

# Electronic Supplementary Information

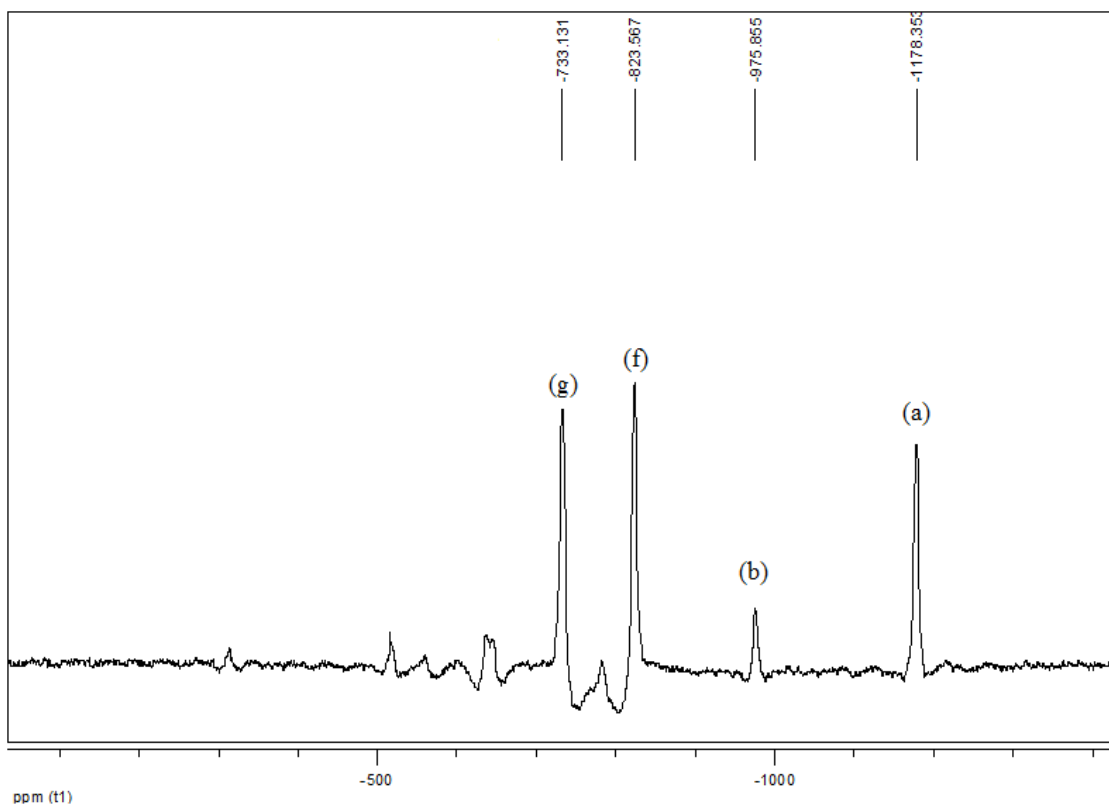
## Synthesis and structures of novel 1-methylcytosinato-bridged (ethylenediamine)platinum(II) and platinum(III) dinuclear complexes

Vesna M. Djinovic, Markus Galanski, Vladimir B. Arion, and Bernhard K. Keppler\*

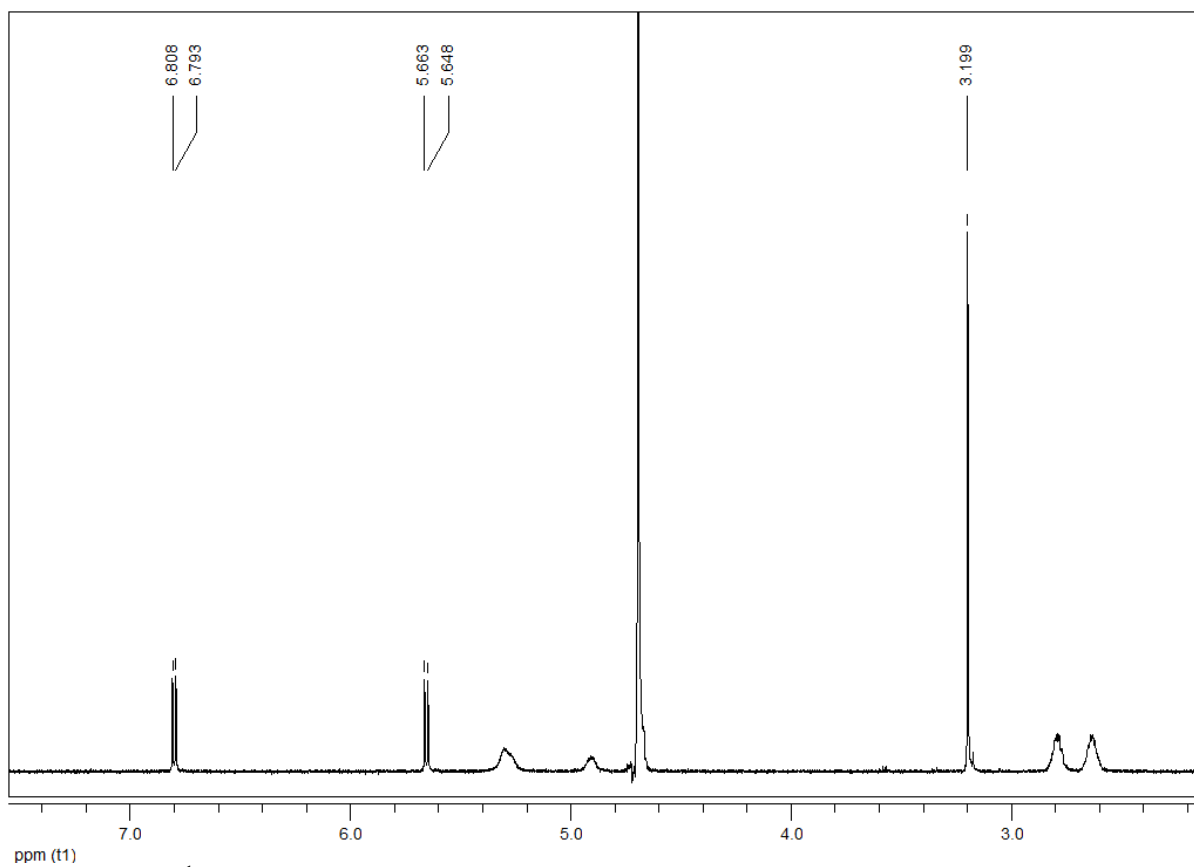
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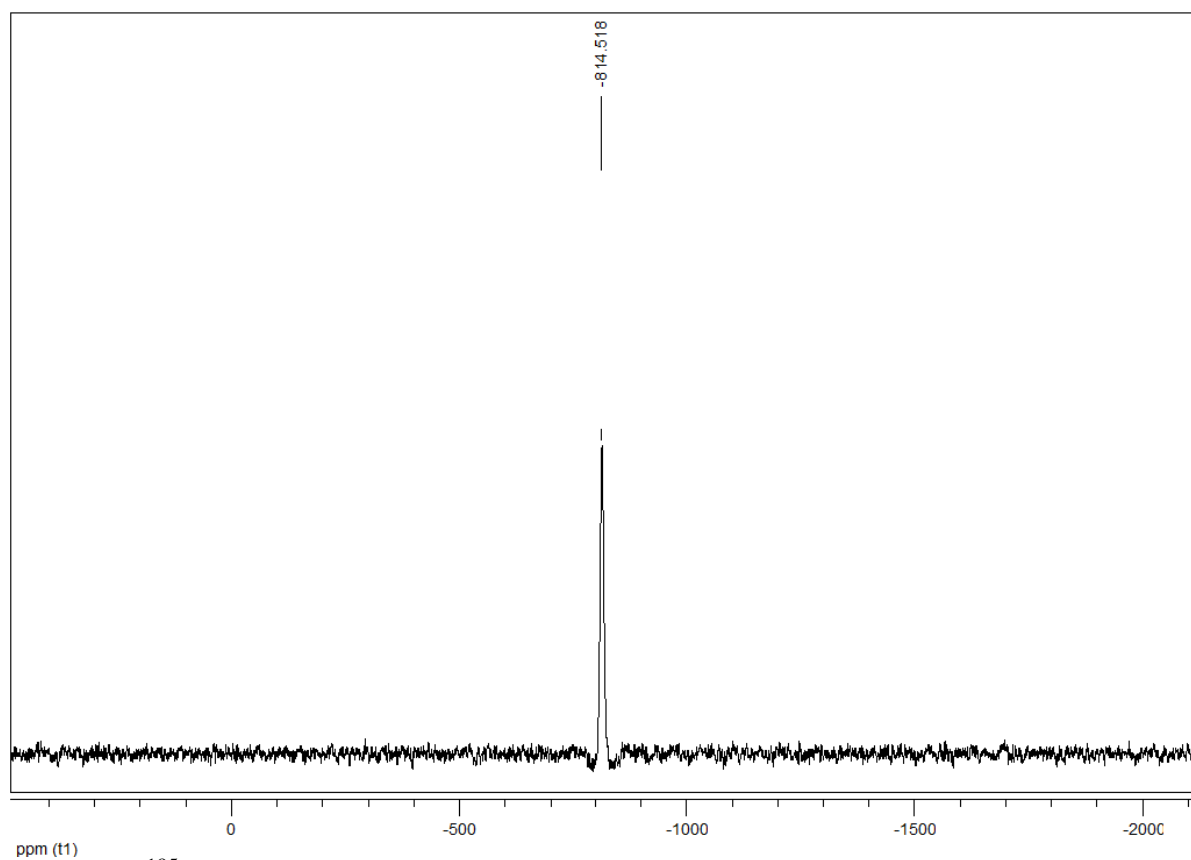
- Figure S1.**  $^{195}\text{Pt}$  NMR (9:1  $\text{H}_2\text{O}:\text{D}_2\text{O}$ ) spectrum of the products obtained from the reaction of  $[\text{Pt}(\text{en})(\text{H}_2\text{O})_2]^{2+}$  with 1 equiv of 1-MeCyt.
- Figure S2.**  $^1\text{H}$  NMR spectrum (9:1  $\text{H}_2\text{O}:\text{D}_2\text{O}$ ) of  $\text{ht}-[(\text{en})\text{Pt}(\text{MetCyt-H})_2\text{Pt}(\text{en})](\text{NO}_3)_2\cdot\text{H}_2\text{O}$  (**1**).
- Figure S3.**  $^{195}\text{Pt}$  NMR (9:1  $\text{H}_2\text{O}:\text{D}_2\text{O}$ ) spectrum of  $\text{ht}-[(\text{en})\text{Pt}(\text{MetCyt-H})_2\text{Pt}(\text{en})](\text{NO}_3)_2\cdot\text{H}_2\text{O}$  (**1**).
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- Figure S9.**  $^{195}\text{Pt}$  NMR spectrum ( $\text{D}_2\text{O}$ ) of  $[\text{Pt}^{\text{II}}(\text{en})(\text{MetCyt})\text{Cl}]\text{NO}_3$  (**4**).
- Figure S10.**  $^1\text{H}$  NMR spectrum ( $\text{D}_2\text{O}$ ) of  $\text{ht}-[\text{H}_2\text{O}(\text{en})\text{Pt}(\text{MetCyt-H})_2\text{Pt}(\text{en})\text{OH}](\text{ClO}_4)_3$  (**6**).
- Figure S11.**  $^{195}\text{Pt}$  NMR spectrum ( $\text{D}_2\text{O}$ ) of  $\text{ht}-[\text{H}_2\text{O}(\text{en})\text{Pt}(\text{MetCyt-H})_2\text{Pt}(\text{en})\text{OH}](\text{ClO}_4)_3$  (**6**).
- Table S1.** Comparison of Geometric Parameters of Head-to-Head  $\alpha$ -Pyridonate and Head-to-Tail 1-Methylcytosinate-Bridged Platinum Dimers
- Synthesis, Characterization and X-ray structure analysis of  $[\text{Pt}^{\text{II}}(\text{dmen})(\text{MetCyt})\text{Cl}]\text{NO}_3$  (**S1**)**
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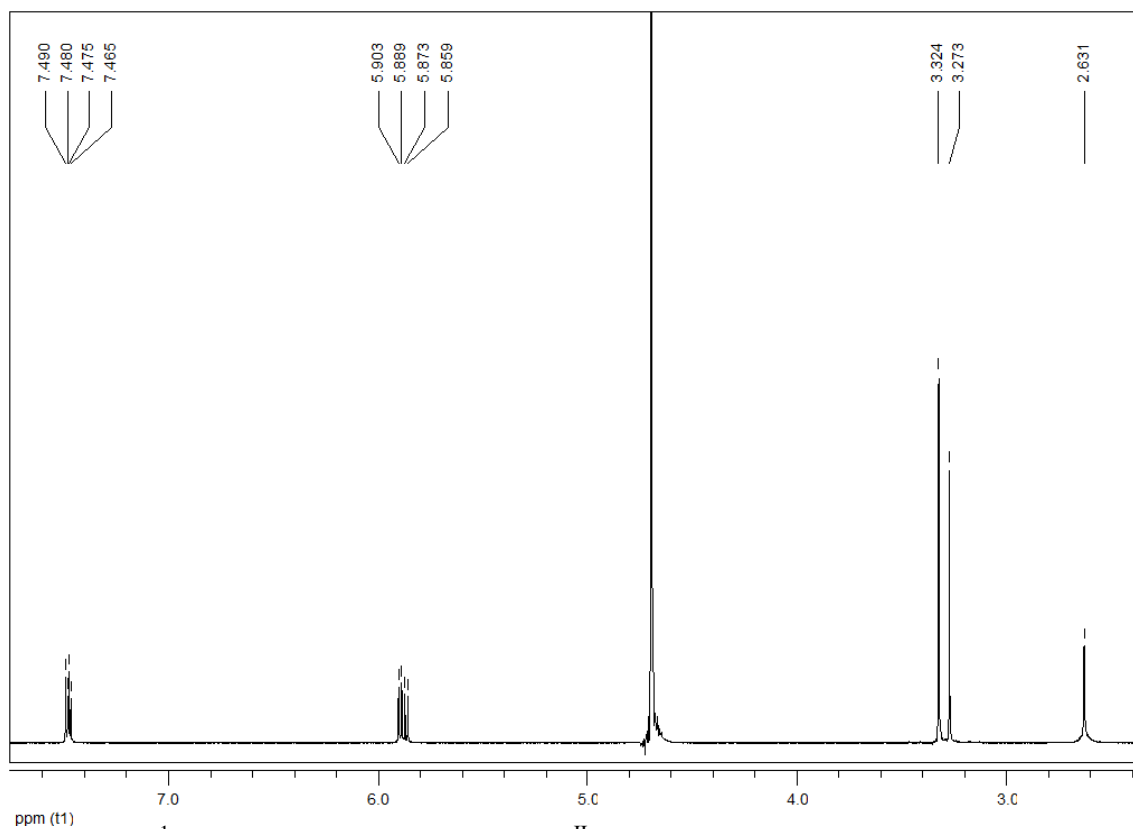
**Figure S1.**  $^{195}\text{Pt}$  NMR (9:1  $\text{H}_2\text{O}:\text{D}_2\text{O}$ ) spectrum of the products obtained from the reaction of  $[\text{Pt}(\text{en})(\text{H}_2\text{O})_2]^{2+}$  with 1 equiv of 1-MeCyt (as described in the Experimental Section) after 24 h at 40 °C. The pH of the solution was 3. The chemical shifts are referenced to  $\text{K}_2[\text{PtCl}_4]$ . The resonances are assigned as follows: (a)  $[\text{Pt}(\text{en})(\text{MeCyt})_2]^{2+}$  (**3**), -1178 ppm; (b)  $[\text{Pt}(\text{en})(\text{MetCyt})\text{Cl}]^+$  (**4**), -975 ppm; (f)  $\text{ht}-[(\text{en})\text{Pt}(\text{MetCyt-H})_2\text{Pt}(\text{en})]^{2+}$  (**1**), -823 ppm; (g)  $[\text{Pt}(\text{en})(\text{MetCyt-H})(\text{H}_2\text{O})]^+$ , -733 ppm.



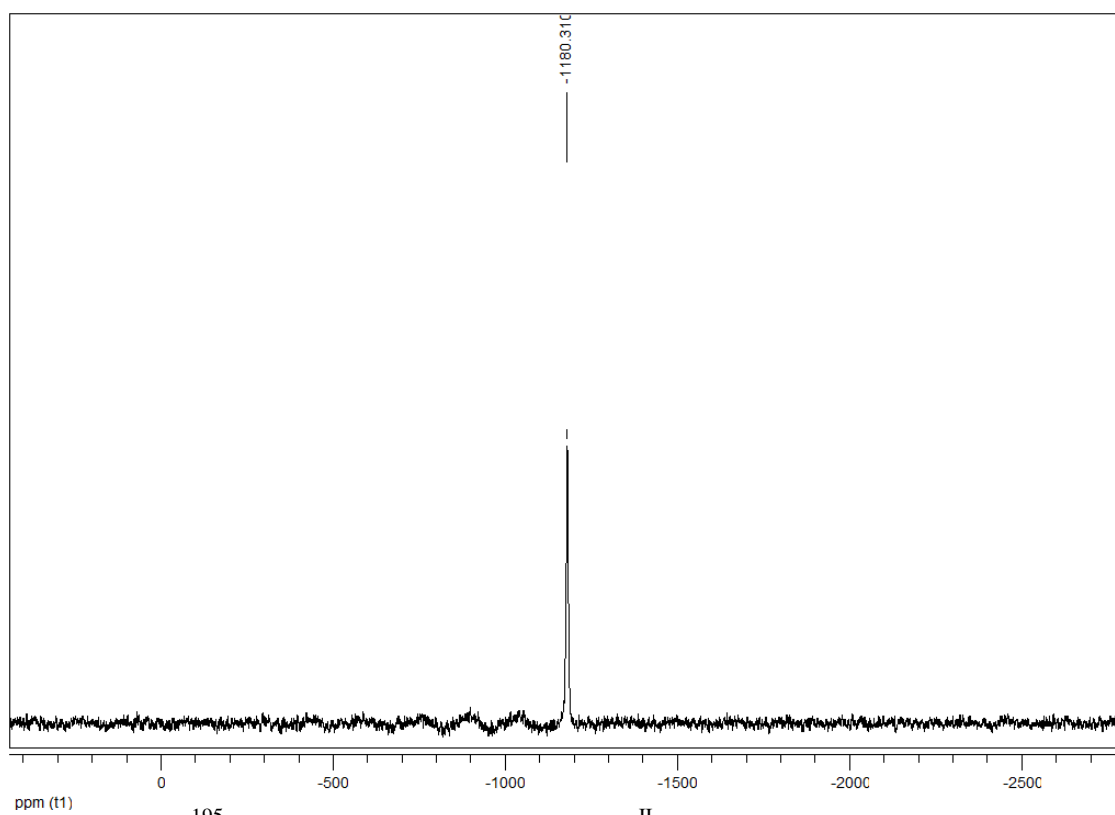
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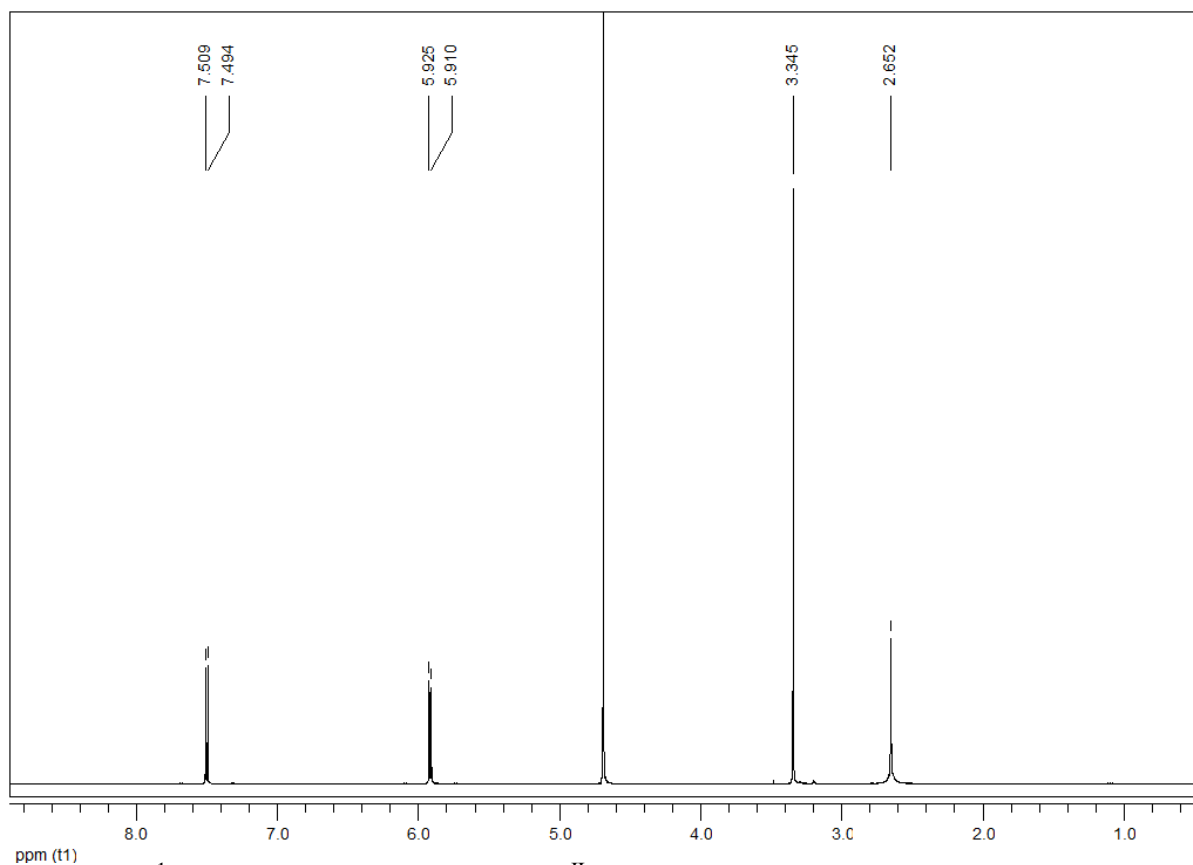
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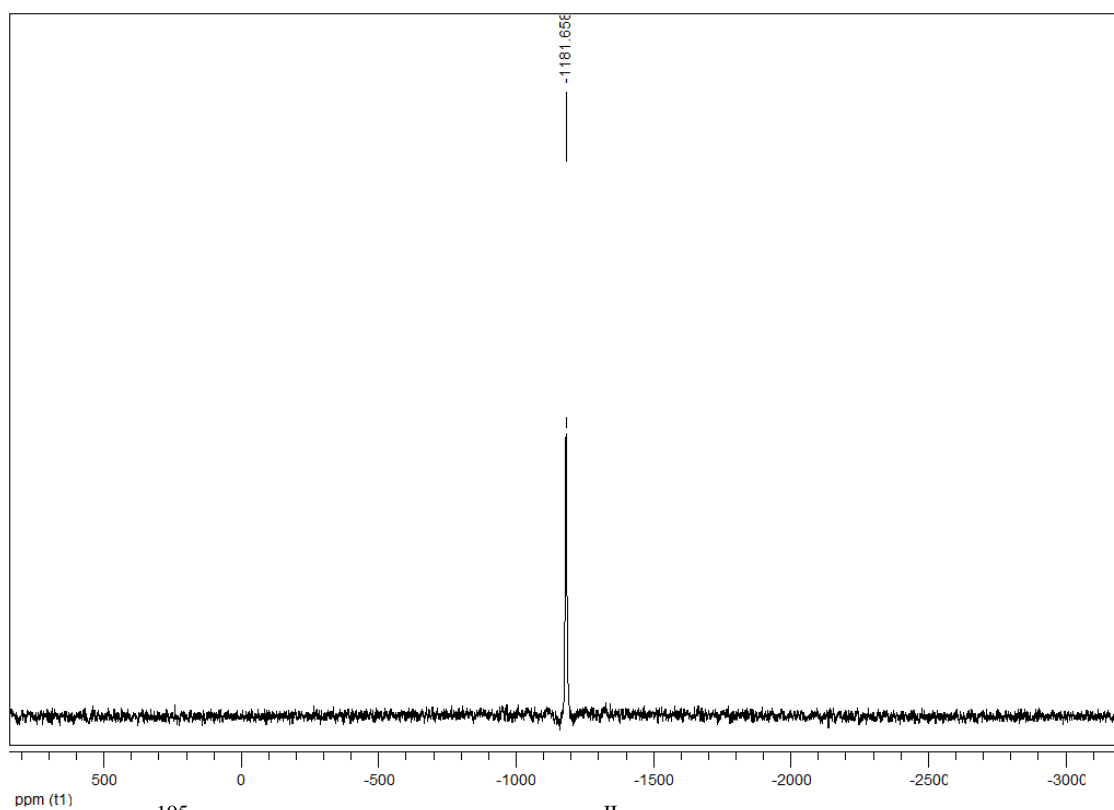
**Figure S4.**  $^1\text{H}$  NMR spectrum ( $\text{D}_2\text{O}$ ) of  $[\text{Pt}^{\text{II}}(\text{en})(\text{MetCyt})_2](\text{NO}_3)_2 \cdot \text{MetCyt}$  (**2**).



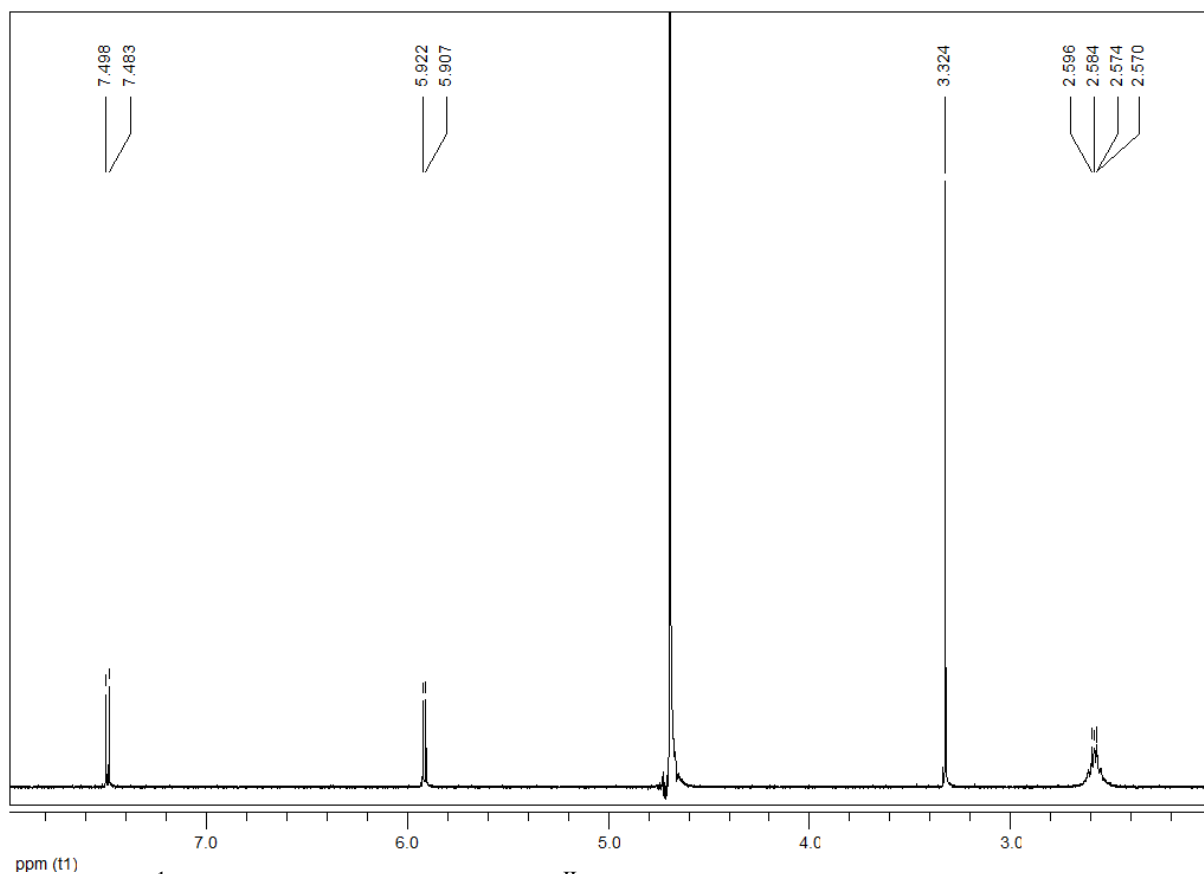
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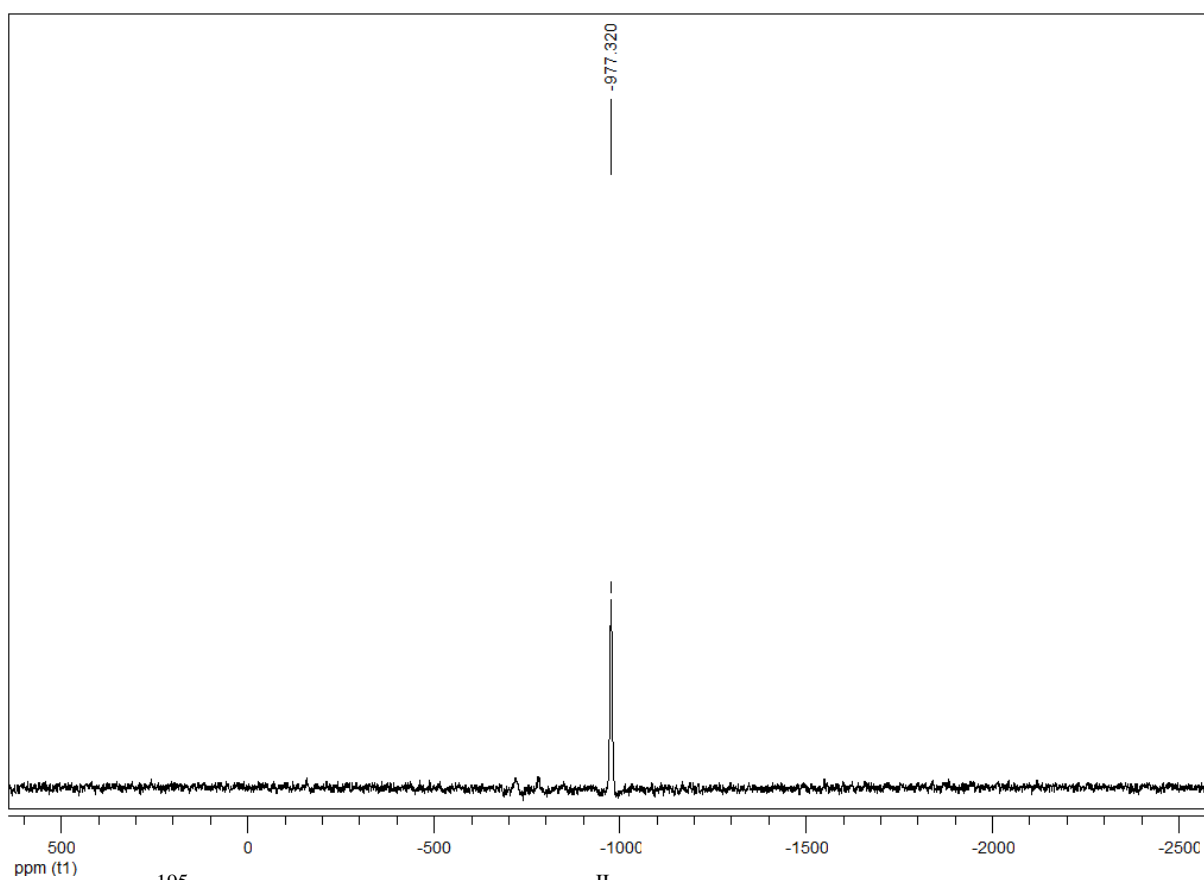
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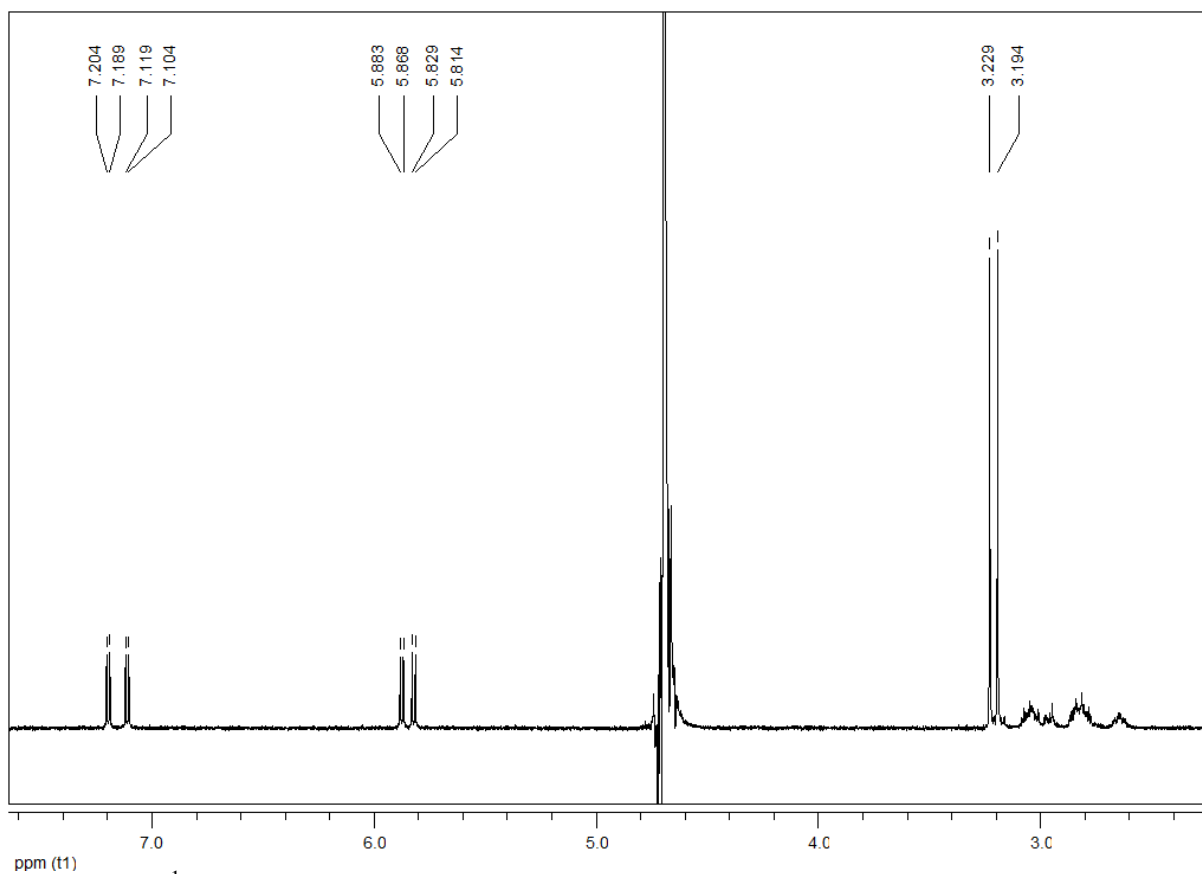
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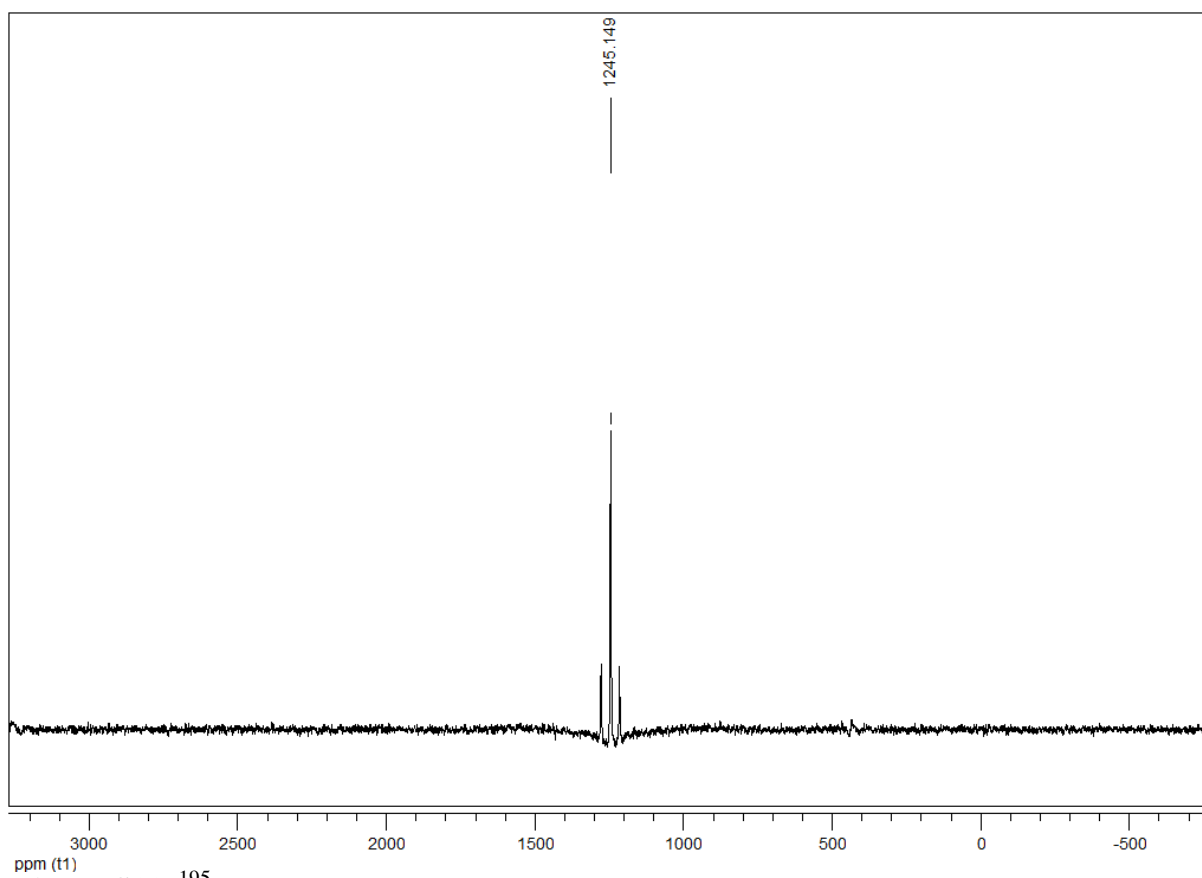
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**Figure S9.**  $^{195}\text{Pt}$  NMR spectrum ( $\text{D}_2\text{O}$ ) of  $[\text{Pt}^{\text{II}}(\text{en})(\text{MetCyt})\text{Cl}]\text{NO}_3$  (**4**).



**Figure S10.**  $^1\text{H}$  NMR spectrum ( $\text{D}_2\text{O}$ ) of  $\text{ht-}[\text{H}_2\text{O}(\text{en})\text{Pt}(\text{MetCyt-H})_2\text{Pt}(\text{en})\text{OH}](\text{ClO}_4)_3$  (**6**).



**Figure S11.**  $^{195}\text{Pt}$  NMR spectrum ( $\text{D}_2\text{O}$ ) of  $\text{ht-}[\text{H}_2\text{O}(\text{en})\text{Pt}(\text{MetCyt-H})_2\text{Pt}(\text{en})\text{OH}](\text{ClO}_4)_3$  (**6**).

**Table S1.** Comparison of Geometric Parameters of Head-to-Head  $\alpha$ -Pyridonate and Head-to-Tail 1-Methylcytosinate-Bridged Platinum Dimers

Compound	Formal oxidation state	Pt-Pt Distance (Å)	$\tau(^{\circ})^a$	$\omega(^{\circ})^b$	Ref.
Head-Head $\alpha$ -Pyridonate Bridged Platinum Dimers					
[Pt <sub>2</sub> (en) <sub>2</sub> (C <sub>5</sub> H <sub>4</sub> NO) <sub>2</sub> ](NO <sub>3</sub> ) <sub>4</sub> ( <b>9</b> )	2	2.992(1)	39.6	24.9	33
[Pt <sub>2</sub> (en) <sub>2</sub> (C <sub>5</sub> H <sub>4</sub> NO) <sub>2</sub> (NO <sub>2</sub> )(NO <sub>3</sub> ) <sub>2</sub> ](NO <sub>3</sub> ) <sub>5</sub> ( <b>10</b> )	3	2.6382(6)	30.7	36.2	17
[Pt <sub>2</sub> (NH <sub>3</sub> ) <sub>4</sub> (C <sub>5</sub> H <sub>4</sub> NO) <sub>2</sub> ](NO <sub>3</sub> ) <sub>4</sub> ( <b>11</b> )	2	2.877(1)	30.0	20.3	33
[Pt <sub>2</sub> (NH <sub>3</sub> ) <sub>4</sub> (C <sub>5</sub> H <sub>4</sub> NO) <sub>2</sub> (H <sub>2</sub> O)(NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>3</sub> ( <b>12</b> )	3	2.540(1)	20.0	23.2	33
Head-Tail 1-Methylcytosinate-Bridged Platinum Dimers					
[Pt <sub>2</sub> (en) <sub>2</sub> (MetCyt-H) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> ( <b>1</b> )	2	2.9816(3)	34.4	18.7	c
[(SO <sub>4</sub> )(en)Pt(MeCyt-H) <sub>2</sub> Pt(en)(SO <sub>4</sub> )] ( <b>5</b> )	3	2.5982(4)	26.6	28.1	c
[H <sub>2</sub> O(en)Pt(MeCyt-H) <sub>2</sub> Pt(en)OH](ClO <sub>4</sub> ) <sub>3</sub> ( <b>6</b> )	3	2.5569(3)	26.5	24.4	c
[Pt <sub>2</sub> (NH <sub>3</sub> ) <sub>4</sub> (MeCyt-H) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> ( <b>7</b> )	2	2.981(2)	34.0	16.0	22
[Pt <sub>2</sub> (NH <sub>3</sub> ) <sub>4</sub> (MeCyt-H) <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> ( <b>8</b> )	3	2.584(1)	21.0	25.0	22

<sup>a</sup>  $\tau$  is the tilt angle between adjacent platinum coordination planes in the dinuclear complex. <sup>b</sup>

$\omega$  is the average torsion (or twist) angle about the Pt(1)-Pt(2) vector. <sup>c</sup> This work.



## Synthesis, Characterization and X-ray structure analysis of [Pt<sup>II</sup>(dmen)(MetCyt)Cl]NO<sub>3</sub> (**S1**)

**Materials and Methods.** All reagents and solvents were obtained from commercial suppliers and were used as received. The starting compound [Pt<sup>II</sup>(dmen)Cl<sub>2</sub>] was synthesized according to standard literature procedures. <sup>1</sup>H and <sup>195</sup>Pt NMR spectra were recorded with a Bruker Avance III 500 MHz NMR spectrometer at 500.32 (<sup>1</sup>H) and 107.55 MHz (<sup>195</sup>Pt) in D<sub>2</sub>O at 298 K, using the solvent residual peak for <sup>1</sup>H as internal reference. <sup>195</sup>Pt chemical shifts were referenced relative to external K<sub>2</sub>[PtCl<sub>4</sub>]. 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<sup>II</sup>(dmen)(MetCyt)Cl]NO<sub>3</sub> (**S1**):** [Pt<sup>II</sup>(dmen)Cl<sub>2</sub>] (0.109 g, 3.068·10<sup>-4</sup> mol) was dissolved in 40 ml of *N,N*-dimethylformamide, and to this solution 1 equiv. of AgNO<sub>3</sub> (0.0521 g, 3.068·10<sup>-4</sup> 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<sup>II</sup>(dmen)(H<sub>2</sub>O)Cl]NO<sub>3</sub>, 1 equiv. of MeCyt (0.0384 g, 3.068·10<sup>-4</sup> 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 obtain the product **S1**. A pale yellow product **3** was filtered, washed with CH<sub>2</sub>Cl<sub>2</sub> and acetone. Crystals of **S1**·H<sub>2</sub>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<sub>9</sub>H<sub>19</sub>N<sub>6</sub>ClO<sub>4</sub>Pt: C 21.36; H 3.76; N 16.62. Found: C 21.47; H 3.63; N 16.77. <sup>1</sup>H NMR (D<sub>2</sub>O): δ = 7.52 (m, H; C<sub>6</sub>H), 5.94 (m, H; C<sub>5</sub>H), 3.34 (s, 3H; CH<sub>3</sub>), 3.33 (s, 3H; CH<sub>3</sub>), 2.92-2.27 (m, 4H; CH<sub>2</sub>). <sup>195</sup>Pt NMR (400 MHz, D<sub>2</sub>O, 23 °C): δ = -983 ppm.

### Crystallographic Structure Determination.

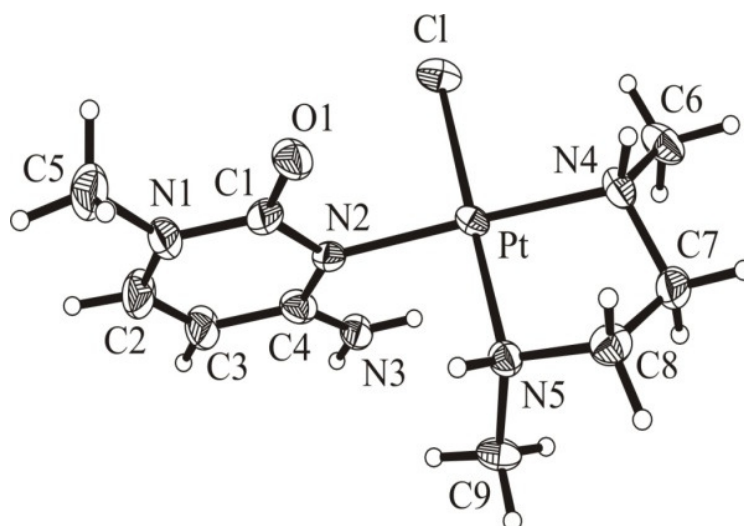
X-ray diffraction measurements for **S1** were performed on a Bruker X8 APEXII CCD diffractometer. A single crystal was positioned at 40 mm from the detector, and 2204 frames were measured, each for 20 s over 1° scan width. The data were processed using SAINT software.<sup>1</sup> Crystal data, data 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*;<sup>2</sup> refinement, *SHELXL-97*;<sup>3</sup> molecular diagrams, *ORTEP*;<sup>4</sup> computer, Pentium IV; scattering factors.<sup>5</sup> 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<sub>2</sub>O**

Complex	<b>S1·H<sub>2</sub>O</b>
Empirical formula	C <sub>9</sub> H <sub>21</sub> ClN <sub>6</sub> O <sub>5</sub> Pt
Fw	523.86
space group	<i>P2<sub>1</sub>/c</i>
<i>a</i> [Å]	12.4934(4)
<i>b</i> [Å]	12.7860(4)
<i>c</i> [Å]	12.6634(4)
<i>V</i> [Å <sup>3</sup> ]	1771.37(10)
<i>Z</i>	4
$\lambda$ [Å]	0.71073
$\rho_{\text{calcd}}$ [g cm <sup>-3</sup> ]	1.964
crystal size [mm <sup>3</sup> ]	0.13 × 0.10 × 0.02
<i>T</i> [K]	100
$\mu$ [cm <sup>-1</sup> ]	81.01
R1 <sup>[a]</sup>	0.0279
wR2 <sup>[b]</sup>	0.0735
GOF <sup>[c]</sup>	1.068

[a]  $R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ . [b]  $wR2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$ .

[c]  $GOF = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{(n - p)} \right\}^{1/2}$ , where *n* is the number of reflections and *p* is the total number of parameters refined.



**Figure S12.** Structure of the cation  $[\text{Pt}^{\text{II}}(\text{dmen})(\text{MeCyt})\text{Cl}]^+$  in **S1** displaying ellipsoids at 50% probability. Selected bond lengths ( $\text{\AA}$ ) 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).

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

<sup>2</sup> G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*; University of Göttingen, Göttingen, Germany, 1997.

<sup>3</sup> G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, 1997.

<sup>4</sup> G. K. Johnson, Report ORNL-5138; OAK Ridge National Laboratory; Oak Ridge, TN, 1976.

<sup>5</sup> *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.