Supporting information

The impact of counterion on metastable states properties in nitrosyl ruthenium complexes

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Table S1. Experimental and refinement details.

Complex	$[RuNO(NH_3)_4F][PtCl_6]$	$[RuNO(NH_3)_4F][PdCl_4]$	$[RuNO(NH_3)_4F][PtCl_4]$	$[RuNO(NH_3)_4F](ClO_4)_2$
Empirical formula	$Cl_6FH_{12}N_5OPtRu$	$Cl_4FH_{12}N_5OPdRu$	$Cl_4H_{12}FN_5OPtRu$	$Cl_2H_{12}FN_5O_9Ru$
Formula weight	626.01	466.42	555.11	417.12
Temperature/K	150(2)	150(2)	150(2)	150(2)
Crystal system	orthorhombic	orthorhombic	orthorhombic	triclinic
Space group	$P2_12_12_1$	$Cmc2_1$	$Cmc2_1$	$P\bar{1}$
a/Å	7.0583(5)	8.1541(3)	8.1354(13)	8.0038(5)
b/Å	8.7624(6)	17.4696(10)	17.5637(18)	11.8995(5)
c/Å	22.0421(14)	8.1730(5)	8.1749(8)	13.8054(8)
α/°	90	90	90	70.720(2)
β/°	90	90	90	86.091(2)
γ/°	90	90	90	88.040(2)
Volume/Å^3	1363.25(16)	1164.23(11)	1168.1(2)	1238.12(12)
Z	4	4	4	4
ρ_{calc}g/cm^3	3.050	2.661	3.157	2.238
μ/mm^{-1}	12.528	3.745	14.157	1.759
F(000)	1152.0	888.0	1016.0	824.0
Crystal size/mm^3	0.07 × 0.03 × 0.03	0.17 × 0.08 × 0.02	0.11 × 0.08 × 0.03	0.1 × 0.08 × 0.04
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.696 to 61.3	4.664 to 59.27	4.638 to 52.69	3.936 to 66.314
Index ranges	-9 ≤ h ≤ 9, -12 ≤ k ≤ 12, -31 ≤ l ≤ 30	-11 ≤ h ≤ 10, -24 ≤ k ≤ 23, -11 ≤ l ≤ 11	-10 ≤ h ≤ 9, -21 ≤ k ≤ 20, -10 ≤ l ≤ 10	-12 ≤ h ≤ 12, -18 ≤ k ≤ 18, -20 ≤ l ≤ 21
Reflections collected	44736	11486	2669	24099
Independent reflections	4053 [R_{int} = 0.0534, R_{sigma} = 0.0340]	1750 [R_{int} = 0.0400, R_{sigma} = 0.0290]	1253 [R_{int} = 0.0465, R_{sigma} = 0.0880]	24099 [R_{int} = 0.0373, R_{sigma} = 0.0448]
Data/restraints/parameters	4053/0/137	1750/1/73	1253/7/72	24099/0/334
Goodness-of-fit on F^2	1.056	1.053	0.833	1.080
Final R indexes [I>=2σ (I)]	R_1 = 0.0251, wR_2 = 0.0340	R_1 = 0.0200, wR_2 = 0.0359	R_1 = 0.0336, wR_2 = 0.0629	R_1 = 0.0385, wR_2 = 0.0988
Final R indexes [all data]	R_1 = 0.0329, wR_2 = 0.0359	R_1 = 0.0220, wR_2 = 0.0371	R_1 = 0.0444, wR_2 = 0.0685	R_1 = 0.0586, wR_2 = 0.1088
Largest diff. peak/hole / e Å^{-3}	1.08/-1.78	0.41/-0.41	1.23/-1.33	0.81/-1.01
Flack parameter	-0.011(3)	-0.07(3)	0.020(12)	-

Table S2. Selected bond lengths (Å) in obtained complexes.

Distance/complex					
$A[PtCl_4]$		$A[PdCl_4]$		$A[PtCl_6]$	
Pt-Cl1	2.310(6)	Pd-Cl1	2.312(1)	Pt-Cl1	2.330(1)
Pt-Cl2	2.302(2)	Pd-Cl2	2.298(1)	Pt-Cl2	2.314(2)
Pt-Cl3	3.339(6)	Pd-Cl3	2.344(2)	Pt-Cl3	2.321(1)
Pt-Cl4	2.302(2)	Pd-Cl4	2.298(1)	Pt-Cl4	2.328(2)
				Pt-Cl5	2.323(2)
				Pt-Cl6	2.313(2)

Table S3. Bond lengths (Å) in the ClO_4^- anions of the $A(ClO_4)_2$.

Bond/ Distance							
Cl1-O3	1.427(2)	Cl2-O7	1.449(3)	Cl3-O11	1.438(3)	Cl4-O15	1.409(2)
Cl1-O4	1.441(3)	Cl2-O8	1.434(2)	Cl3-O12	1.432(3)	Cl4-O16	1.438(3)
Cl1-O5	1.433(3)	Cl2-O9	1.426(3)	Cl3-O13	1.434(3)	Cl4-O17	1.440(3)
Cl1-O6	1.449(3)	Cl2-O10	1.428(4)	Cl3-O14	1.443(2)	Cl4-O18	1.441(3)

Table S4. Found hydrogen bond lengths (Å) and angles (°).

Distance, angle/complex					
$A[PdCl_4]$			$A[PtCl_4]$		
N1-H···Cl2	2.844	112.0	N1-H···Cl2	2.534	156.9
N1-H···Cl3	2.526	171.6	N1-H···Cl2	2.813	119.7
N1-H···Cl2	2.528	151.3	N1-H···Cl3	2.614	163.1
N3-H···Cl2	2.804	145.8	N3-H···Cl1	2.572	158.3
N3-H···Cl3	2.637	138.5	N3-H···Cl2	2.854	121.7
N3-H···Cl2	2.908	149.8	N3-H···Cl3	2.547	159.3
N3-H···Cl1	2.912	114.9	N1-H···F1	2.148	142.2
N3-H···Cl2	2.458	169.9			
N1-H···F1	2.046	149.1			
$A(ClO_4)_2$			$A[PtCl_6]$		
N1-H···O13	2.365	128.1	N1-H···Cl4	2.886	127.9
N1-H···O7	2.422	144.1	N1-H···Cl6	2.649	152.9
N1-H···O15	2.484	114.3	N1-H···Cl6	2.927	122.6
N1-H···O9	2.639	117.3	N1-H···Cl3	2.787	140.1
N1-H···O14	2.613	139.4	N1-H···Cl2	2.759	133.1
N1-H···O11	2.617	116.8	N1-H···Cl3	2.916	126.9
N2-H···O8	2.701	134.0	N1-H···Cl5	2.776	148.2
N2-H···O7	2.265	163.6	N2-H···Cl1	2.774	139.2
N2-H···O8	2.243	138.4	N2-H···Cl4	2.669	152.5
N2-H···O6	2.537	132.3	N2-H··Cl5	2.701	131.1
N2-H···O3	2.648	130.4	N2-H···Cl5	2.433	176.4
N2-H···13	2.395	116.1	N3-H···Cl1	2.672	151.3
N3-H···O6	2.591	124.1	N3-H···Cl2	2.515	172.4
N3-H···O8	2.463	142.1	N3-H···Cl6	2.819	126.6
N3-H···O10	2.417	145.6	N4-H···Cl3	2.600	156.2
N3-H···O4	2.218	142.9	N4-H···Cl2	2.884	82.9

N3-H···O18	2.652	116.3	N4-H···Cl1	2.926	101.5
N3-H···O16	2.212	146.4	N4-H···Cl6	2.530	158.5
N4-H···O4	2.632	132.4	N4-H···F1	2.399	114.6
N4-H···O3	2.365	144.5			
N4-H···O18	2.317	145.3			
N4-H···O13	2.476	110.0			
N4-H···O11	2.272	152.7			
N4-H···O13	2.535	105.7			
N6-H···O18	2.371	166.6			
N6-H···O12	2.409	118.9			
N6-H···O16	2.130	155.3			
N7-H···O5	2.203	150.3			
N7-H···O12	2.092	158.5			
N7-H···O6	2.173	172.6			
N7-H···O5	2.691	121.2			
N8-H···O9	2.244	143.2			
N8-H···O12	2.631	100.6			
N8-H···O12	2.595	103.7			
N8-H···O7	2.208	171.9			
N8-H···O6	2.377	145.2			
N8-H···O4	2.344	153.3			
N9-H···O17	2.679	119.7			
N9-H···O12	2.255	135.2			
N9-H···O7	2.523	137.8			
N9-H···O17	2.111	164.6			
N1-H···F1	1.992	176.6			
N6-H···F2	2.160	156.0			
N9-H···F2	2.128	159.2			

Table S5. Intermolecular contacts shorter than the sum of the van der Waals radii (contacting atoms are underlined).

Contact length (Å)/complex									
A(SiF_6)		A[$PtCl_6$]		A[$PdCl_4$]		A[$PtCl_4$]		A(ClO_4)$_2$*	
N<u>O</u>···NH_3	2.66	N<u>O</u>···Cl	3.12	N<u>O</u>···Cl	3.19	N<u>O</u>···Cl	3.17	N<u>O</u>···O	2.91; 2.92
N<u>O</u>···F	2.66	N<u>O</u>···Cl	3.17	N<u>O</u>···Cl	3.19	N<u>O</u>···Cl	3.17	N<u>O</u>···O	3.04; 3.01
N<u>O</u>···F	2.86	N<u>O</u>···Cl	3.17			<u>N</u>O···Cl	3.29	<u>N</u>O···O	2.94; 3.01
<u>N</u>O···F	2.97	<u>N</u>O···Cl	3.30			<u>N</u>O···Cl	3.29	<u>N</u>O···O	2.97; 3.04
* The values related to the Ru1; Ru2 parts									

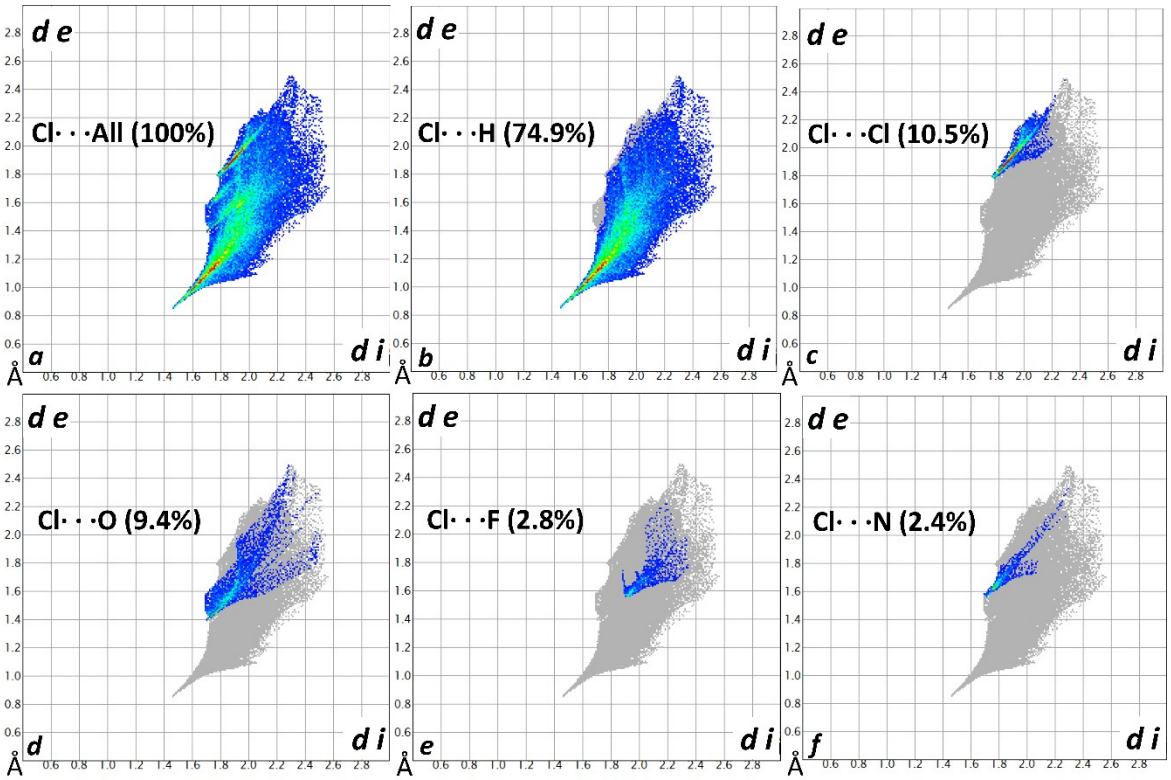

Fig. S1. The two-dimensional fingerprints of Hirshfeld surface of the $[PtCl_6]^{2-}$ in $A[PtCl_6]$.

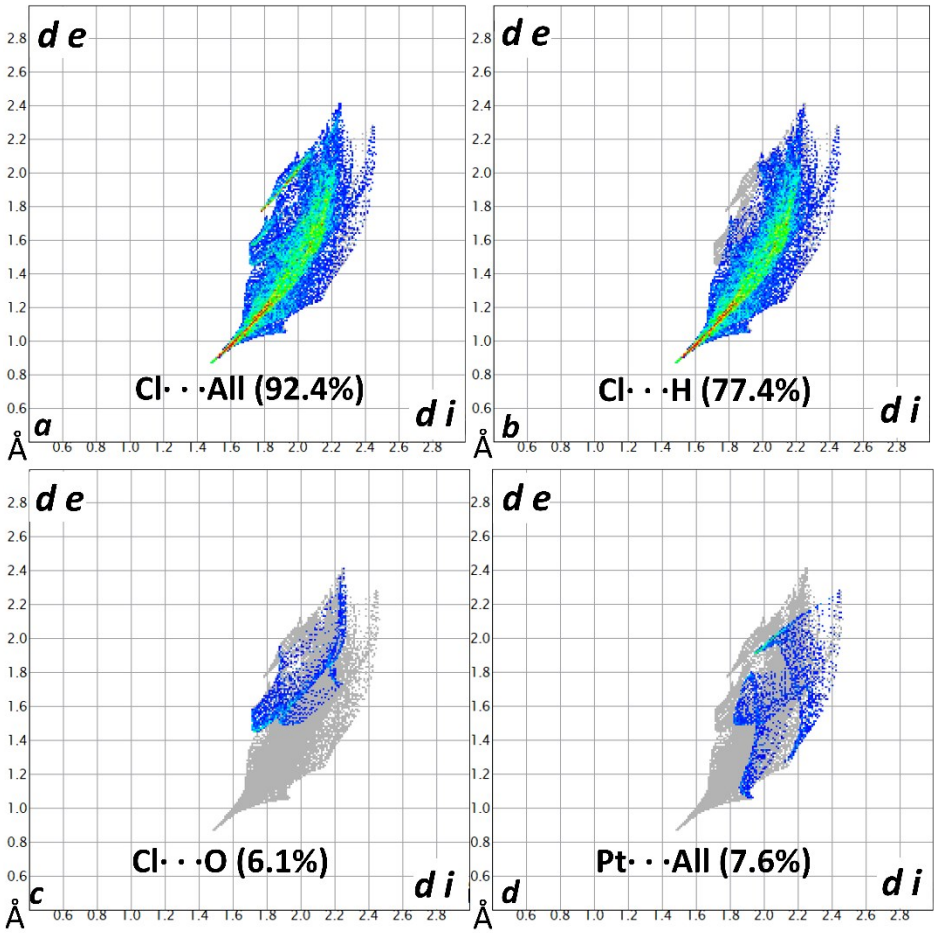

Fig. S2. The two-dimensional fingerprints of Hirshfeld surface of the $[PdCl_4]^{2-}$ in $A[PdCl_4]$.

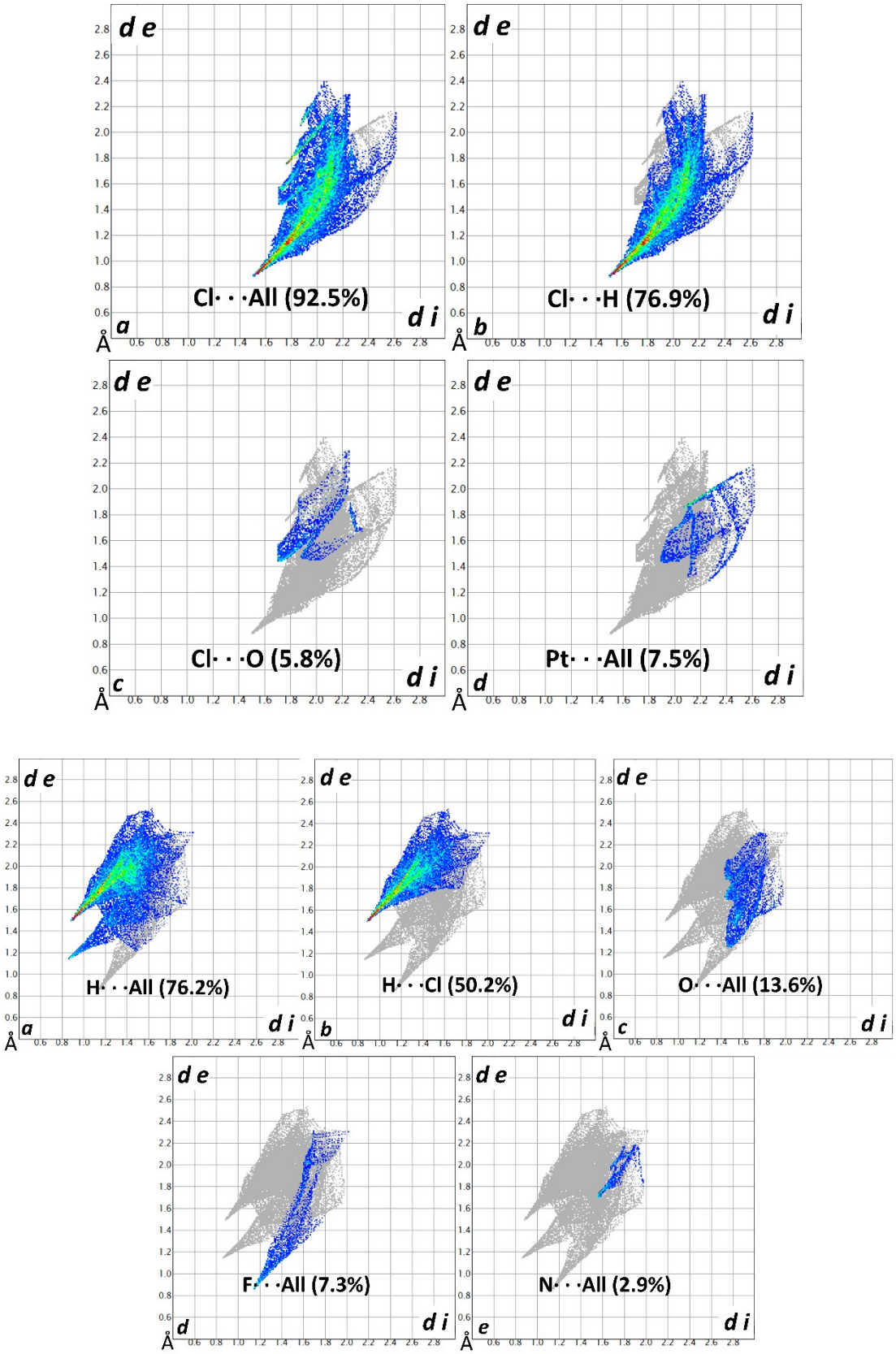

Fig. S3. The two-dimensional fingerprints of Hirshfeld surface of the $[PtCl_4]^{2-}$ (top panels) and $[RuNO(NH_3)_4F]^{2+}$ (bottom panels) in $A[PtCl_4]$.

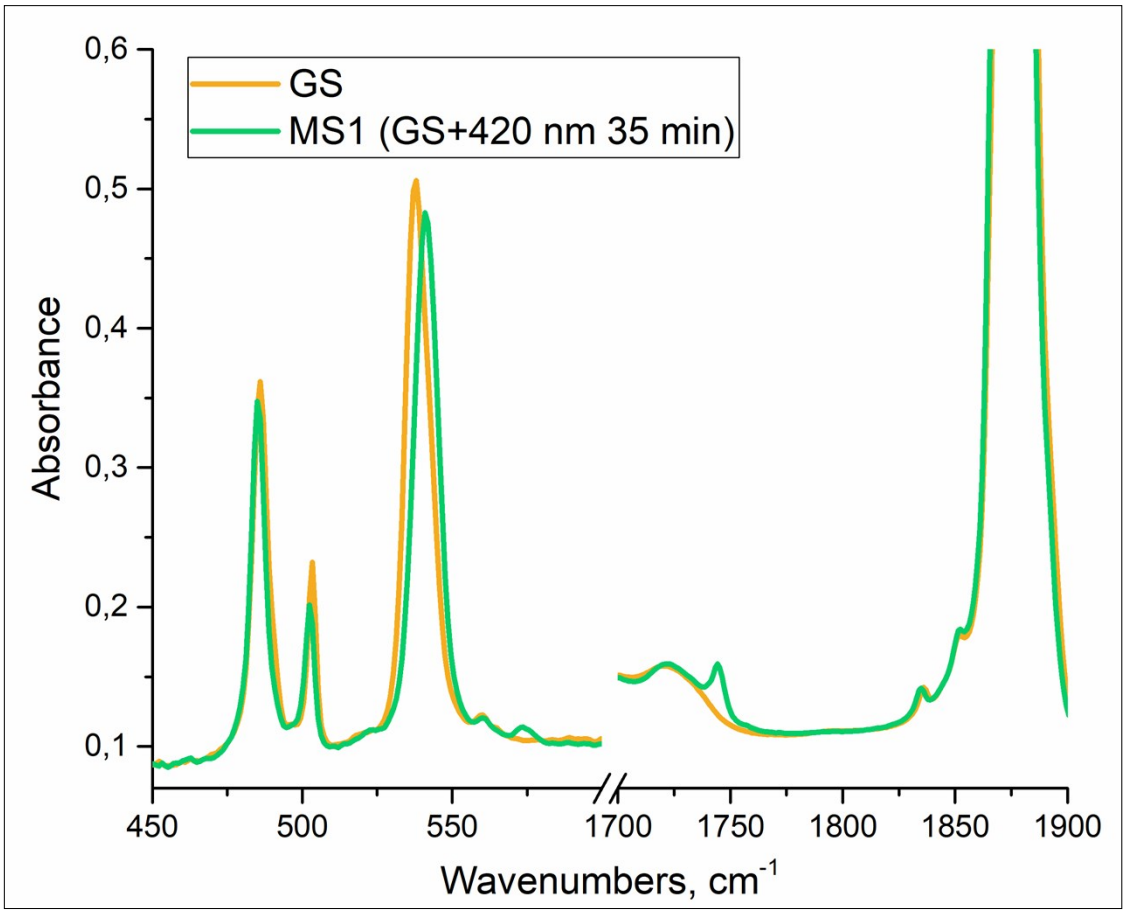

Fig. S4. IR-spectrum of A[$PtCl_6$] at 10 K before (GS, yellow) and after 420 nm irradiation (MS1, green).

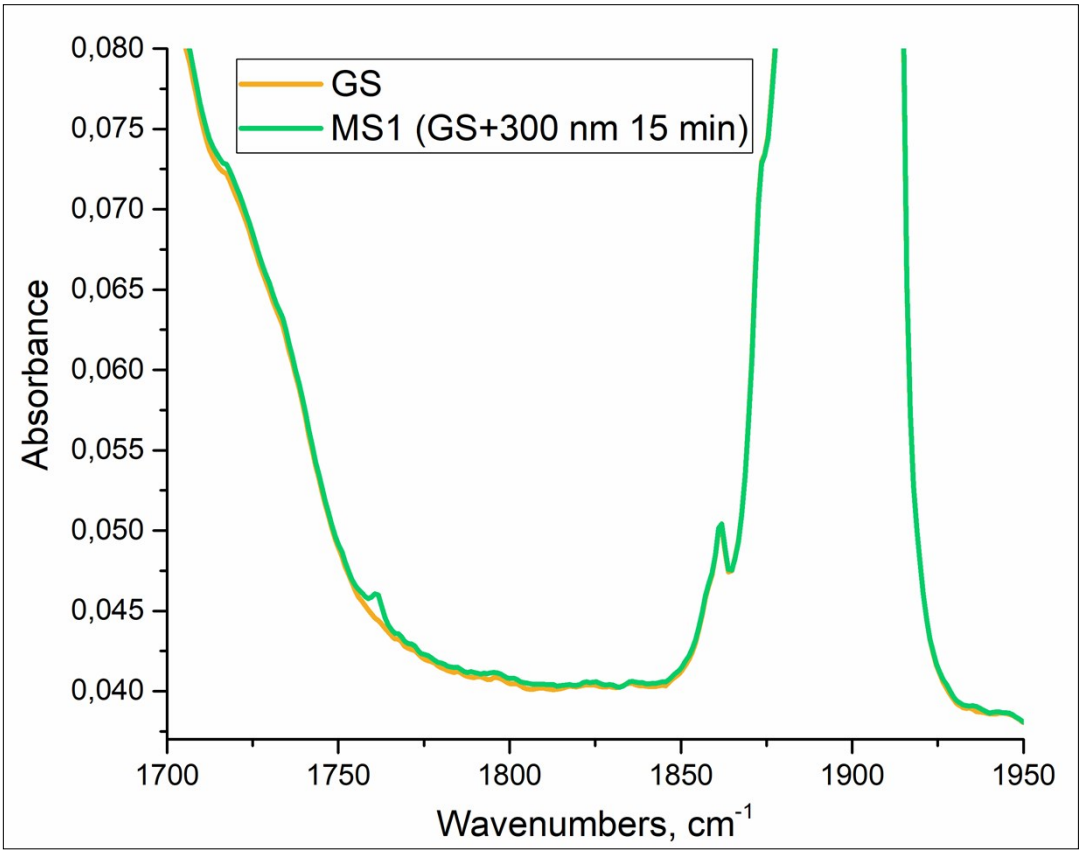

Fig. S5. IR-spectrum of A[$PtCl_4$] at 10 K before (GS, yellow) and after 300 nm irradiation (MS1, green).

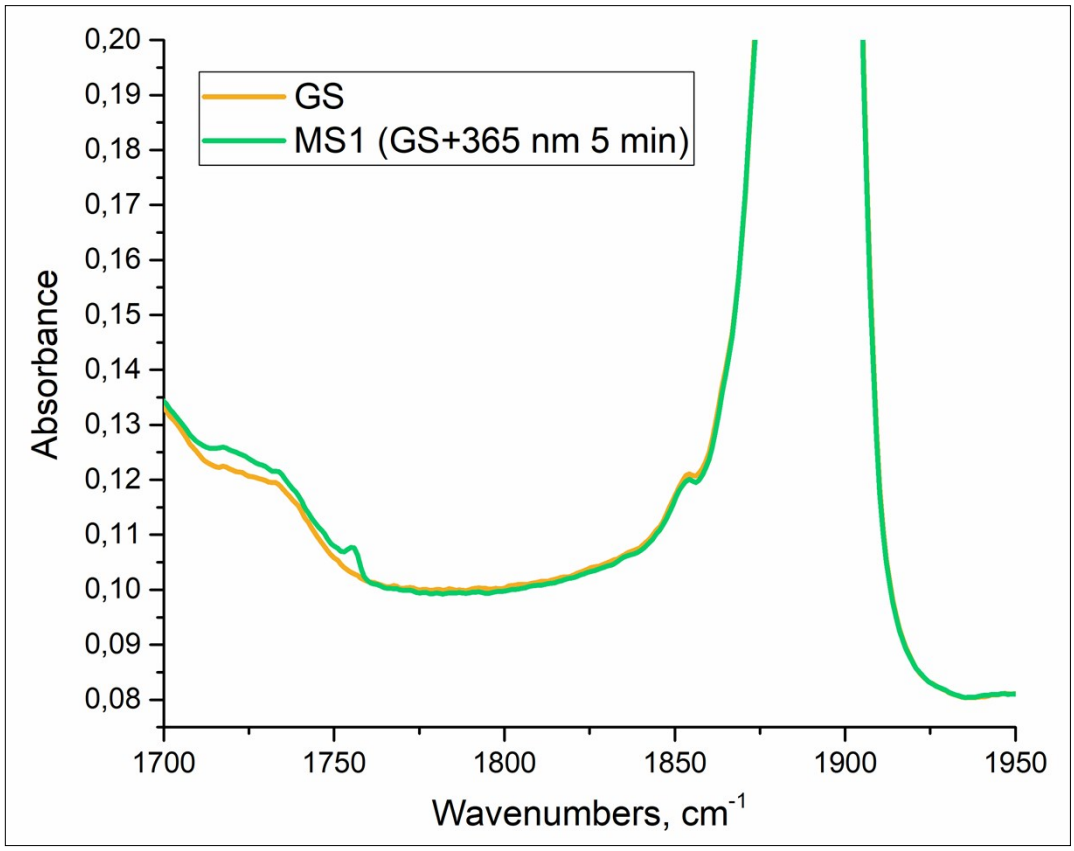

Fig. S6. IR-spectrum of A[$PdCl_4$] at 10 K before (GS, yellow) and after 365 nm irradiation (MS1, green).

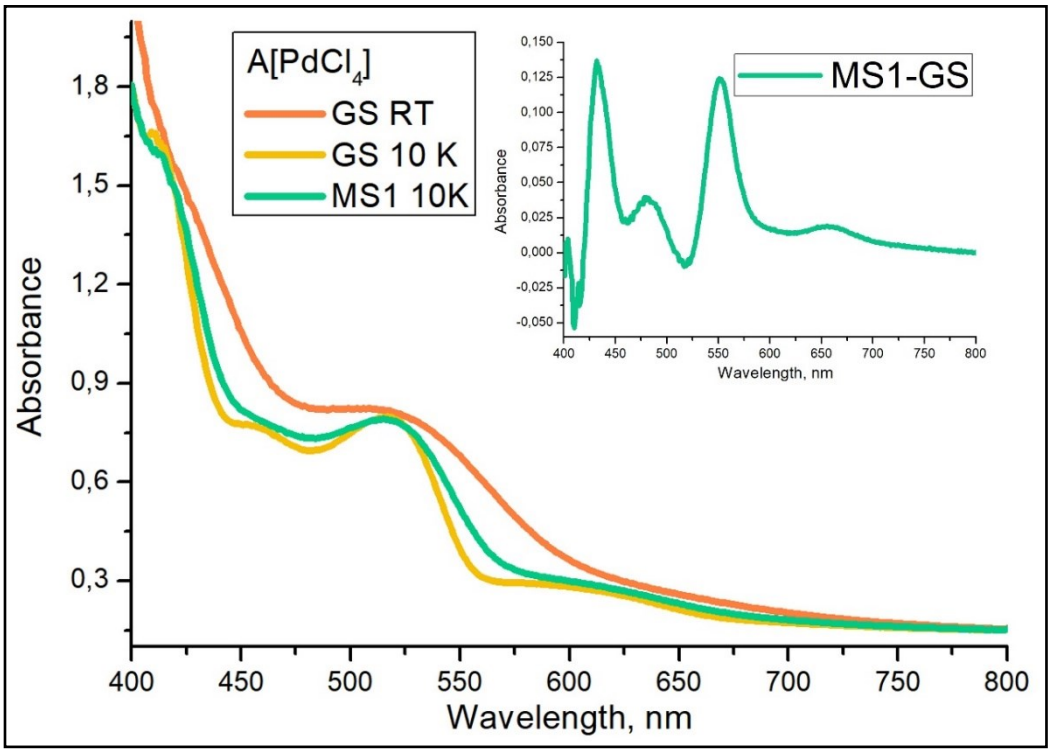

Fig. S7. UV/vis spectra of A[$PdCl_4$] in KBr at room temperature (orange), 10 K (yellow) and after MS1 generation at 10 K (green).

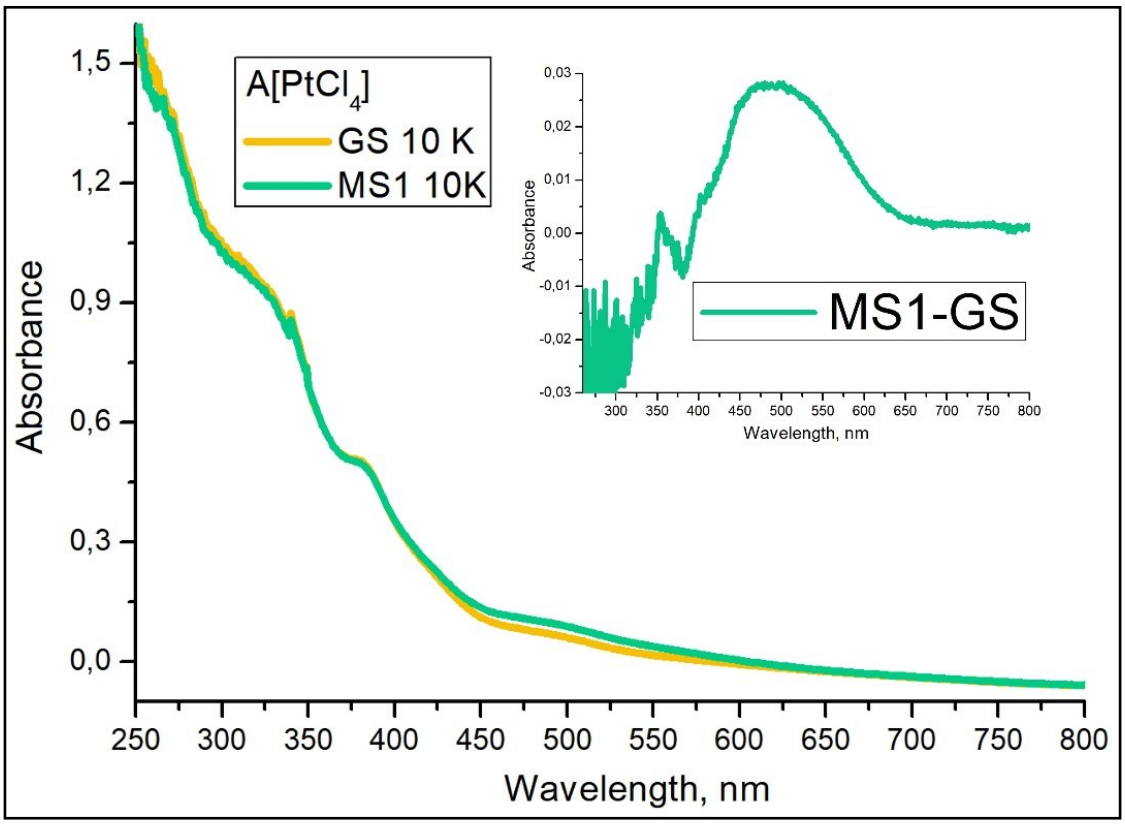

Fig. S8. UV/vis spectra of $A[PtCl_4]$ in KBr at 10 K (yellow) and after MS1 generation at 10 K (green).

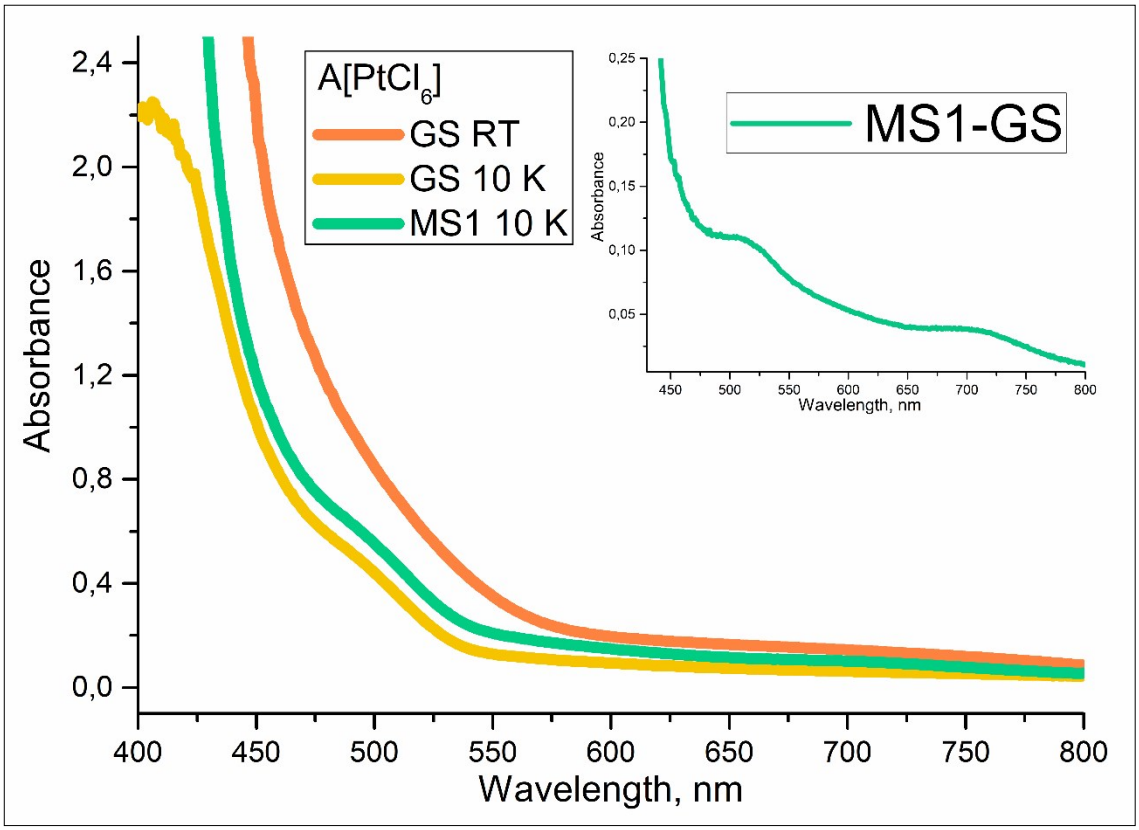

Fig. S9. UV/vis spectra of $A[PtCl_6]$ in KBr at room temperature (orange), 10 K (yellow) and after MS1 generation at 10 K (green).

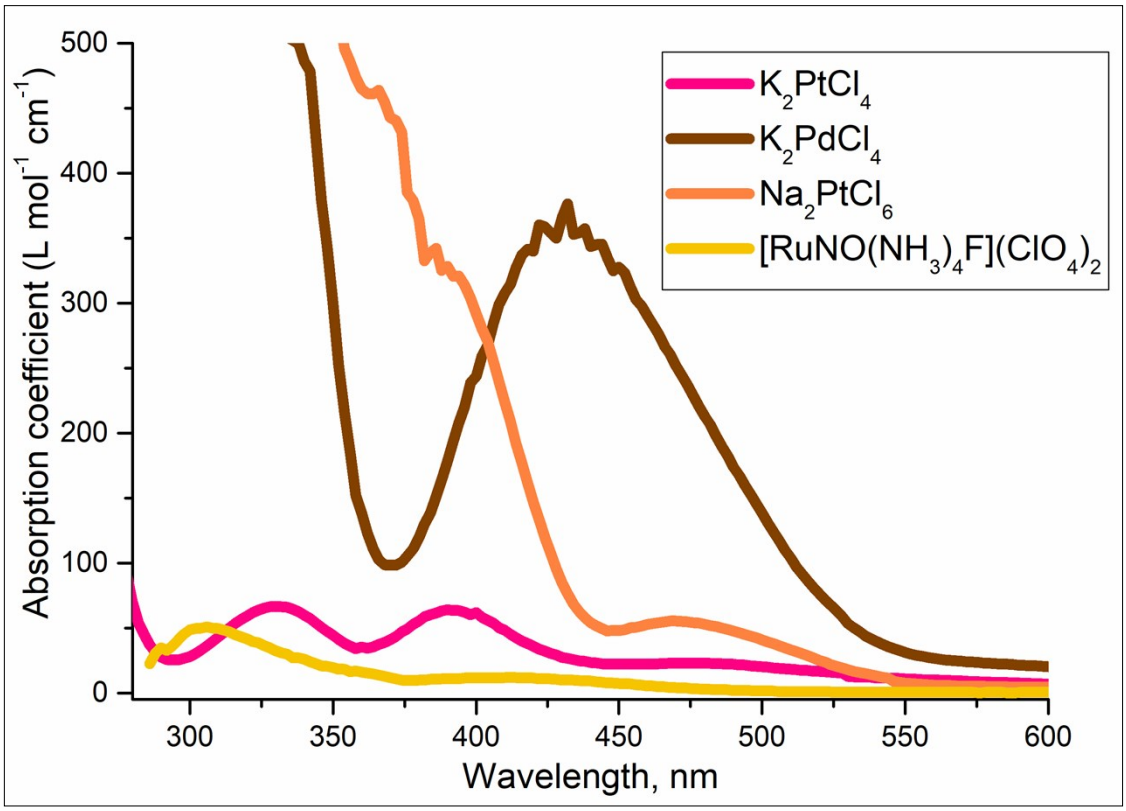

Fig. S10. UV/vis spectra of water solutions of K_2PtCl_4 (pink), K_2PdCl_4 (brown), Na_2PtCl_6 (orange) and $[RuNO(NH_3)_4F](ClO_4)_2$ (yellow).