$ (**5**)	3	2.5982(4)	26.6	28.1	c
$[H_2O(en)Pt(MetCyt\text{-}H)_2Pt(en)OH](ClO_4)_3$ (**6**)	3	2.5569(3)	26.5	24.4	c
$[Pt_2(NH_3)_4(MeCyt\text{-}H)_2](NO_3)_2$ (**7**)	2	2.981(2)	34.0	16.0	22
$[Pt_2(NH_3)_4(MeCyt\text{-}H)_2(NO_2)_2](NO_3)_2$ (**8**)	3	2.584(1)	21.0	25.0	22

[a] τ is the tilt angle between adjacent platinum coordination planes in the dinuclear complex. [b] ω is the average torsion (or twist) angle about the Pt(1)-Pt(2) vector. [c] This work.

Synthesis, Characterization and X-ray structure analysis of [Pt^{II}(dmen)(MetCyt)Cl]NO_3 (S1)

Materials and Methods. All reagents and solvents were obtained from commercial suppliers and were used as received. The starting compound [Pt^{II}(dmen)Cl_2] was synthesized according to standard literature procedures. ^{1}H and ^{195}Pt NMR spectra were recorded with a Bruker Avance III 500 MHz NMR spectrometer at 500.32 (^{1}H) and 107.55 MHz (^{195}Pt) in D_2O at 298 K, using the solvent residual peak for ^{1}H as internal reference. ^{195}Pt chemical shifts were referenced relative to external $K_2[PtCl_4]$. Elemental analyses were performed using a Perkin-Elmer 2400CHN elemental analyzer by the micro laboratory of the Institute of Physical Chemistry, University of Vienna.

[Pt^{II}(dmen)(MetCyt)Cl]NO_3 (S1): [Pt^{II}(dmen)Cl_2] (0.109 g, $3.068{\cdot}10^{-4}$ mol) was dissolved in 40 ml of *N,N*-dimethylformamide, and to this solution 1 equiv. of $AgNO_3$ (0.0521g, $3{\cdot}068.10^{-4}$ mol) was added. The reaction mixture was then continuously stirred in the dark for 24h at room temperature. The AgCl precipitate was filtered off, using celite as a filter. To the filtrate [Pt^{II}(dmen)(H_2O)Cl]NO_3, 1 equiv. of MeCyt (0.0384 g, $3.068{\cdot}10^{-4}$ mol) was added. The reaction mixture was then stirred for 24 h at room temperature. A pale yellow solution was obtained. This solution was filtered and concentrated to 3 ml under reduced pressure; acetone was then added to obtained the product **S1**. A pale yellow product **3** was filtered, washed with CH_2Cl_2 and acetone. Crystals of **S1·H$_2$O** suitable for X-ray data collection were grown via vapor diffusion of acetone into a solution of **S1** in DMF. The final product was dried in vacuo. Yield 101 mg, 65 %. Anal. Calcd. for $C_9H_{19}N_6ClO_4Pt$: C 21.36; H 3.76; N 16.62. Found: C 21.47; H 3.63; N 16.77. ^{1}H NMR (D_2O): δ = 7.52 (m, H; C_6H), 5.94 (m, H; C_5H), 3.34 (s, 3H; CH_3), 3.33 (s, 3H; CH_3), 2.92-2.27 (m, 4H; CH_2). ^{195}Pt NMR (400 MHz, D_2O, 23 °C): δ = -983 ppm.

Crystallographic Structure Determination.

X-ray diffraction measurements for **S1** were performed on a Bruker X8 APEXII CCD diffractometer. A single crystal was positioned at 40 mm from the detector, and 2204 frames were measured, each for 20 s over 1° scan width. The data were processed using SAINT software.[1] Crystal data, data collection parameters, and structure refinement details are given in Table S2. The structure was solved by direct methods and refined by full-matrix least-squares techniques. Non-H atoms were refined with anisotropic displacement parameters. H atoms were inserted in calculated positions and refined with a riding model. The positions of H atoms in the disordered water molecule have not been calculated. The following software, computer and table were used: structure solution, *SHELXS-97*;[2] refinement, *SHELXL-97*;[3] molecular diagrams, *ORTEP*;[4] computer, Pentium IV; scattering factors.[5] Crystal data, data collection parameters, and structure refinement details are given in Table S2.

Table S2. Crystal data and details of data collection for **S1·H$_2$O**

Complex	**S1·H$_2$O**
Empirical formula	$C_9H_{21}ClN_6O_5Pt$
Fw	523.86
space group	$P2_1/c$
a [Å]	12.4934(4)
b [Å]	12.7860(4)
c [Å]	12.6634(4)
V [Å^3]	1771.37(10)
Z	4
λ [Å]	0.71073
ρ_{calcd} [g cm^{-3}]	1.964
crystal size [mm^3]	$0.13 \times 0.10 \times 0.02$
T [K]	100
μ [cm^{-1}]	81.01
R1[a]	0.0279
wR2[b]	0.0735
GOF[c]	1.068

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.
[c] $GOF = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

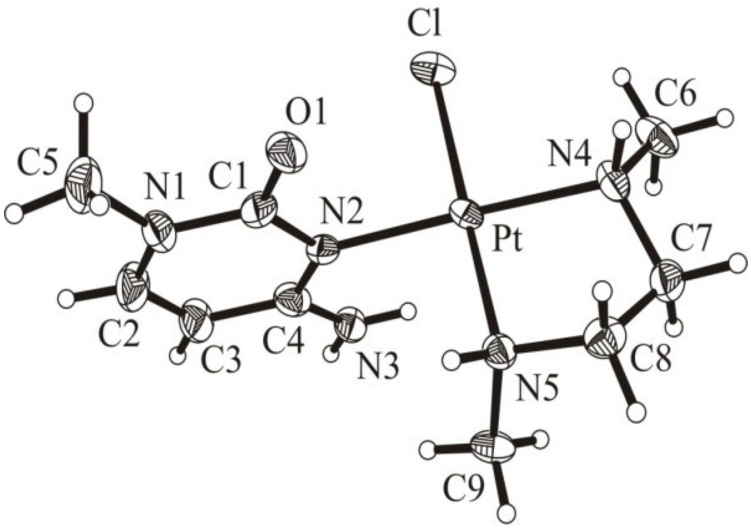

Figure S12. Structure of the cation [Pt^{II}(dmen)(MeCyt)Cl]$^+$ in **S1** displaying ellipsoids at 50% probability. Selected bond lengths (Å) and angles (deg): Pt–N4, 2.042(5); Pt–N5, 2.054(5); Pt–N2, 2.030(5); Pt–Cl, 2.3050(14); N2–Pt–N5, 92.62(18); N4–Pt–N5, 84.48(19); N2–Pt–Cl, 87.90(13); N4–Pt–Cl, 94.94(14).

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[1] *SAINT-Plus (Version 7.06a) and APEX2;* Bruker-Nonius AXS Inc.: Madison, Wisconsin, USA, 2004.

[2] G. M. Sheldrick, *SHELXS-97*, *Program for Crystal Structure Solution*; University of Göttingen, Göttingen, Germany, 1997.

[3] G. M. Sheldrick, *SHELXL-97*, *Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, 1997.

[4] G. K. Johnson, Report ORNL-5138; OAK Ridge National Laboratory; Oak Ridge, TN, 1976.

[5] *International Tables for X-ray Crystallography*; Kluwer Academic Press: Dordrecht, The Netherlands, 1992; Vol. C, Tables 4.2.6.8 and 6.1.1.4.