Electronic Supporting Information for

Oxidative Halogenation of Cisplatin and Carboplatin: Synthesis, Spectroscopy, and Crystal and Molecular Structures of Pt(IV) Prodrugs

Timothy C. Johnstone, Sarah M. Alexander, Justin J. Wilson, and Stephen J. Lippard*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Correspondence to: lippard@mit.edu

Contents

Figure S1. ^{1}H NMR spectrum of **1** in DMF-d_7.
Figure S2. ^{1}H NMR spectrum of **1** in DMSO-d_6.
Figure S3. ^{14}N NMR spectrum of **1** in DMSO-d_6.
Figure S4. ^{14}N{^{1}H} NMR spectrum of **1** in DMSO-d_6.
Figure S5. ^{195}N NMR spectrum of **1** in DMF-d_7.
Figure S6. ^{195}N NMR spectrum of **1** in DMSO-d_6.
Figure S8. ^{1}H NMR spectrum of **2** in DMSO-d_6.
Figure S7. ^{1}H NMR spectrum of **2** in DMF-d_7.
Figure S9. ^{14}N NMR spectrum of **2** in DMSO-d_6.
Figure S10. ^{195}Pt NMR spectrum of **2** in DMSO-d_6.
Figure S11. ^{1}H NMR spectrum of **3** in DMF-d_7.
Figure S12. ^{195}Pt NMR spectrum of **3** in DMSO-d_6 .
Figure S13. ^{1}H NMR spectrum of **4** in DMF-d_7.
Figure S14. ^{13}C{^{1}H} NMR spectrum of **4** in DMF-d_7.
Figure S15. ^{195}Pt NMR spectrum of **4** in DMF-d_7.
Figure S16. ^{1}H NMR spectrum of **5** in DMF-d_7.
Figure S17. ^{13}C{^{1}H} NMR spectrum of **5** in DMF-d_7.
Figure S18. ^{195}Pt NMR spectrum of **5** in DMF-d_7.
Figure S19. ^{1}H NMR spectrum of **6** in DMF-d_7.
Figure S20. ^{13}C{^{1}H} NMR spectrum of **6** in DMF-d_7.
Figure S21. ^{195}Pt NMR spectrum of **6** in DMF-d_7.
Figure S22. ^{1}H NMR spectrum in DMSO-d_6 of the side product from the synthesis of **6**.
Figure S23. Depiction of the molecules from the crystal structure of **1**·3DMF·½Et_2O.
Figure S24. Depiction of the molecules from the crystal structure of **1**·2DMSO.
Figure S25. Depiction of the molecules from the crystal structure of *cis,trans*-[Pt(CBDCA)$(NH_3)_2(OH)_2$].
Figure S26. Depiction of the molecules from the crystal structure of *fac*-[Pt$(NH_3)_3Br_3$]Br·DMF.
Figure S27. Depiction of the molecules from the crystal structure of *fac*-[Pt$(NH_3)_3Cl_3$]Cl·DMF.
Table S1. Crystal data and structure refinement for *cis*-[Pt$(NH_3)_2Cl_4$]·3DMF·½Et_2O.
Table S2. Crystal data and structure refinement for *cis*-[Pt$(NH_3)_2Cl_4$]·3DMSO.
Table S3. Crystal data and structure refinement for *cis*,*trans*-[Pt$(NH_3)_2(OH)_2$CBDCA]·3H_2O.
Table S4. Crystal data and structure refinement for *fac*-[Pt$(NH_3)_3Br_3$]Br·DMF.

Table S5. Crystal data and structure refinement for *fac*-[$Pt(NH_3)_3Cl_3$]Cl·DMF.
Table S6. Cartesian coordinates (Å) of the DFT-optimized structure of **4**.
Table S7. Cartesian coordinates (Å) of the DFT-optimized structure of **5**.
Table S8. Cartesian coordinates (Å) of the DFT-optimized structure of **6**.
Table S9. Hydrogen bonding metrics of **1**·3DMF.
Table S10. Hydrogen bonding metrics **3**·3DMF.
Table S11. Hydrogen bonding metrics of **4**·DMF.
Table S12. Hydrogen bonding metrics of **5**·DMF.
Table S13. Hydrogen bonding metrics of **7**·3DMF·Et_2O.
Table S14. Hydrogen bonding metrics of *cis*-[$Pt(NH_3)_2Cl_4$]·3DMF·½Et_2O (ESI1).
Table S15. Hydrogen bonding metrics of *cis*-[$Pt(NH_3)_2Cl_4$]·3DMSO (ESI2).
Table S16. Hydrogen bonding metrics of *cis*,*trans*-[$Pt(NH_3)_2(OH)_2$CBDCA]·$3H_2O$ (ESI3).
Table S17. Hydrogen bonding metrics of *fac*-[$Pt(NH_3)_3Br_3$]Br·DMF (ESI4).
Table S18. Hydrogen bonding metrics of *fac*-[$Pt(NH_3)_3Br_3$]Br·DMF (ESI5).

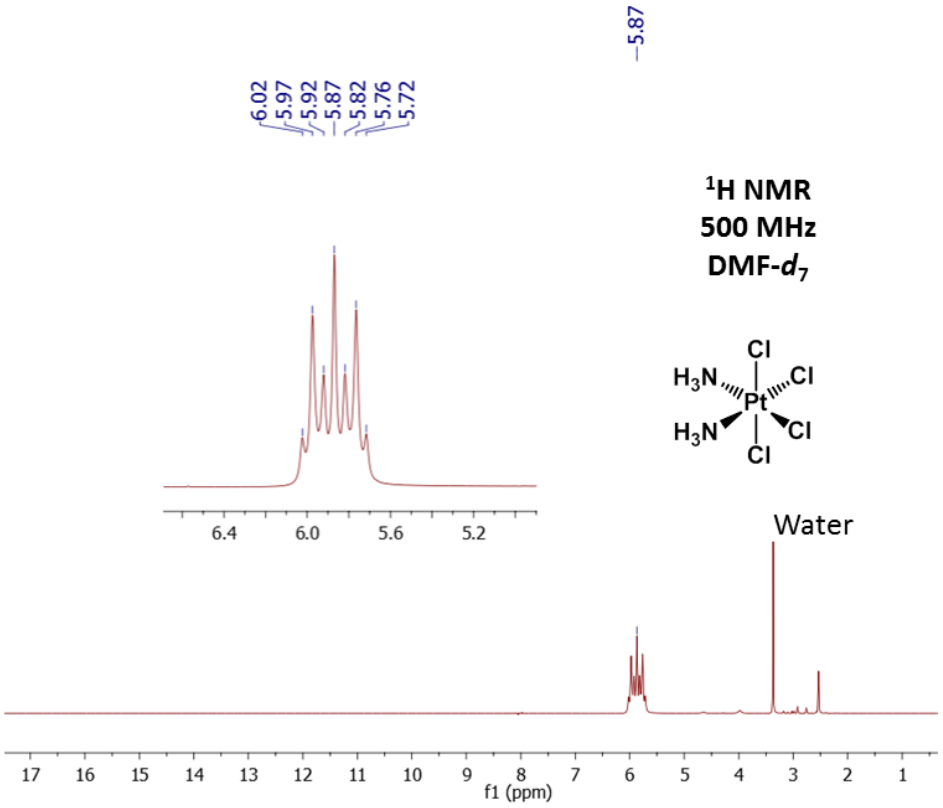

Figure S1. ^{1}H NMR spectrum of **1** in DMF-d_7.

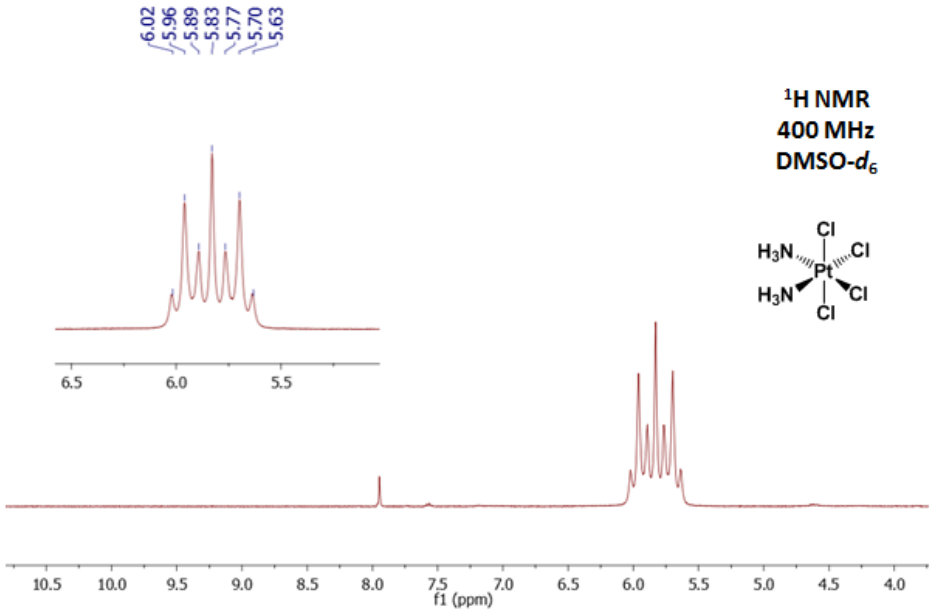

Figure S2. ^{1}H NMR spectrum of **1** in DMSO-d_6.

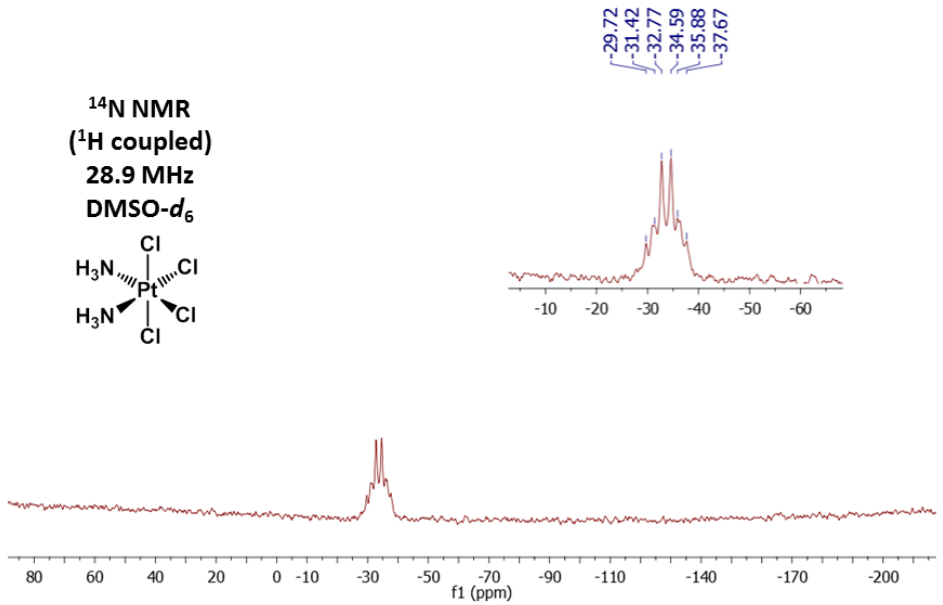

Figure S3. ^{14}N NMR spectrum of **1** in DMSO-d_6.

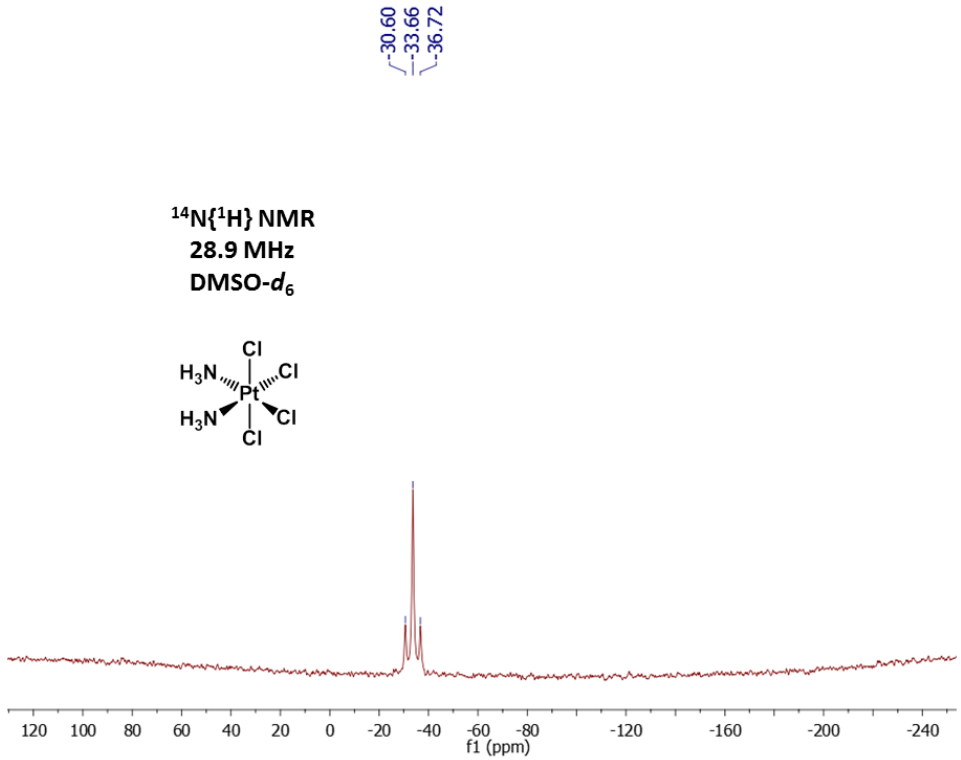

Figure S4. ^{14}N{^{1}H} NMR spectrum of **1** in DMSO-d_6.

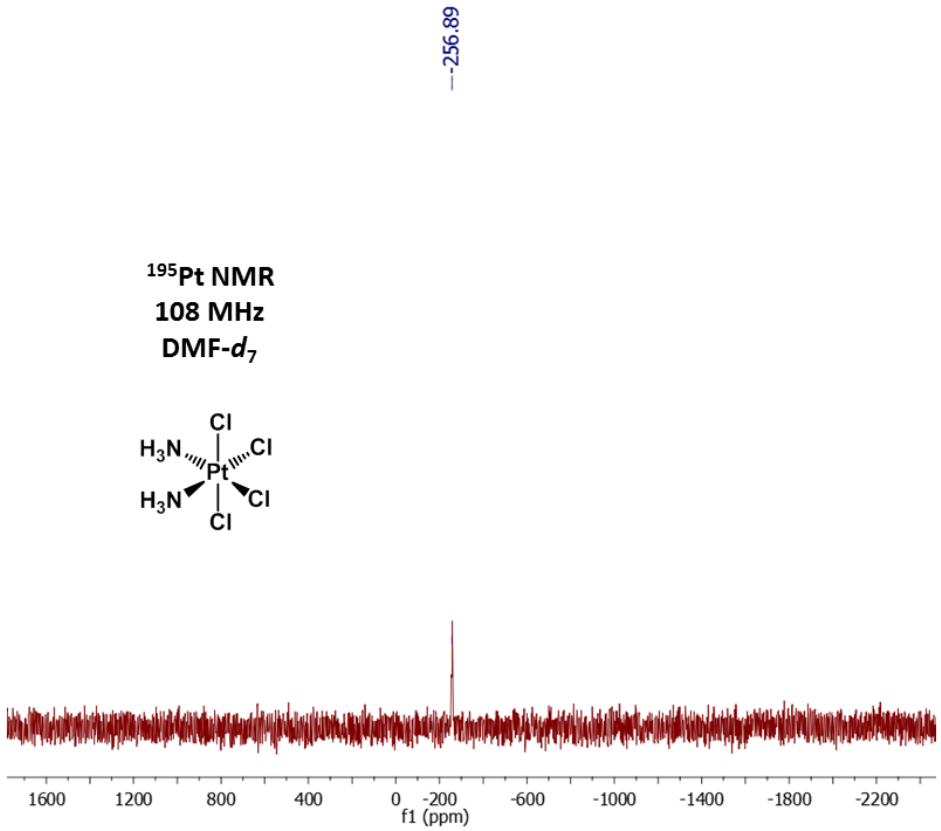

Figure S5. ^{195}Pt NMR spectrum of **1** in DMF-d_7.

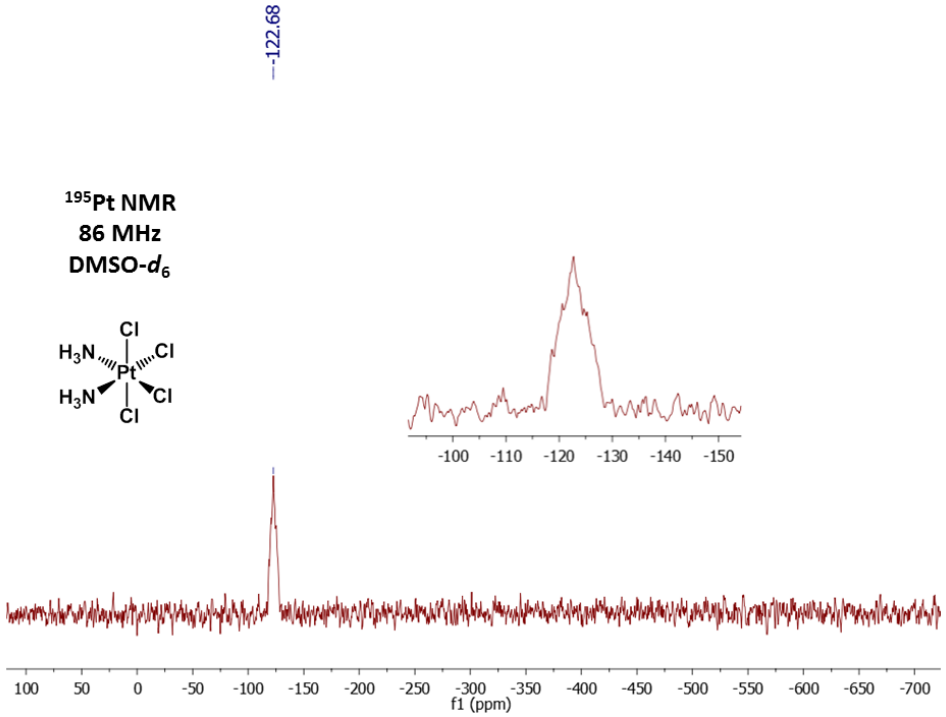

Figure S6. ^{195}Pt NMR spectrum of **1** in DMSO-d_6.

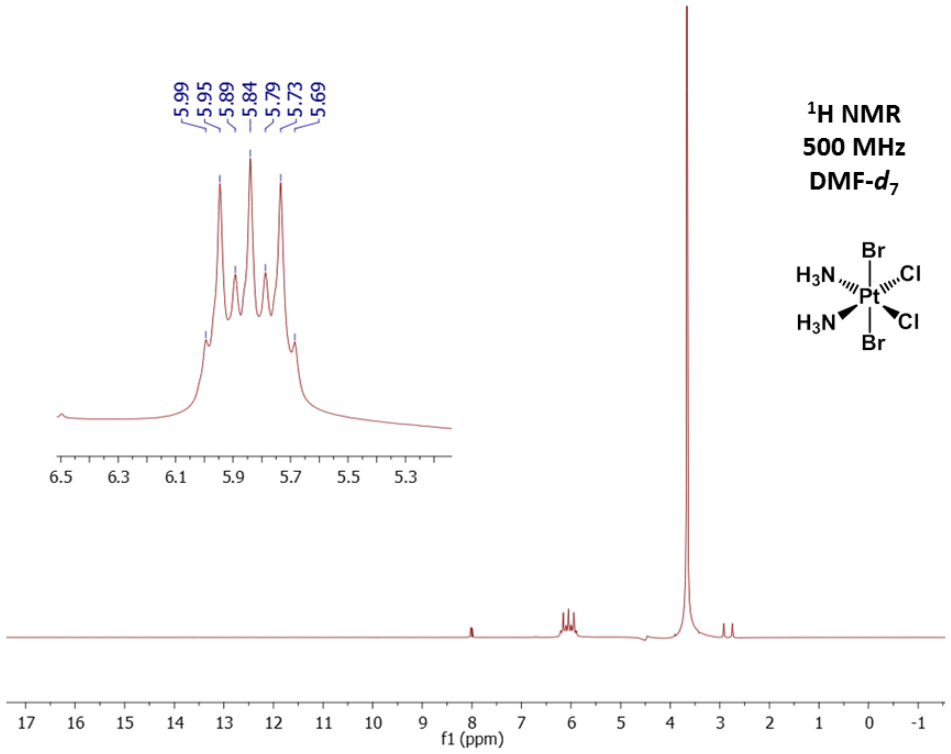

Figure S7. ^{1}H NMR spectrum of **2** in DMF-d_7.

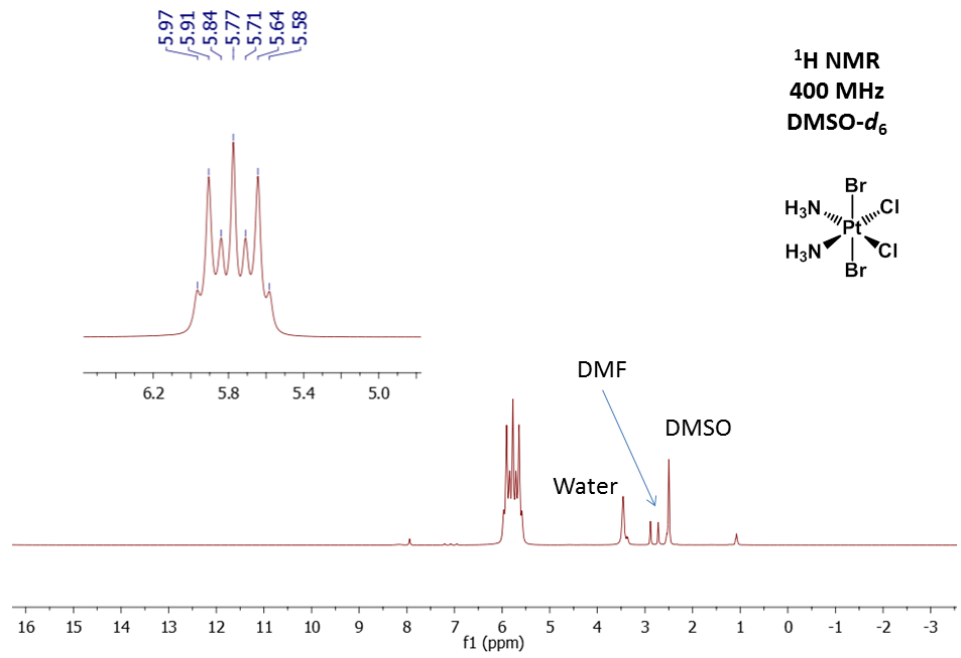

Figure S8. ^{1}H NMR spectrum of **2** in DMSO-d_6.

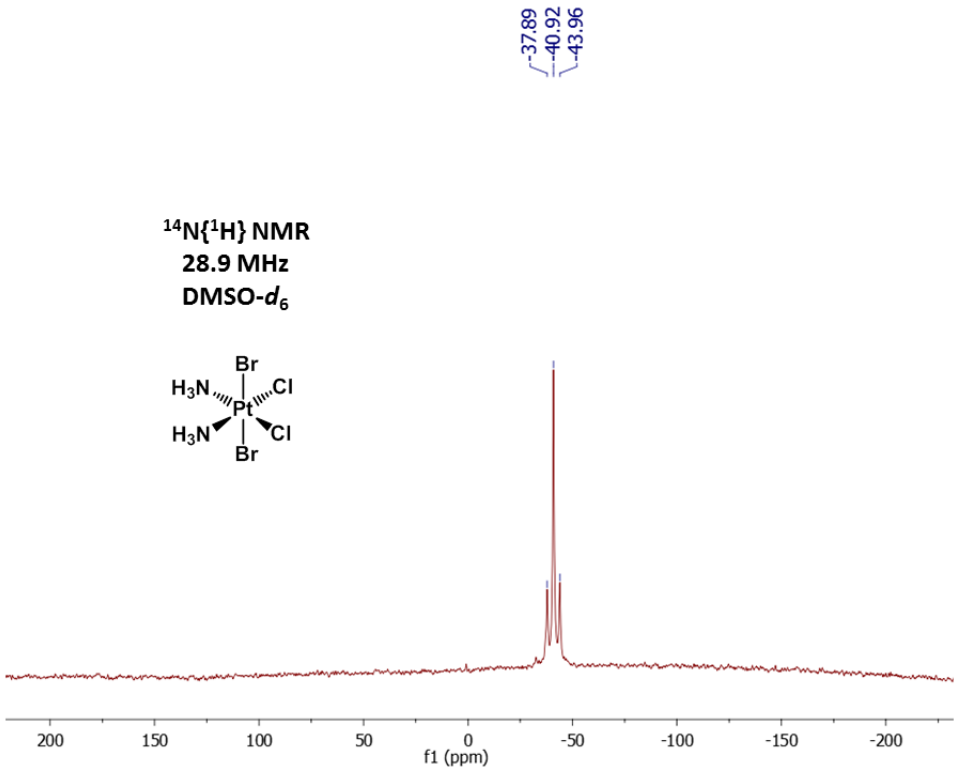

Figure S9. ^{14}N NMR spectrum of **2** in DMSO-d_6.

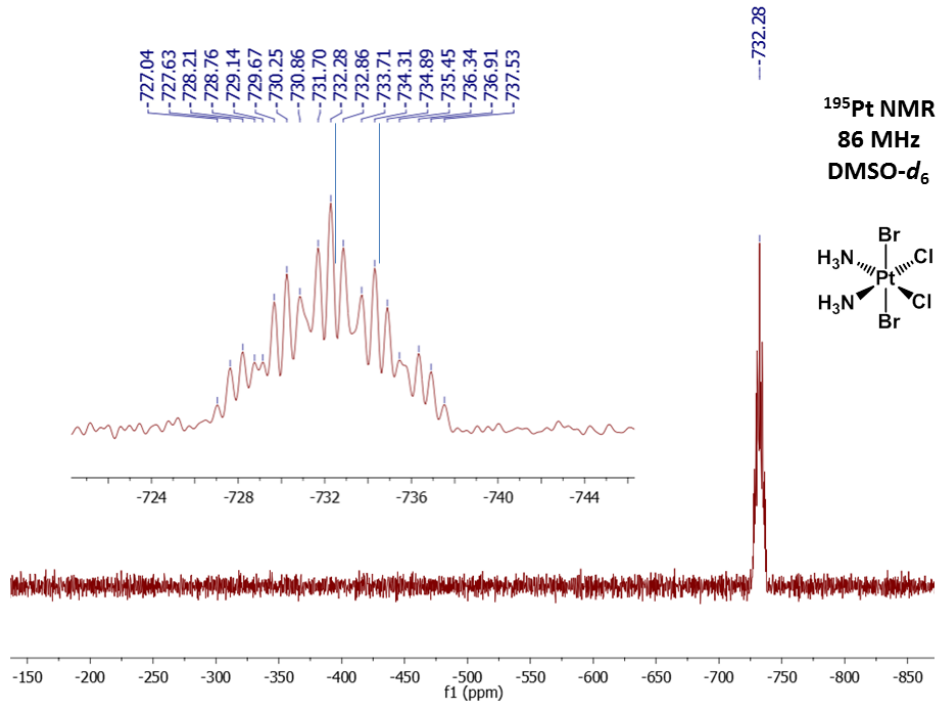

Figure S10. ^{195}Pt NMR spectrum of **2** in DMSO-d_6.

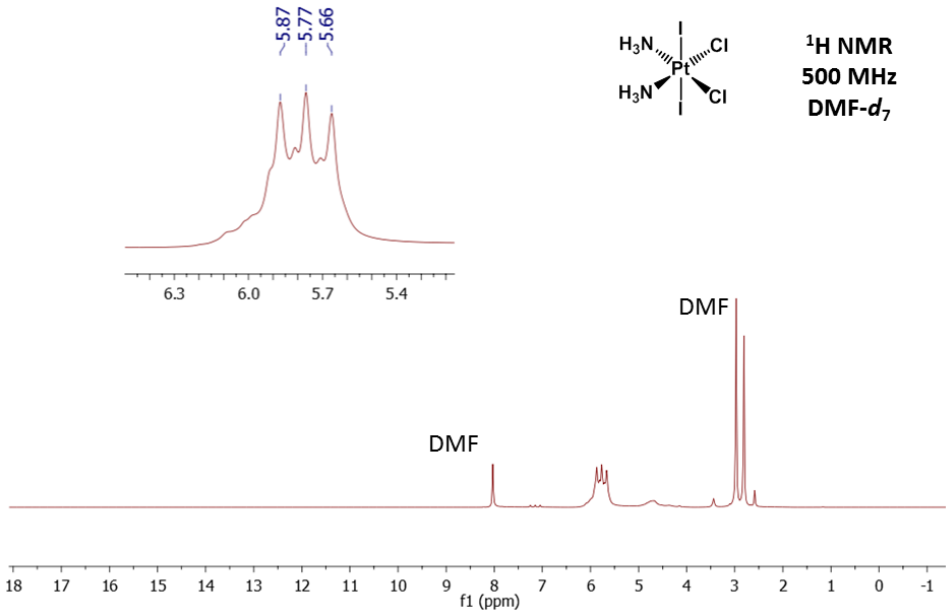

Figure S11. ^{1}H NMR spectrum of **3** in DMF-d_7.

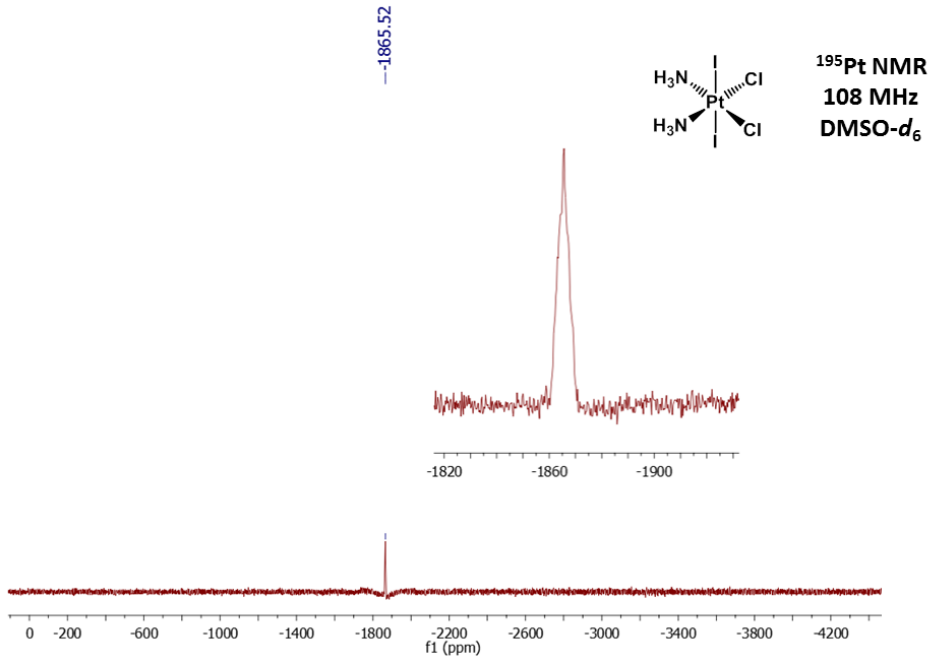

Figure S12. ^{195}Pt NMR spectrum of **3** in DMSO-d_6 .

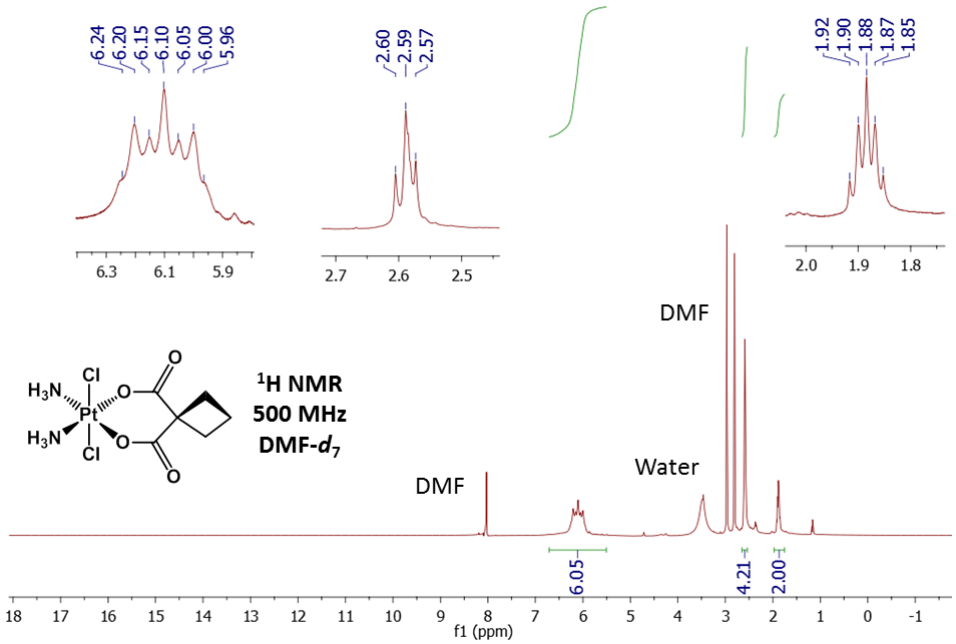

Figure S13. ^{1}H NMR spectrum of **4** in DMF-d_7.

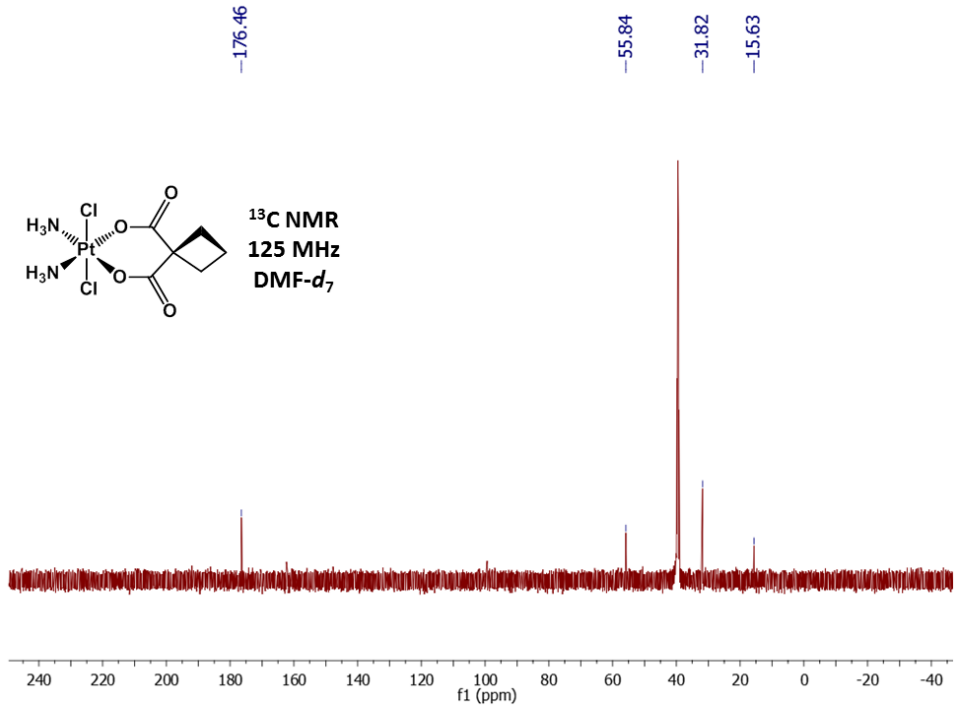

Figure S14. ^{13}C{^{1}H} NMR spectrum of **4** in DMF-d_7.

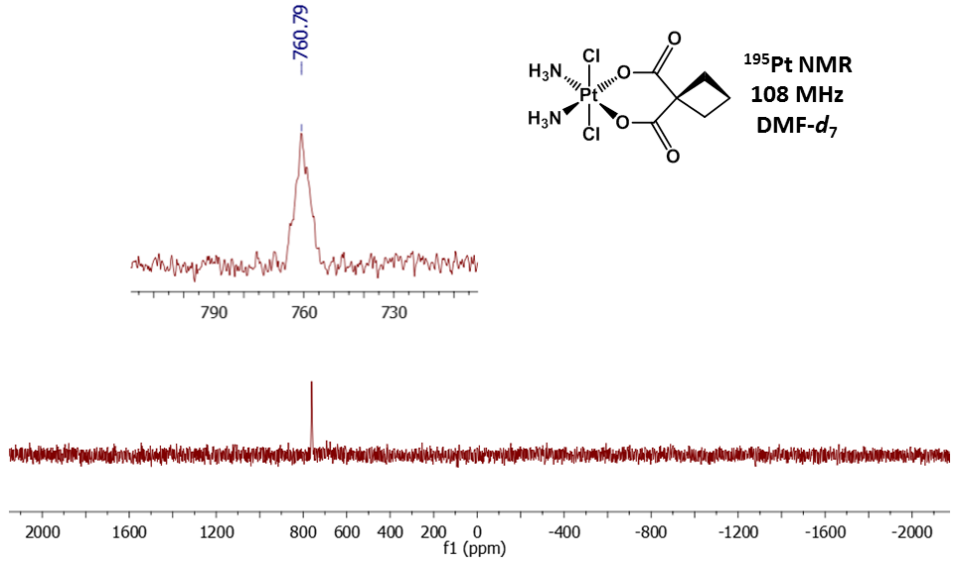

Figure S15. ^{195}Pt NMR spectrum of **4** in DMF-d_7.

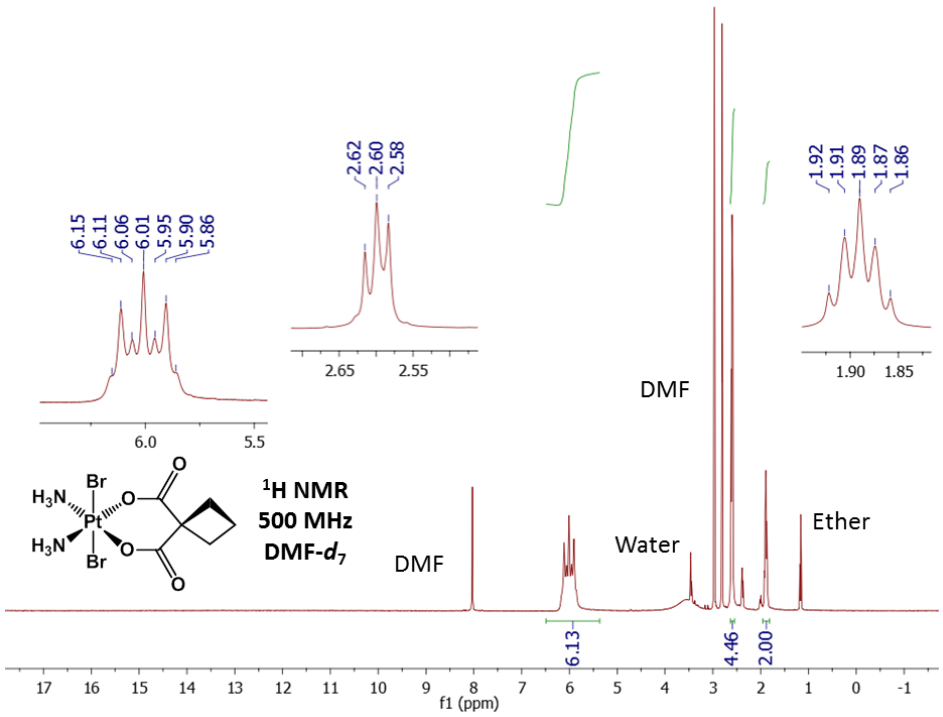

Figure S16. ^{1}H NMR spectrum of **5** in DMF-d_7.

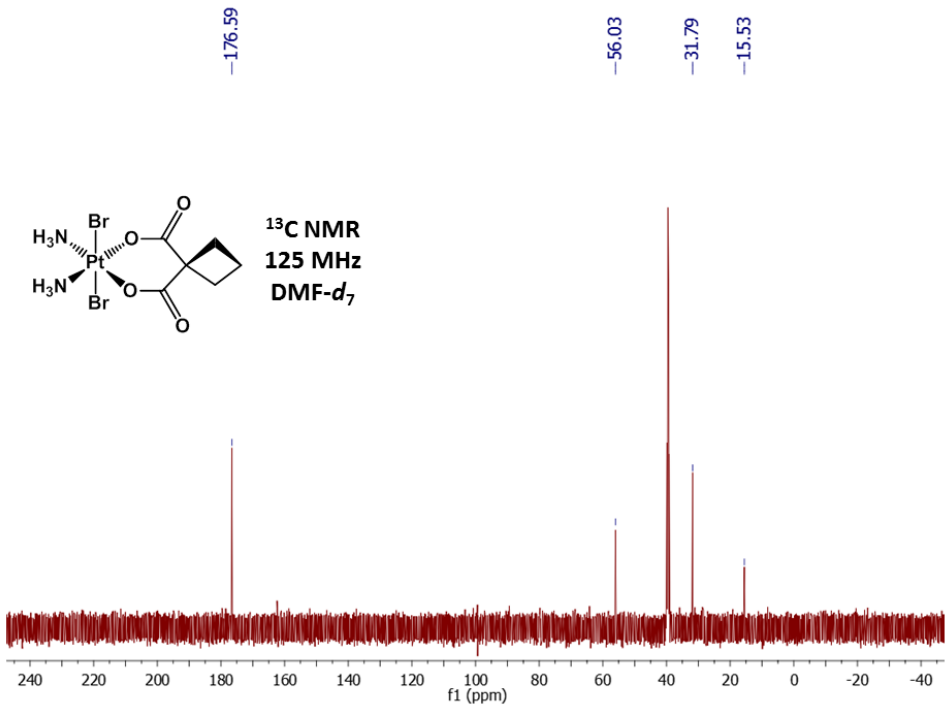

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in DMF-d_7.

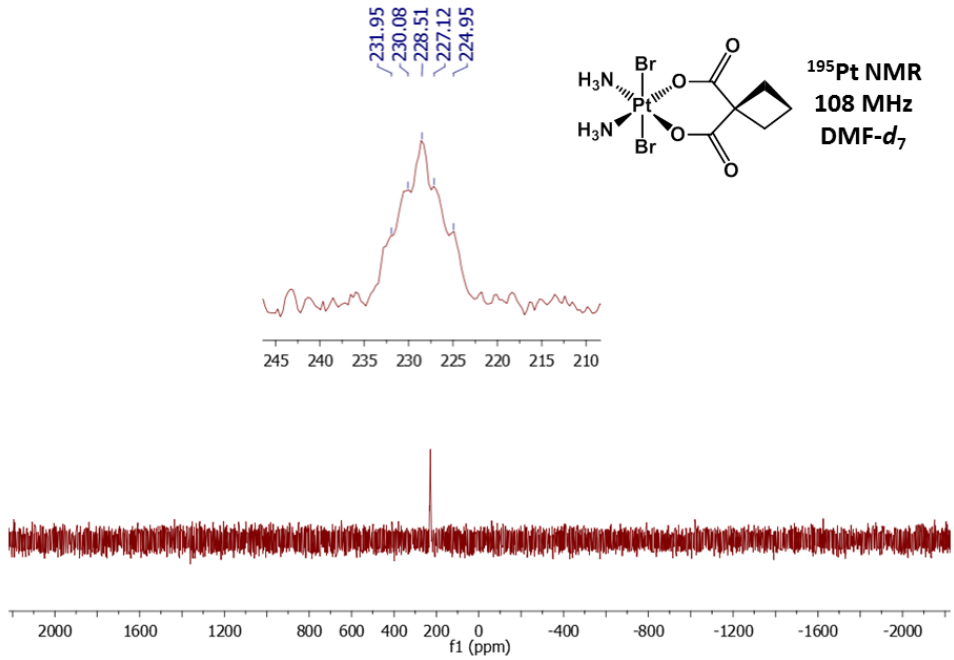

Figure S18. ^{195}Pt NMR spectrum of **5** in DMF-d_7.

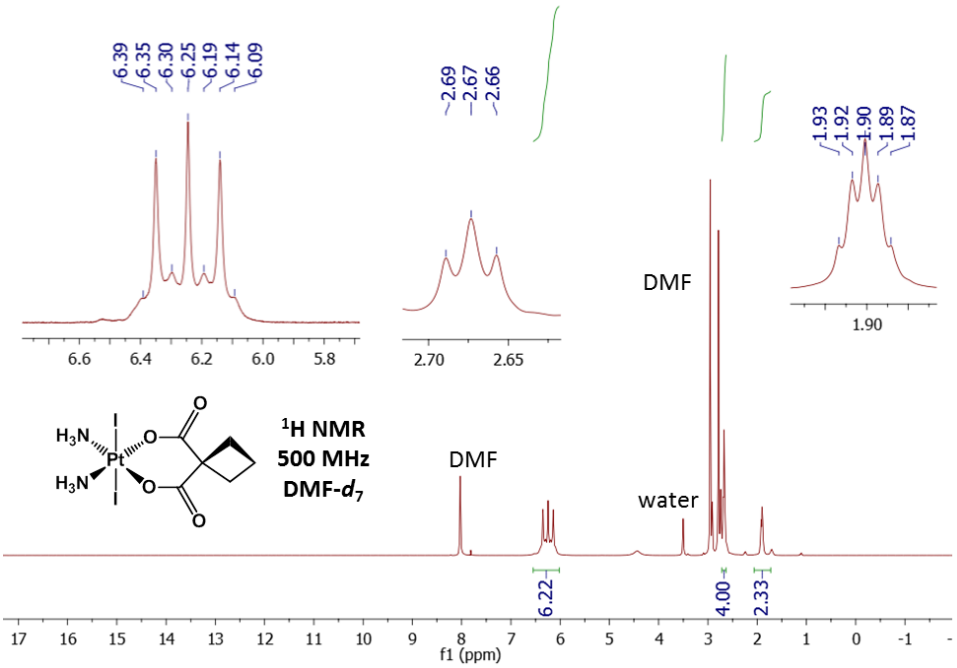

Figure S19. ^{1}H NMR spectrum of **6** in DMF-d_7.

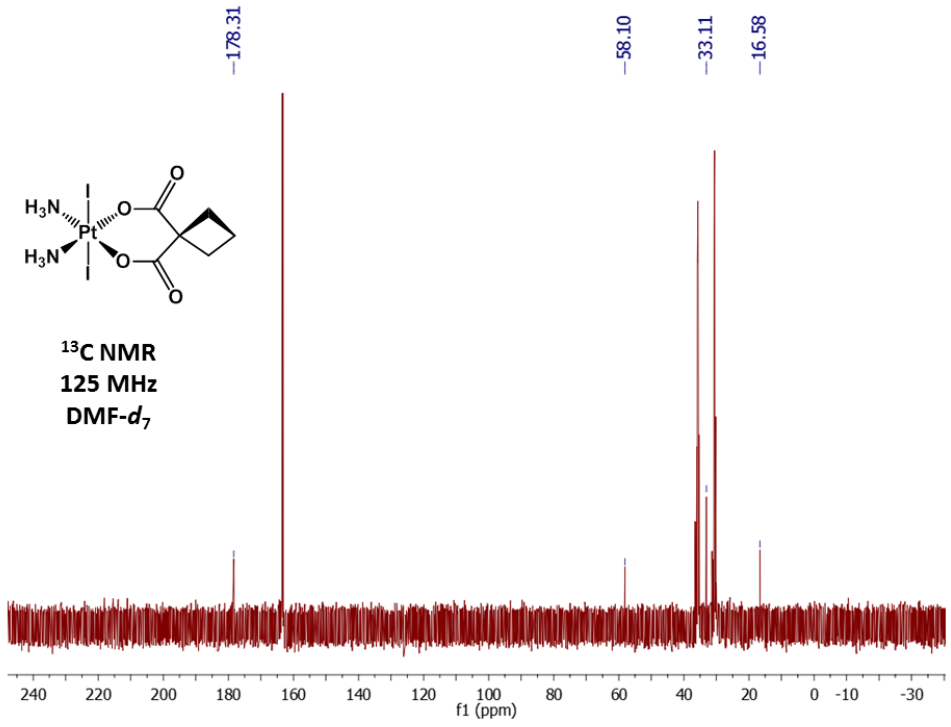

Figure S20. ^{13}C{^{1}H} NMR spectrum of **6** in DMF-d_7.

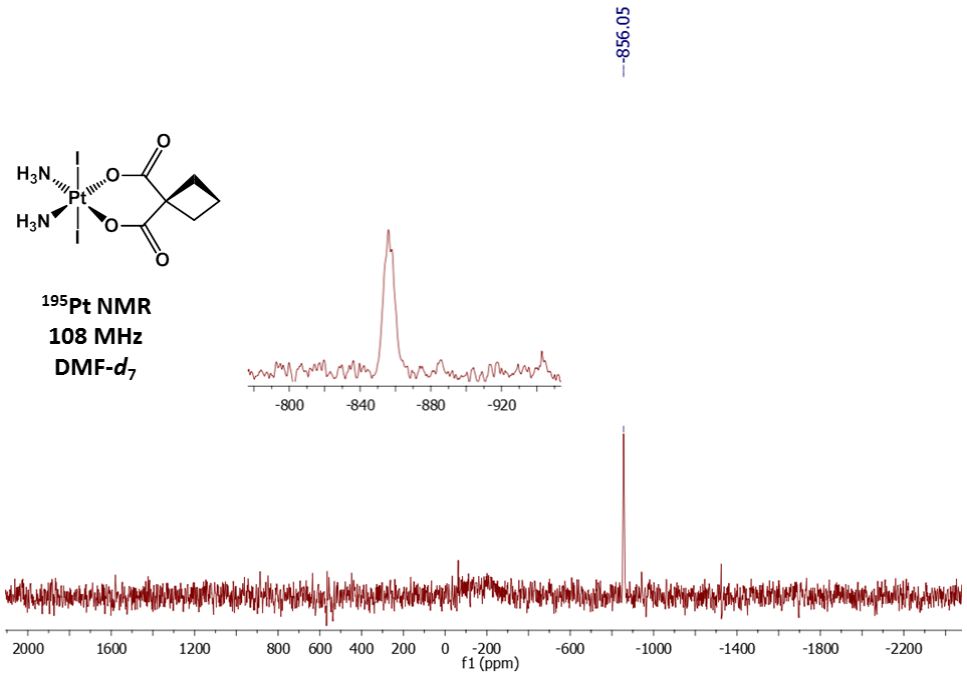

Figure S21. ^{195}Pt NMR spectrum of **6** in DMF-d_7.

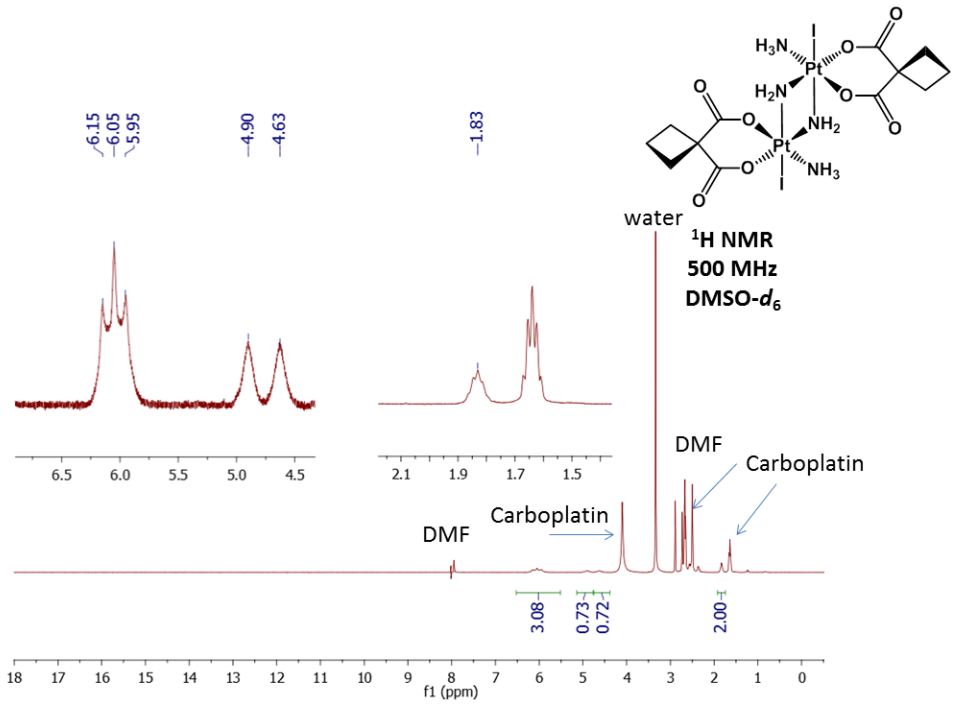

Figure S22. ^{1}H NMR spectrum in DMSO-d_6 of the side product from the synthesis of **6** showing evidence for the formation of **7**.

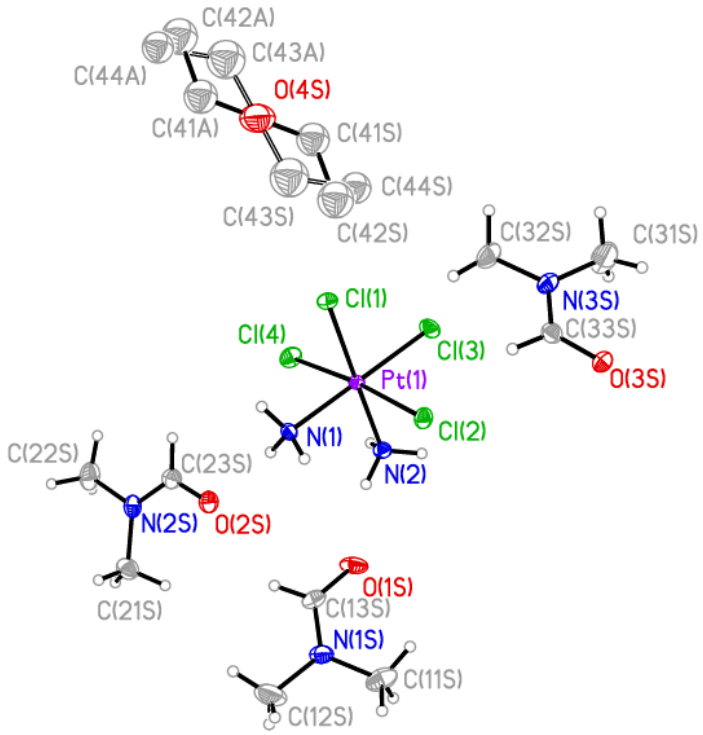

Figure S23. Depiction of the molecules from the crystal structure of **1**·3DMF·½Et_2O. Thermal ellipsoids are depicted at the 50% probability level.

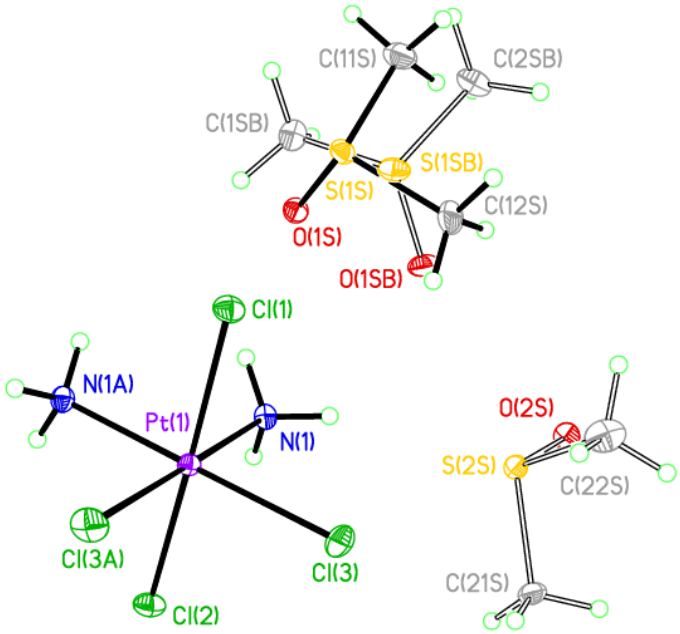

Figure S24. Depiction of the molecules from the crystal structure of **1**·2DMSO. Thermal ellipsoids are depicted at the 50% probability level.

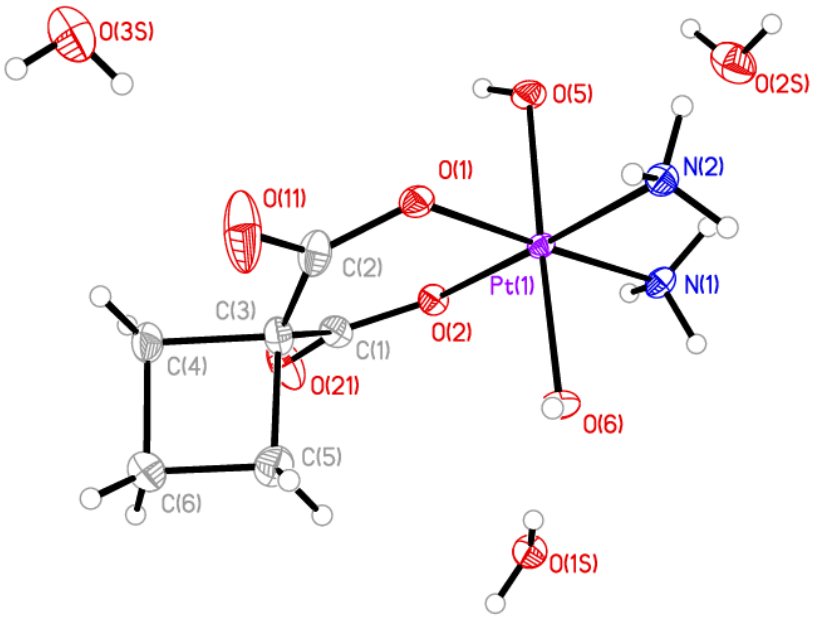

Figure S25. Depiction of the molecules from the crystal structure of *cis,trans*-[Pt(CBDCA)$(NH_3)_2(OH)_2$]. Thermal ellipsoids are depicted at the 50% probability level

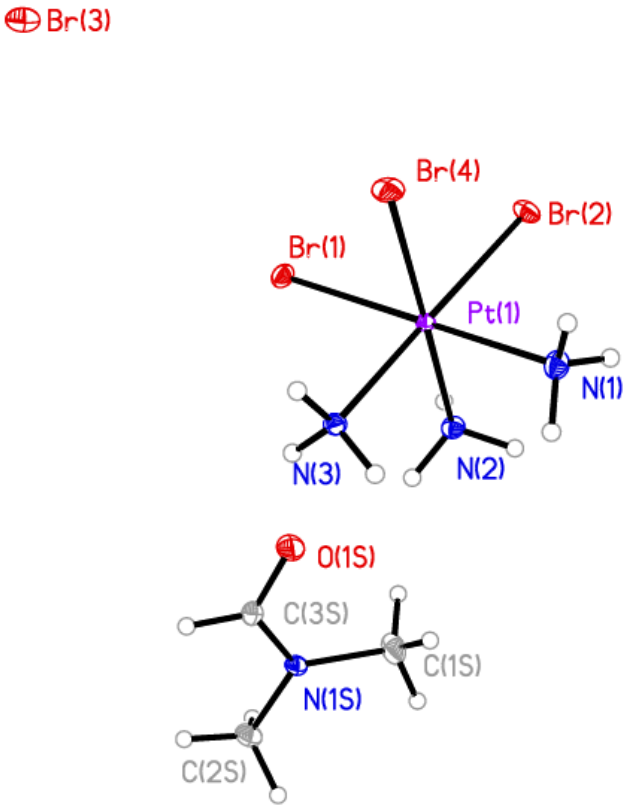

Figure S26. Depiction of the molecules from the crystal structure of *fac*-[Pt$(NH_3)_3Br_3$]Br·DMF. Thermal ellipsoids are depicted at the 50% probability level

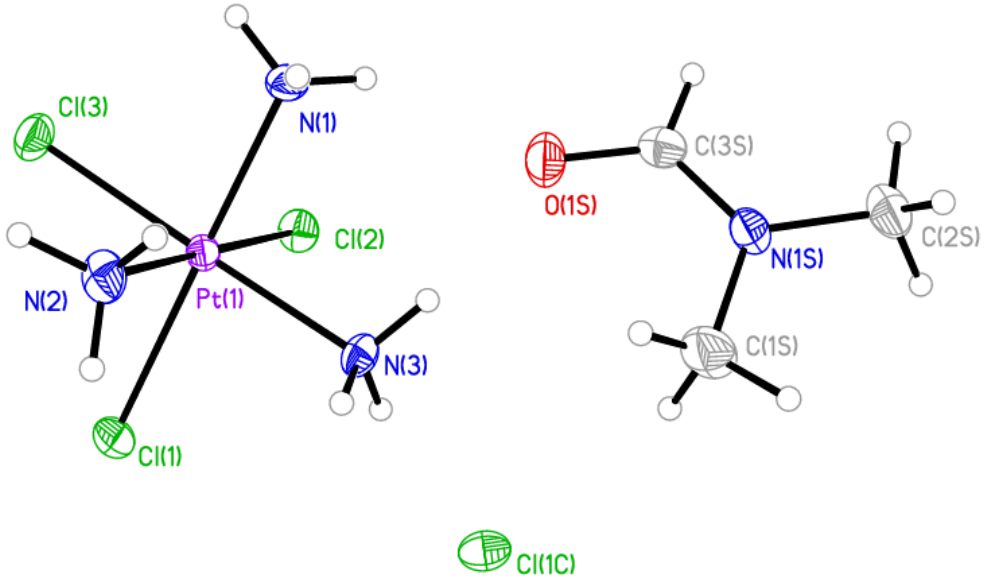

Figure S27. Depiction of the molecules from the crystal structure of *fac*-$[Pt(NH_3)_3Cl_3]Cl \cdot DMF$. Thermal ellipsoids are depicted at the 50% probability level.

Table S1. Crystal data and structure refinement for *cis*-$[Pt(NH_3)_2Cl_4]\cdot 3DMF\cdot \frac{1}{2}Et_2O$.

Empirical formula	$C_{11}H_{27}Cl_4N_5O_{3.5}Pt$
Formula weight	622.27
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 11.548(2) Å
	b = 10.8403(19) Å β = 93.380(3)°
	c = 18.077(3) Å
Volume	2259.0(7) $Å^3$
Z	4
Density (calculated)	1.830 Mg/m^3
Absorption coefficient	6.705 mm^{-1}
F(000)	1208
Crystal size	0.44 x 0.32 x 0.15 mm^3
Theta range for data collection	1.77 to 28.22°.
Index ranges	-15<=h<=15, -14<=k<=14, -23<=l<=24
Reflections collected	43406
Independent reflections	5533 [R(int) = 0.0446]
Completeness to theta = 28.22°	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.4756
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5533 / 3 / 230
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0232, wR2 = 0.0428
R indices (all data)	R1 = 0.0291, wR2 = 0.0455
Largest diff. peak and hole	0.770 and -0.760 e $Å^{-3}$

Comment: The disorder of the ether molecule about a special position, in conjunction with its reduced occupancy precluded stable anisotropic refinement with inclusion of hydrogen atoms.

Table S2. Crystal data and structure refinement for *cis*-$[Pt(NH_3)_2Cl_4]\cdot 3DMSO$.

Empirical formula	$C_6H_{24}Cl_4N_2O_3PtS_3$
Formula weight	605.34
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/m$
Unit cell dimensions	a = 9.5555(12) Å
	b = 10.4647(13) Å β = 109.763(2)°
	c = 10.0797(12) Å
Volume	948.6(2) $Å^3$
Z	2
Density (calculated)	2.119 Mg/m^3
Absorption coefficient	8.292 mm^{-1}
F(000)	584
Crystal size	0.30 x 0.20 x 0.11 mm^3
Theta range for data collection	2.15 to 28.77°.
Index ranges	-12<=h<=12, -14<=k<=14, -13<=l<=13
Reflections collected	19728
Independent reflections	2598 [R(int) = 0.0335]
Completeness to theta = 28.77°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7458 and 0.4041
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2598 / 0 / 152
Goodness-of-fit on F^2	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0139, wR2 = 0.0314
R indices (all data)	R1 = 0.0154, wR2 = 0.0322
Largest diff. peak and hole	1.177 and -0.933 e $Å^{-3}$

Table S3. Crystal data and structure refinement for cis,trans-[Pt(NH_3)$_2$(OH)$_2$CBDCA]·3H_2O.

Empirical formula	$C_6H_{26}N_2O_9Pt$	
Formula weight	465.33	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P***Error!**	
Unit cell dimensions	a = 6.0601(3) Å	α = 97.405(1)°
	b = 9.5144(4) Å	β = 99.999(1)°
	c = 11.3376(5) Å	γ = 91.296(1)°
Volume	637.73(5) Å^3	
Z	2	
Density (calculated)	2.392 Mg/m^3	
Absorption coefficient	11.043 mm^{-1}	
F(000)	440	
Crystal size	0.15 x 0.05 x 0.02 mm^3	
Theta range for data collection	1.84 to 27.88°.	
Index ranges	-7<=h<=7, -12<=k<=12, -14<=l<=14	
Reflections collected	12172	
Independent reflections	3016 [R(int) = 0.0187]	
Completeness to theta = 27.88°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8094 and 0.2882	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3016 / 10 / 185	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0139, wR2 = 0.0346	
R indices (all data)	R1 = 0.0148, wR2 = 0.0350	
Largest diff. peak and hole	1.578 and -0.653 e Å^{-3}	

Comment: This crystal structure is almost isostructural with that of the tetrahydrate of the same molecule deposited in the CSD as a private communication by Sadler and coworkers (CCDC 276872).The two structures have different unit cell parameters and volumes. The structure reported here has no significant voids or residual electron density which might correspond to an missing water molecule. This curiosity has not been investigated further.

Table S4. Crystal data and structure refinement for *fac*-$[Pt(NH_3)_3Br_3]Br \cdot DMF$.

Empirical formula	$C_3H_{16}Br_4N_4OPt$
Formula weight	638.88
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 6.5922(5) Å
	b = 11.0012(8) Å β = 97.3610(10)°
	c = 18.9288(13) Å
Volume	1361.44(17) $Å^3$
Z	4
Density (calculated)	3.117 Mg/m^3
Absorption coefficient	22.017 mm^{-1}
F(000)	1152.0
Crystal size	0.12 x 0.06 x 0.06 mm^3
Theta range for data collection	2.15 to 28.68°.
Index ranges	-8<=h<=8, -14<=k<=14, -25<=l<=25
Reflections collected	27014
Independent reflections	3508 [R(int) = 0.0297]
Completeness to theta = 28.68°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.3590
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3508 / 0 / 123
Goodness-of-fit on F^2	1.106
Final R indices [I>2sigma(I)]	R1 = 0.0153, wR2 = 0.0322
R indices (all data)	R1 = 0.0177, wR2 = 0.0327
Largest diff. peak and hole	1.766 and -0.732 e $Å^{-3}$

Table S5. Crystal data and structure refinement for *fac*-$[Pt(NH_3)_3Cl_3]Cl \cdot DMF$.

Empirical formula	$C_3H_{16}Cl_4N_4OPt$
Formula weight	461.09
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 6.3996(14) Å
	b = 10.711(2) Å β = 96.665(3)°
	c = 18.334(4) Å
Volume	1248.3(5) $Å^3$
Z	4
Density (calculated)	2.453 Mg/m^3
Absorption coefficient	12.070 mm^{-1}
F(000)	864
Crystal size	0.09 x 0.05 x 0.02 mm^3
Theta range for data collection	2.21 to 28.54°.
Index ranges	-8<=h<=8, -14<=k<=14, -24<=l<=24
Reflections collected	23701
Independent reflections	3185 [R(int) = 0.0696]
Completeness to theta = 28.54°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7943 and 0.4097
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3185 / 0 / 123
Goodness-of-fit on F^2	1.073
Final R indices [I>2sigma(I)]	R1 = 0.0325, wR2 = 0.0674
R indices (all data)	R1 = 0.0456, wR2 = 0.0728
Largest diff. peak and hole	2.064 and -1.050 e $Å^{-3}$

Table S6. Cartesian coordinates (Å) of the DFT-optimized structure of **4**.

Pt	0.967300	0.069800	-0.013100
Cl	1.629500	-2.187500	-0.127100
O	-2.273700	-0.943100	-2.181800
C	-2.778200	1.260600	0.085400
H	-2.754400	1.680500	1.094700
H	-2.254900	1.940600	-0.590000
C	-1.524000	-0.575200	1.394900
N	2.318700	0.310400	1.563000
H	3.082000	-0.362200	1.535200
H	1.731000	0.105200	2.375900
H	2.667700	1.263300	1.640800
O	-0.219900	-0.335800	1.515700
C	-3.751500	-0.670800	0.110000
H	-3.995500	-1.488500	-0.570000
H	-4.057100	-0.916100	1.128500
N	2.183100	0.435400	-1.674400
H	1.521200	0.320200	-2.446800
H	2.923100	-0.256000	-1.775800
H	2.555400	1.382200	-1.695600
O	-0.345600	-0.222800	-1.464500
C	-2.265800	-0.237600	0.106500
C	-1.622100	-0.534700	-1.244300
C	-4.172000	0.748100	-0.316700
H	-4.337800	0.819300	-1.394600
H	-5.022800	1.193000	0.206500
O	-2.115500	-0.971400	2.376600
Cl	0.564400	2.393300	0.098500

Table S7. Cartesian coordinates (Å) of the DFT-optimized structure of **5**.

Pt	0.782500	0.180400	-0.011500
Br	1.775300	-2.166600	-0.036300
O	-2.252600	-1.365600	-2.161600
C	-3.116300	0.776400	0.052600
H	-3.156000	1.227900	1.047700
H	-2.711900	1.509200	-0.649000
C	-1.588400	-0.797900	1.406400
N	2.084500	0.639200	1.561100
H	2.928900	0.071100	1.558500
H	1.522900	0.384100	2.378500
H	2.309800	1.630600	1.613200
O	-0.358900	-0.301800	1.528500
C	-3.765100	-1.287800	0.127000
H	-3.872900	-2.147000	-0.536800
H	-4.026500	-1.561500	1.150600
N	1.960500	0.621900	-1.684100
H	1.342900	0.346000	-2.452900
H	2.810200	0.064200	-1.735600
H	2.168700	1.614800	-1.769300
O	-0.472200	-0.324500	-1.455100
C	-2.370700	-0.618900	0.110800
C	-1.681100	-0.837300	-1.231900
C	-4.411400	0.035300	-0.324600
H	-4.595200	0.055600	-1.401700
H	-5.319100	0.347900	0.198900
O	-2.099400	-1.286500	2.391500
Br	0.062100	2.628500	0.010100

Table S8. Cartesian coordinates (Å) of the DFT-optimized structure of **6**.

Pt	0.967300	0.069800	-0.013100
Cl	1.629500	-2.187500	-0.127100
O	-2.273700	-0.943100	-2.181800
C	-2.778200	1.260600	0.085400
H	-2.754400	1.680500	1.094700
H	-2.254900	1.940600	-0.590000
C	-1.524000	-0.575200	1.394900
N	2.318700	0.310400	1.563000
H	3.082000	-0.362200	1.535200
H	1.731000	0.105200	2.375900
H	2.667700	1.263300	1.640800
O	-0.219900	-0.335800	1.515700
C	-3.751500	-0.670800	0.110000
H	-3.995500	-1.488500	-0.570000
H	-4.057100	-0.916100	1.128500
N	2.183100	0.435400	-1.674400
H	1.521200	0.320200	-2.446800
H	2.923100	-0.256000	-1.775800
H	2.555400	1.382200	-1.695600
O	-0.345600	-0.222800	-1.464500
C	-2.265800	-0.237600	0.106500
C	-1.622100	-0.534700	-1.244300
C	-4.172000	0.748100	-0.316700
H	-4.337800	0.819300	-1.394600
H	-5.022800	1.193000	0.206500
O	-2.115500	-0.971400	2.376600
Cl	0.564400	2.393300	0.098500

Table S9. Hydrogen bonding metrics of **1**·3DMF.

Donor	---	H	....Acceptor	[ARU]	D - H	H...A	D...A	D - H...A
N(1)	--H(1A)	..O(2S)	[1455.03]		0.91	1.92	2.8149(19)	168
N(1)	--H(1B)	..O(3S)	[4565.04]		0.91	2.04	2.9142(18)	162
N(1)	--H(1C)	..O(1S)	[2646.02]		0.91	2.27	2.9506(18)	131
N(2)	--H(2A)	..Cl(2)	[ ]		0.91	2.76	3.0738(15)	101
N(2)	--H(2A)	..O(3S)	[3676.04]		0.91	1.98	2.8070(19)	149
N(2)	--H(2B)	..O(1S)	[ ]		0.91	2.00	2.9027(18)	171
N(2)	--H(2C)	..O(2S)	[1455.03]		0.91	2.01	2.8612(19)	156
C(11S)	--H(11A)	..O(1S)	[ ]		0.98	2.41	2.813(2)	104
C(13S)	--H(13S)	..Cl(1)	[ ]		0.95	2.77	3.5984(17)	146
C(21S)	--H(21A)	..O(2S)	[ ]		0.98	2.43	2.771(2)	100
C(31S)	--H(31A)	..O(3S)	[ ]		0.98	2.40	2.815(2)	105

Translation of ARU-Code to CIF and Equivalent Position Code

[4565.]	=	[4_576]	=x,3/2-y,1/2+z
[2646.]	=	[2_646]	=1-x,-1/2+y,3/2-z
[3676.]	=	[3_676]	=1-x,2-y,1-z
[1455.]	=	[1_455]	=-1+x,y,z

Table S10. Hydrogen bonding metrics **3**·3DMF.

Donor	---	H	....Acceptor	[ARU]	D - H	H...A	D...A	D - H...A
N(11)	--H(11A)	..I(11)	[ ]		0.91	2.96	3.344(4)	107

```
N(11) --H(11A) ..O(51S) [         ]       0.91       2.13   2.868(5)        138
N(11) --H(11B) ..O(41S) [  3665.06]       0.91       2.21   2.929(5)        135
N(11) --H(11C) ..O(61S) [         ]       0.91       1.93   2.815(6)        164
N(12) --H(12A) ..O(61S) [         ]       0.91       1.90   2.795(6)        167
N(12) --H(12B) ..O(51S) [  2645.07]       0.91       2.08   2.914(5)        151
N(12) --H(12C) ..I(11)  [         ]       0.91       3.04   3.371(4)        103
N(12) --H(12C) ..O(41S) [  4555.06]       0.91       2.28   3.022(5)        138
N(21) --H(21A) ..I(21)  [         ]       0.91       3.04   3.414(4)        107
N(21) --H(21A) ..O(21S) [  2555.04]       0.91       2.10   2.919(5)        150
N(21) --H(21B) ..O(11S) [  1565.03]       0.91       2.08   2.918(5)        152
N(21) --H(21C) ..O(31S) [         ]       0.91       1.99   2.887(5)        167
N(22) --H(22A) ..O(31S) [         ]       0.91       2.10   2.879(6)        143
N(22) --H(22B) ..Cl(21) [         ]       0.91       2.71   3.033(4)        102
N(22) --H(22B) ..O(21S) [         ]       0.91       2.22   3.007(5)        145
N(22) --H(22C) ..I(21)  [         ]       0.91       3.03   3.389(4)        105
N(22) --H(22C) ..O(11S) [  2555.03]       0.91       1.99   2.832(5)        152

C(12S)--H(19A) ..O(11S) [         ]       0.98       2.37   2.787(8)        105
C(23S)--H(23A) ..O(21S) [         ]       0.98       2.43   2.818(7)        103
C(23S)--H(23B) ..Cl(12) [  4555.01]       0.98       2.77   3.667(6)        153
C(33S)--H(33C) ..O(31S) [         ]       0.98       2.42   2.783(8)        102
C(43S)--H(43A) ..O(41S) [         ]       0.98       2.42   2.827(8)        104
C(52S)--H(52A) ..O(51S) [         ]       0.98       2.39   2.797(8)        104
C(61S)--H(61S) ..Cl(11) [  2645.01]       0.95       2.69   3.564(6)        153
C(62S)--H(62C) ..O(61S) [         ]       0.98       2.40   2.792(9)        103
C(63S)--H(63C) ..Cl(21) [  2645.02]       0.98       2.79   3.727(7)        160

Translation of ARU-Code to CIF and Equivalent Position Code
============================================================
   [  4555.] = [  4_566] =x,1/2-y,1/2+z
   [  2645.] = [  2_645] =1-x,-1/2+y,1/2-z
   [  3665.] = [  3_665] =1-x,1-y,-z
   [  2555.] = [  2_555] =-x,1/2+y,1/2-z
   [  1565.] = [  1_565] =x,1+y,z
```

Table S11. Hydrogen bonding metrics of **4**·DMF.

```
Donor --- H....Acceptor [    ARU  ]      D - H      H...A      D...A  D - H...A
N1    --H1A    ..O2     [  2655.01]       0.91       2.31   3.143(2)        153
N1    --H1A    ..O3     [  2655.01]       0.91       2.57   2.879(2)        101
N1    --H1B    ..O1S    [  2645.02]       0.91       1.96   2.841(2)        163
N1    --H1C    ..Cl12   [         ]       0.91       2.73 3.0219(18)        100
```

```
N1    --H1C    ..O4     [  1655.01]       0.91       2.04   2.910(2)        160
N2    --H2A    ..O4     [  2545.01]       0.91       2.24   2.973(2)        137
N2    --H2B    ..Cl11   [  2545.01]       0.91       2.70 3.6045(19)        174
N2    --H2C    ..O1S    [         ]       0.91       1.96   2.818(2)        157

C1S   --H1S1   ..O1S    [         ]       0.98       2.45   2.794(3)        100
C1S   --H1S2   ..Cl12   [  2646.01]       0.98       2.80   3.738(3)        161
C14   --H14A   ..O3     [         ]       0.99       2.39   2.741(3)        100
C14   --H14A   ..Cl11   [  2555.01]       0.99       2.75   3.653(2)        152
C14   --H14B   ..O4     [         ]       0.99       2.46   2.832(3)        102

Translation of ARU-Code to CIF and Equivalent Position Code
============================================================
   [  2645.] = [  2_645] =1-x,-1-y,-z
   [  2545.] = [  2_545] =-x,-1-y,-z
   [  2555.] = [  2_555] =-x,-y,-z
   [  1655.] = [  1_655] =1+x,y,z
   [  2655.] = [  2_655] =1-x,-y,-z
   [  2646.] = [  2_646] =1-x,-1-y,1-z
```

Table S12. Hydrogen bonding metrics of **5**·DMF.

```
Donor --- H....Acceptor [    ARU  ]      D - H      H...A      D...A  D - H...A
N(1)  --H(1A)  ..Br(2)  [         ]       0.91       2.82   3.154(3)        103
N(1)  --H(1A)  ..O(4)   [  1655.01]       0.91       2.07   2.916(3)        154
N(1)  --H(1B)  ..O(1S)  [  1645.02]       0.91       1.97   2.822(4)        155
N(1)  --H(1C)  ..O(3)   [  2666.01]       0.91       2.13   2.970(3)        154
N(2)  --H(2A)  ..Br(2)  [         ]       0.91       2.85   3.138(3)        100
N(2)  --H(2A)  ..O(1S)  [  2565.02]       0.91       1.97   2.842(3)        159
N(2)  --H(2B)  ..Br(1)  [  2555.01]       0.91       2.92   3.817(2)        168
```

N(2) --H(2C)	..O(1S)	[1645.02]	0.91	2.37	3.080(3)	135
N(2) --H(2C)	..O(4)	[2555.01]	0.91	2.38	3.001(3)	126
C(4) --H(4A)	..O(4)	[ ]	0.99	2.45	2.830(4)	103
C(11S)--H(11A)	..O(1S)	[ ]	0.98	2.42	2.761(4)	100
C(12S)--H(12C)	..Br(2)	[1455.01]	0.98	2.84	3.766(3)	157

Translation of ARU-Code to CIF and Equivalent Position Code

[1645.]	= [1_645]	=1+x,-1+y,z
[2555.]	= [2_555]	=-x,-y,-z
[2565.]	= [2_565]	=-x,1-y,-z
[2666.]	= [2_666]	=1-x,1-y,1-z
[1455.]	= [1_455]	=-1+x,y,z
[1655.]	= [1_655]	=1+x,y,z

Table S13. Hydrogen bonding metrics of **7**·3DMF·Et_2O.

Donor --- H....Acceptor	[ARU]	D - H	H...A	D...A	D - H...A
N(11) --H(51A) ..O(211)	[2665.02]	0.92	2.50	3.287(4)	144
N(11) --H(51A) ..O(214)	[2665.02]	0.92	2.07	2.954(4)	160
N(11) --H(51B) ..O(3S)	[2675.06]	0.92	2.10	2.960(4)	156
N(111)--H(51C) ..O(112)	[2675.01]	0.91	2.17	2.938(4)	142
N(111)--H(51D) ..O(1S)	[ ]	0.91	1.88	2.759(5)	162
N(111)--H(51E) ..O(214)	[2665.02]	0.91	2.10	2.822(4)	136
N(21) --H(61A) ..O(3S)	[2666.06]	0.92	2.10	2.991(4)	163
N(21) --H(61B) ..O(2S)	[2656.05]	0.92	2.00	2.890(4)	162
N(211)--H(61C) ..O(2S)	[2656.05]	0.91	2.02	2.910(4)	164

```
N(211)--H(61D) ..O(114) [  1545.01]       0.91       1.91   2.811(4)        169
N(211)--H(61E) ..O(3S)  [  1545.06]       0.91       2.06   2.958(4)        168

C(3)  --H(3A)  ..O(114) [         ]       0.99       2.54   3.344(5)        138
C(115)--H(11C) ..O(113) [         ]       0.99       2.42   2.775(5)        100
C(115)--H(11D) ..O(114) [         ]       0.99       2.30   2.748(6)        106
C(11S)--H(11E) ..O(1S)  [         ]       0.98       2.37   2.787(6)        105
C(13S)--H(13S) ..O(111) [         ]       0.95       2.55   3.276(6)        134
C(214)--H(21A) ..O(214) [         ]       0.99       2.34   2.720(5)        102
C(214)--H(21B) ..O(213) [         ]       0.99       2.43   2.829(5)        103
C(21S)--H(21H) ..O(213) [  2766.02]       0.98       2.52   3.499(5)        174
C(31S)--H(31A) ..O(3S)  [         ]       0.98       2.44   2.829(6)        103
C(32S)--H(32B) ..O(113) [  1455.01]       0.98       2.54   3.328(7)        137

Translation of ARU-Code to CIF and Equivalent Position Code
============================================================
   [  2675.] = [  2_675] =1-x,2-y,-z
   [  2665.] = [  2_665] =1-x,1-y,-z
   [  1545.] = [  1_545] =x,-1+y,z
   [  2666.] = [  2_666] =1-x,1-y,1-z
   [  2656.] = [  2_656] =1-x,-y,1-z
   [  2766.] = [  2_766] =2-x,1-y,1-z
   [  1455.] = [  1_455] =-1+x,y,z
```

Table S14. Hydrogen bonding metrics of *cis*-$[Pt(NH_3)_2Cl_4]\cdot 3DMF\cdot \frac{1}{2}Et_2O$ (ESI1).

```
Donor --- H....Acceptor [    ARU  ]      D - H      H...A      D...A  D - H...A
N(1)  --H(1A)  ..O(2S)  [         ]       0.91       2.01   2.865(3)        156
N(1)  --H(1B)  ..Cl(1)  [         ]       0.91       2.72   3.036(3)        101
N(1)  --H(1B)  ..O(1S)  [  2656.03]       0.91       2.10   2.962(3)        158
N(1)  --H(1C)  ..Cl(2)  [         ]       0.91       2.75   3.067(2)        102
N(1)  --H(1C)  ..O(3S)  [  3667.05]       0.91       2.03   2.868(3)        153
N(2)  --H(2A)  ..O(1S)  [         ]       0.91       1.91   2.792(3)        163
N(2)  --H(2B)  ..O(2S)  [  2646.04]       0.91       2.20   3.059(3)        157
N(2)  --H(2C)  ..Cl(4)  [         ]       0.91       2.76   3.057(2)        100
N(2)  --H(2C)  ..O(3S)  [  4554.05]       0.91       2.12   2.894(3)        143

C(13S)--H(13S) ..O(2S)  [         ]       0.95       2.45   3.294(4)        148
C(31S)--H(31A) ..O(3S)  [         ]       0.98       2.43   2.772(5)        100
```

```
Translation of ARU-Code to CIF and Equivalent Position Code
============================================================
   [  2656.] = [  2_656] =1-x,1/2+y,3/2-z
   [  2646.] = [  2_646] =1-x,-1/2+y,3/2-z
   [  3667.] = [  3_667] =1-x,1-y,2-z
   [  4554.] = [  4_565] =x,1/2-y,-1/2+z
```

Table S15. Hydrogen bonding metrics of *cis*-$[Pt(NH_3)_2Cl_4]\cdot 3DMSO$ (ESI2).

Donor	---	H....	Acceptor	[ARU]	D - H	H...A	D...A	D - H...A
N1	--H1A	..Cl2	[ ]		0.91	2.76	3.0770(17)	102
N1	--H1A	..O1S	[3676.02]		0.91	2.24	2.914(4)	130
N1	--H1B	..Cl3	[ ]		0.91	2.76	3.0509(17)	100
N1	--H1B	..S2S	[ ]		0.91	2.74	3.601(2)	159
N1	--H1B	..O2S	[4565.03]		0.91	2.18	2.987(4)	147
N1	--H1C	..O1S	[ ]		0.91	2.25	3.035(3)	145
N1	--H1C	..O2S	[2656.03]		0.91	2.10	2.755(3)	128
C11S	--H11A	..Cl2	[2646.01]		0.98	2.74	3.680(5)	160
C11S	--H11C	..Cl2	[1556.01]		0.98	2.77	3.697(4)	158
C12S	--H12B	..Cl1	[2546.01]		0.98	2.69	3.545(5)	146

```
Translation of ARU-Code to CIF and Equivalent Position Code
============================================================
   [  3676.] = [  3_676] =1-x,2-y,1-z
   [  4565.] = [  4_575] =x,3/2-y,z
```

```
[  2656.] = [  2_656] =1-x,1/2+y,1-z
[  2546.] = [  2_546] =-x,-1/2+y,1-z
[  3576.] = [  3_576] =-x,2-y,1-z
[  2646.] = [  2_646] =1-x,-1/2+y,1-z
[  1556.] = [  1_556] =x,y,1+z
[  4576.] = [  4_586] =x,5/2-y,1+z
```

Table S16. Hydrogen bonding metrics of *cis*,*trans*-[Pt(NH_3)$_2$(OH)$_2$CBDCA]·3H_2O (ESI3).

Donor	---	H	....Acceptor	[ARU]	D - H	H...A	D...A	D - H...A
O1S	--H1S1	..O6		[ ]	0.82(3)	1.84(3)	2.644(3)	169(3)
N1	--H1A	..O2S		[ ]	0.91	2.08	2.900(3)	149
N1	--H1B	..O1S		[2656.02]	0.91	2.03	2.869(3)	152
N1	--H1C	..O6		[2556.01]	0.91	2.08	2.942(3)	157
O1S	--H2S1	..O3S		[1545.04]	0.84(2)	1.98(3)	2.795(3)	165(3)
N2	--H2A	..O1		[2566.01]	0.91	2.14	2.957(3)	149
N2	--H2B	..O1S		[2556.02]	0.91	1.94	2.827(3)	164
N2	--H2C	..O2		[1455.01]	0.91	2.57	3.151(3)	122
N2	--H2C	..O5		[2566.01]	0.91	2.21	2.938(3)	137
O2S	--H1S2	..O3S		[2666.04]	0.92(2)	1.98(2)	2.817(3)	150(3)
O2S	--H2S2	..O11		[2566.01]	0.79(4)	2.05(3)	2.826(4)	166(4)
O5	--H5	..O2S		[ ]	0.84	1.93	2.728(3)	157
O3S	--H2S3	..O11		[2565.01]	0.86(2)	2.24(3)	3.036(3)	154(4)
O6	--H6	..O21		[1455.01]	0.84	1.88	2.707(3)	170
O3S	--H1S3	..O11		[ ]	0.85(3)	2.17(3)	3.005(4)	168(4)
C4	--H4A	..O11		[ ]	0.99	2.37	2.779(4)	104
C4	--H4B	..O21		[ ]	0.99	2.36	2.720(4)	101

```
Translation of ARU-Code to CIF and Equivalent Position Code
============================================================
   [  2566.] = [  2_566] =-x,1-y,1-z
   [  1455.] = [  1_455] =-1+x,y,z
   [  2556.] = [  2_556] =-x,-y,1-z
   [  2656.] = [  2_656] =1-x,-y,1-z
   [  1545.] = [  1_545] =x,-1+y,z
   [  2666.] = [  2_666] =1-x,1-y,1-z
   [  2565.] = [  2_565] =-x,1-y,-z
```

Table S17. Hydrogen bonding metrics of *fac*-[Pt(NH_3)$_3$$Br_3$]Br·DMF (ESI4).

```
Donor --- H....Acceptor [    ARU  ]      D - H      H...A      D...A  D - H...A
N1    --H1A    ..Br3    [  4355.03]       0.91       2.54   3.402(2)        158
N1    --H1B    ..Br4    [         ]       0.91       2.84   3.193(2)        104
N1    --H1C    ..Br3    [  2345.03]       0.91       2.78   3.492(2)        136
N2    --H2A    ..Br3    [  2345.03]       0.91       2.55   3.442(2)        167
N2    --H2B    ..Br3    [  4455.03]       0.91       2.51   3.374(2)        158
N2    --H2C    ..O1S    [         ]       0.91       1.96   2.830(3)        159
N3    --H3A    ..O1S    [         ]       0.91       2.02   2.791(3)        142
N3    --H3B    ..Br4    [         ]       0.91       2.81   3.161(2)        104
N3    --H3B    ..Br2    [  2256.01]       0.91       2.78   3.610(2)        152
N3    --H3C    ..Br3    [  4355.03]       0.91       2.64   3.446(2)        148

Translation of ARU-Code to CIF and Equivalent Position Code
============================================================
   [  2256.] = [  2_256] =-5/2-x,1/2+y,3/2-z
   [  2345.] = [  2_345] =-3/2-x,-1/2+y,1/2-z
   [  4355.] = [  4_466] =-3/2+x,1/2-y,1/2+z
   [  4455.] = [  4_566] =-1/2+x,1/2-y,1/2+z
```

Table S18. Hydrogen bonding metrics of *fac*-[$Pt(NH_3)_3Br_3$]Br·DMF (ESI5).

Donor	--- H....	Acceptor	[ARU]	D - H	H...A	D...A	D - H...A
N1	--H1A	..Cl1C	[1655.03]	0.91	2.46	3.301(5)	153
N1	--H1B	..Cl3	[ ]	0.91	2.71	3.042(5)	103
N1	--H1B	..Cl1	[2745.01]	0.91	2.70	3.478(5)	144
N1	--H1C	..O1S	[ ]	0.91	2.09	2.798(7)	134
N2	--H2A	..Cl1C	[3766.03]	0.91	2.74	3.409(6)	131
N2	--H2B	..Cl3	[ ]	0.91	2.74	3.067(6)	103
N2	--H2C	..Cl1C	[1655.03]	0.91	2.41	3.268(6)	157
N3	--H3A	..O1S	[ ]	0.91	1.94	2.809(7)	160
N3	--H3B	..Cl1C	[ ]	0.91	2.35	3.218(5)	161
N3	--H3C	..Cl1C	[3766.03]	0.91	2.38	3.278(6)	170

Translation of ARU-Code to CIF and Equivalent Position Code

[2745.] = [2_745] =5/2-x,-1/2+y,1/2-z
[1655.] = [1_655] =1+x,y,z
[3766.] = [3_766] =2-x,1-y,1-z