Supporting Information

Sequential Photooxidation of a Pt(II)(Diimine)Cysteamine Complex: Intermolecular Oxygen Atom Transfer vs. Sulfinate Formation

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General Procedures

Solvents and chemicals used for synthetic procedures and photochemical studies were of reagent grade and were not purified unless noted otherwise. $PtCl_2$(2,2'-bipyridine) and 2-aminoethanethiol hydrochloride were purchased from Aldrich Chemical Company. All deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. NMR spectra were recorded on a 400 MHz Brucker Avance II NMR spectrometer. The [195]Pt-NMR spectra were referenced against K_2PtCl_4 in D_2O with a chemical shift $\delta = 0.0$ ppm. IR spectra were obtained from Nicolet AVATAR 320 FT-IR. UV-Vis spectra were recorded using a Varian Cary 300 Bio Spectrophotometer. Mass spectrometry was performed on a Thermo Scientific LCQ Fleet Ion Trap Mass Spectrometer.

Synthesis of Complexes 1-3

Complex **1** was prepared by using the literature method developed by Jensen et al. (Scheme 1).[1]
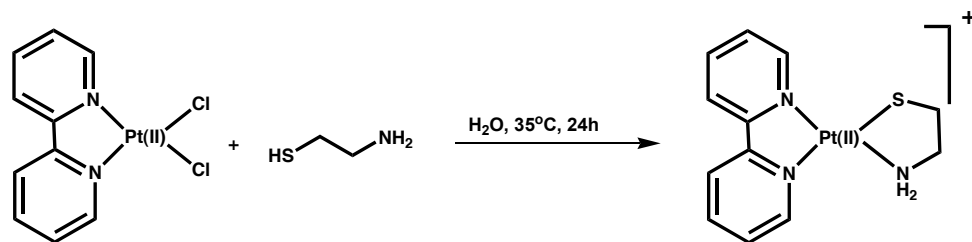

Scheme 1. Synthesis of Complex **1.**

Complexes **2** and **3** were prepared by reaction of **1** with singlet oxygen as described in the main text. Alternatively, for complex **2**, one molar equivalent of H_2O_2 (30%) was added to compound **1** previously dissolved in D_2O. For complex **3**, two equivalents of H_2O_2 (30%) were added to compound **1** dissolved in D_2O. D_2O was subsequently removed from the reaction mixture at room temperature under vacuum for approximately 5-7 hrs. [195]Pt NMR data, FTIR data for the sulfenate or sulfinato stretches of **2** and **3** and UV/vis spectra for complexes **1-3** are shown below.

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[1] Mitchell, K. A.; Jensen, C. M. *Inorg. Chem.* **1995**, *34*, 4441-4446.

^{195}Pt-NMR Spectra of Complexes (1), (2), and (3)
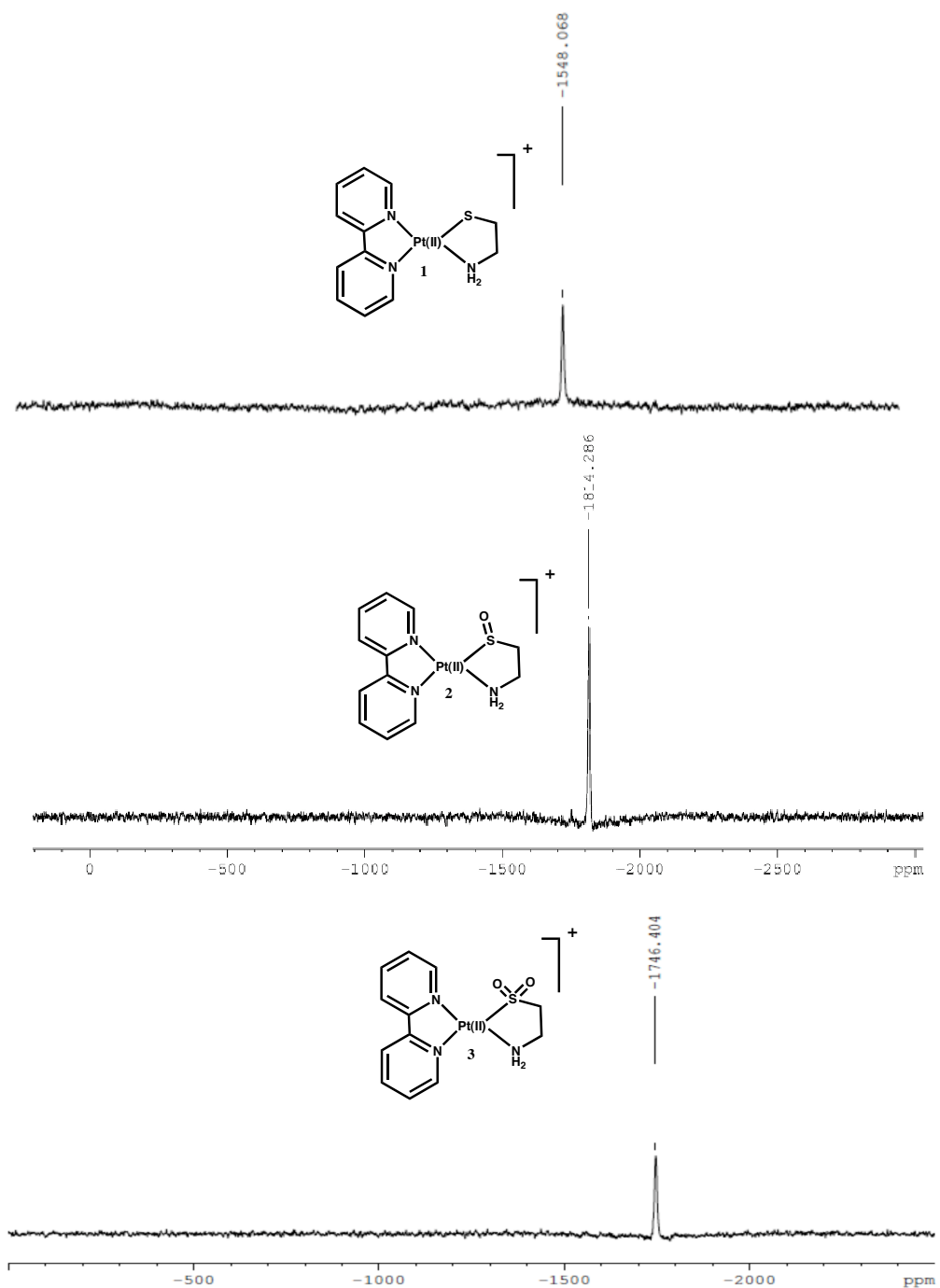
Figure 1. ^{195}Pt-NMR of complexes **1**, **2**, and **3** with chemical shifts of -1548 ppm (**1**), -1814 ppm (**2**), and -1746 ppm (**3**). Samples were obtained by dissolving 10.0 mg (0.0216 mmol) of **1** or 13.0 mg (0.0271 mmol) of **2** or 10.0 mg (0.0202 mmol) of **3** in 1 mL D$_2$O. Reference: K$_2$PtCl$_4$.
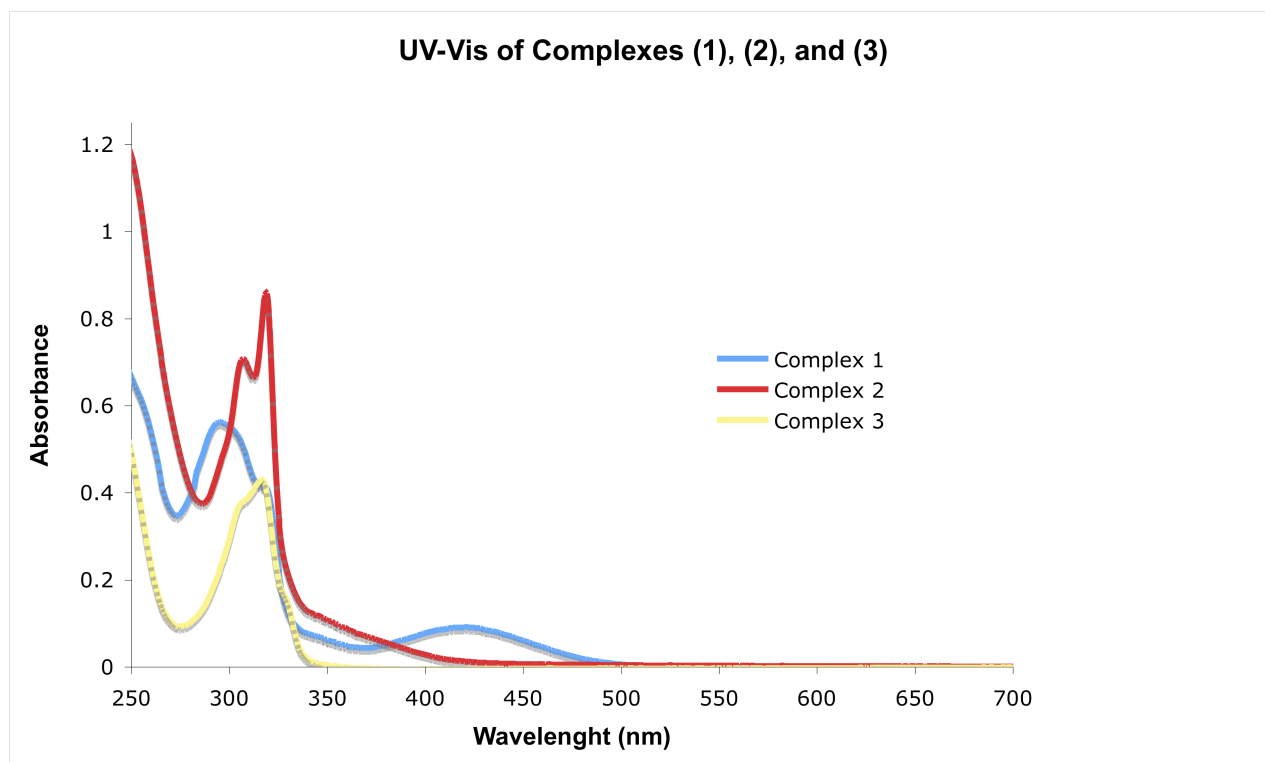
Table 1. Spectroscopic Properties for Complexes **1**, **2**, and **3**.

Complex	^{195}Pt-NMR[a] (ppm)	LC-MS (m/z) $[M - Cl]^+$	IR[b] (cm^{-1}) Pt−S=O	IR[b] (cm^{-1}) Pt−S(=O)(=O)	IR[b] (cm^{-1}) Pt−S(=O^{18})(=O^{18})	UV-Vis[c] [λ max (nm), ε (M^{-1} cm^{-1})]
1	-1548	427	-	-	-	295 (1.25 x 10^4), 421 (2.03 x 10^3)
2	-1814	443	918	-	-	307 (3.72 x 10^4), 319 (4.52 x 10^4)
3	-1746	459	-	1210 1070	1162 1024	316 (1.23 x 10^3)

[a] Ref.: K$_2$PtCl$_4$ in D$_2$O.
[a,c] Samples were dissolved in D$_2$O
[b] KBr pellet

Figure 2. UV-Vis Spectra of complexes **1**, **2**, and **3** in water.

Singlet Oxygen Experiments for Complexes 1-4

Singlet oxygen luminescence quenching experiments were carried out with a nanosecond pulsed Nd:YAG laser at an excitation wavelength of 532 nm. Singlet oxygen luminescence was observed with a liquid nitrogen cooled Ge photodiode detector (Applied Detector Corp. Model 403HS). A combination of several band-pass filters was used to remove undesired radiation outside the NIR emission of singlet oxygen. A Schott color glass filter (model RG850; cut-on 850 nm; Newport, USA) was taped to the sapphire entrance of the detector to block any additional ultraviolet and visible light from entering. The port opening to the detector contained a long wave pass filter (silicon filter model 10LWFw1000; Newport, USA) that transmits in the range of 1100-2220 nm and blocks in the range of 800-954 nm. A band pass filter (model BP-1270-080-B*; CWL 1270 nm; Spectrogen, USA) blocked radiation in the UV, visible, and IR regions and only transmitted in the range of 1200-1310 nm with maximum transmission of 60% at 1270 nm. All $^1O_2$ luminescence experiments were run in air-saturated solvents. For k_T measurements, a 2 ml solution of Methylene Blue in D_2O in a fluorescence cell was used as photosensitizer. Aliquots (10-60 μL) of D_2O stock solutions of complexes **1**, **2**, and **3** were added to this methylene blue solution. Concentrations of the stock solutions ranged from 0.0216 mmol to 0.0271 mmol. $^1O_2$ luminescence decay signals were recorded on a 500 MHz oscilloscope (LeCroy 9350 CM) and fitted to a first order exponential function on Origin 7.0. The k_T value for complex **4** was determined in the same way, except that complex **4** was dissolved in CD_2Cl_2.

A sample plot for the rate of singlet oxygen removal, k_T, of complexes **1** and **2** in D_2O are shown on the next page (Figure 3).

Singlet oxygen quantum yields were determined with the same set-up. Samples were prepared in D_2O (complexes **1-3**) or CD_2Cl_2 (complex **4**) with the OD at 532 nm ranging from 0.1–0.3. Complexes **1-3** showed no near infrared signal for singlet oxygen emission. For complex **4**, the characteristic $^1O_2$ emission signal was observed. The quantum yield of **4** was calculated from the intensity of the singlet oxygen emission signal, using C_{60} as a reference sensitizer. The $^1O_2$ intensity signal was extrapolated to $t = 0$. The data points of the initial 0–5 μs were not used due to electronic interference signals from the detector.

Quenching of $^1O_2$ by Complexes (1) and (2)
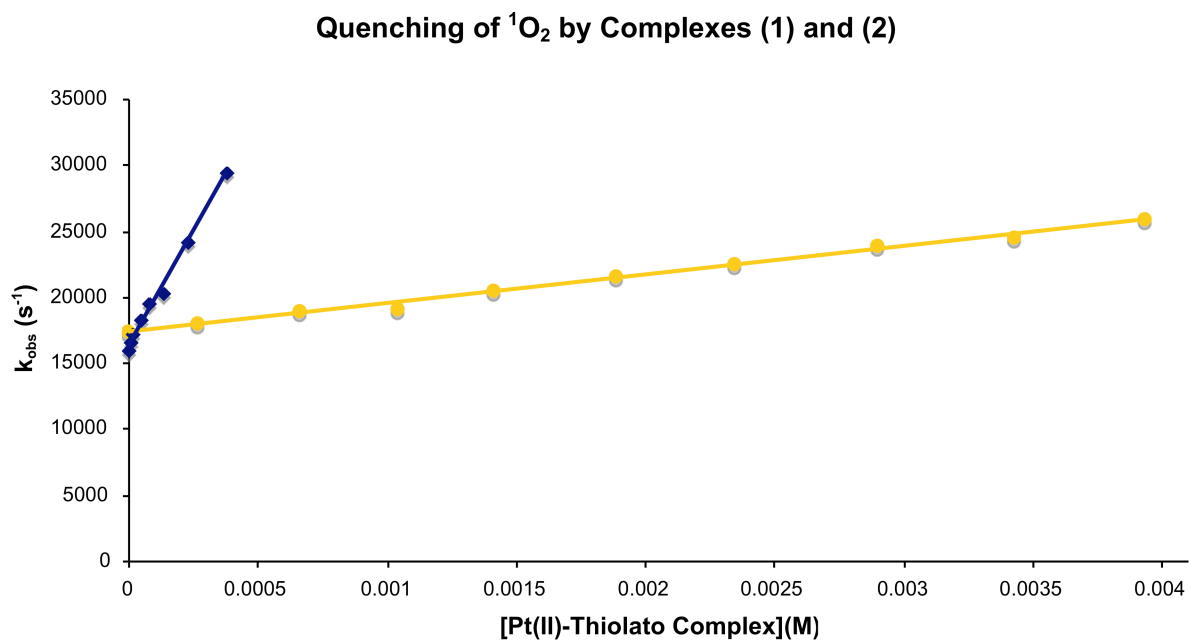
Figure 3. Sample $^1O_2$ luminescence quenching plots for complexes **1** (◆) and **2** (●). The slopes represent the total rate constants of singlet oxygen removal (k_T) by each complex.

X-ray Data Collection, Structure Determination and Refinement for $C_{12}H_{18}ClN_3O_3PtS$.

A yellow rod crystal of approximate dimensions 0.24 x 0.17 x 0.14 mm^3 is mounted on a Cryoloop with Paratone oil and transferred to a Bruker CCD platform diffractometer with graphite fine-focused monochromatic Mo-K_α radiation (λ = 0.71073 Å). The data were collected in a nitrogen gas stream at 143(2) K using phi and omega scans. The crystal-to-detector distance is 60 mm and exposure time of 10 seconds per frame using a scan width of 0.3^o up to a resolution of 0.77 Å. The SMART [1] program package was used to determine the unit-cell parameters and for data collection (20 sec / frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT [2] and SADABS [3] to yield the reflection data file. Subsequent calculations were carried out using the SHEXLTL [4] program. The structure is solved by direct methods (SIR-97) and refined on F^2 by full-matrix least squares techniques to produce a complete heavy-atom phasing model consistent with the proposed structure. The analytical scattering factors [5] for neutral atoms were used throughout the analysis. Data collection was 97.9% complete to 27.53^o in theta. A total of 9,141 reflections were collected covering the -15<= h <=15, -23<= k <=12, -9<= l <=9. 3421 reflections were found to be symmetry independent, with a R(int) of 0.0223. Indexing and unit-cell refinement indicated a primitive, monoclinic Laue group. The space group was found to be P2(1)/c (No. 14). All non-hydrogen atoms were refined anisotropically by the full matrix least-squares (SHELXL-97). Most hydrogen atoms were placed using a riding model corresponding to the respective carbon. Their positions were constrained using an appropriate HFIX cards in SHEXL-97 software.

Final structure refinement for $C_{12}H_{18}ClN_3O_3PtS$ molecule convergence resulted in R_1 = 0.021 and wR_2 = 0.046 for those data I > 2σ(I). The data to parameter ratio is 16 : 1 and Goodness-of-fit on F^2 equals 1.062, Z equals 4, and unit cell dimensions: a = 11.9802(16) Å, b = 17.800(2) Å, c = 7.1567(10) Å, angle β = 95.955(2)^o. There is one molecule in the asymmetric unit. Relevant crystallographic data is summarized in Tables 1 - 5 listed below:

There are two water (H_2O) molecules located in the crystal lattice, the hydrogen atoms were located from the difference Fourier maps and allowed to refine in lease-squares procedure.

Reference.

[1] SMART Software Users Guide, Version 5.1, Bruker Analytical X-Ray Systems, Inc.; Madison, WI, **1999**.

[2] SAINT Software Users Guide, Version 6.0, Bruker Analytical X-Ray Systems, Inc.; Madison, WI, **1999**.

[3] Sheldrick, G.M.: SADABS, Version 2.10, Bruker Analytical X-Ray Systems, Inc.; Madison, WI, **2002**.

[4] Sheldrick, G.M.: SHELXTL, Version 6.12, Bruker Analytical X-Ray Systems, Inc. Madison, WI, **2001**.

[5] International Tables for X-Ray Crystallography **1992**, Vol. C., Dordrecht: Kluwer Academic Publishers.

Table 1. Crystal data and structure refinement for C12H18ClN3O3PtS.

Identification code	ptclm
Empirical formula	C12 H18 Cl N3 O3 Pt S
Formula weight	514.89
Temperature	143(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 11.9802(16) Å $\alpha = 90°$.
	b = 17.800(2) Å $\beta = 95.955(2)°$.
	c = 7.1567(10) Å $\gamma = 90°$.
Volume	1517.9(4) Å^3
Z	4
Density (calculated)	2.253 Mg/m^3
Absorption coefficient	9.570 mm^{-1}
F(000)	984
Crystal size	0.24 x 0.17 x 0.14 mm^3
Theta range for data collection	1.71 to 27.53°.
Index ranges	-15<=h<=15, -23<=k<=12, -9<=l<=9
Reflections collected	9141
Independent reflections	3421 [R(int) = 0.0223]
Completeness to theta = 27.53°	97.9 %
Absorption correction	Empirical
Max. and min. transmission	0.3476 and 0.2072
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3421 / 0 / 206
Goodness-of-fit on F^2	1.062
Final R indices [I>2sigma(I)]	R1 = 0.0207, wR2 = 0.0459
R indices (all data)	R1 = 0.0228, wR2 = 0.0467
Largest diff. peak and hole	1.151 and -0.863 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2x 10^3) for C12H18ClN3O3PtS. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	7510(1)	1276(1)	7237(1)	18(1)
N(1)	6655(2)	290(2)	6852(4)	26(1)
N(2)	8243(2)	2297(2)	7652(4)	19(1)
N(3)	6193(2)	1969(2)	6191(4)	19(1)
O(1)	9997(2)	682(2)	7276(4)	38(1)
S(1)	8996(1)	573(1)	8391(1)	27(1)
C(1)	8417(3)	-335(2)	7554(7)	39(1)
C(2)	7222(4)	-363(2)	7829(7)	41(1)
C(3)	9309(3)	2429(2)	8391(5)	23(1)
C(4)	9722(3)	3145(2)	8717(5)	27(1)
C(5)	9034(3)	3754(2)	8277(5)	25(1)
C(6)	7939(3)	3627(2)	7507(5)	23(1)
C(7)	7566(3)	2903(2)	7201(4)	18(1)
C(8)	6425(3)	2717(2)	6350(5)	20(1)
C(9)	5633(3)	3252(2)	5718(5)	23(1)
C(10)	4595(3)	3019(2)	4888(5)	25(1)
C(11)	4373(3)	2262(2)	4706(5)	26(1)
C(12)	5187(3)	1752(2)	5365(5)	24(1)
Cl(1)	6043(1)	9803(1)	2545(1)	29(1)
O(2)	1964(3)	1408(2)	7580(5)	43(1)
O(3)	8037(3)	7923(2)	8592(5)	45(1)

Table 3.   Bond lengths [Å] and angles [°] for C12H18ClN3O3PtS.

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Pt(1)-N(2)	2.026(3)
Pt(1)-N(1)	2.037(3)
Pt(1)-N(3)	2.080(3)
Pt(1)-S(1)	2.2614(9)
N(1)-C(2)	1.485(5)
N(1)-H(1A)	0.9200
N(1)-H(1B)	0.9200
N(2)-C(3)	1.351(4)
N(2)-C(7)	1.368(4)
N(3)-C(12)	1.343(4)
N(3)-C(8)	1.362(4)
O(1)-S(1)	1.520(3)
S(1)-C(1)	1.834(4)
C(1)-C(2)	1.466(6)
C(1)-H(1C)	0.9900
C(1)-H(1D)	0.9900
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(4)	1.378(5)
C(3)-H(3)	0.9500
C(4)-C(5)	1.378(5)
C(4)-H(4)	0.9500
C(5)-C(6)	1.387(5)
C(5)-H(5)	0.9500
C(6)-C(7)	1.375(5)
C(6)-H(6)	0.9500
C(7)-C(8)	1.474(4)
C(8)-C(9)	1.387(5)
C(9)-C(10)	1.385(5)
C(9)-H(9)	0.9500
C(10)-C(11)	1.376(5)
C(10)-H(10)	0.9500
C(11)-C(12)	1.380(5)
C(11)-H(11)	0.9500

C(12)-H(12)	0.9500
O(2)-H(2C)	0.79(3)
O(2)-H(2D)	0.86(5)
O(3)-H(3C)	0.91(6)
O(3)-H(3D)	0.94(11)
N(2)-Pt(1)-N(1)	175.41(11)
N(2)-Pt(1)-N(3)	79.77(10)
N(1)-Pt(1)-N(3)	96.31(11)
N(2)-Pt(1)-S(1)	97.50(8)
N(1)-Pt(1)-S(1)	86.43(8)
N(3)-Pt(1)-S(1)	177.25(8)
C(2)-N(1)-Pt(1)	114.4(2)
C(2)-N(1)-H(1A)	108.7
Pt(1)-N(1)-H(1A)	108.7
C(2)-N(1)-H(1B)	108.7
Pt(1)-N(1)-H(1B)	108.7
H(1A)-N(1)-H(1B)	107.6
C(3)-N(2)-C(7)	118.0(3)
C(3)-N(2)-Pt(1)	126.2(2)
C(7)-N(2)-Pt(1)	115.8(2)
C(12)-N(3)-C(8)	118.9(3)
C(12)-N(3)-Pt(1)	126.9(2)
C(8)-N(3)-Pt(1)	114.1(2)
O(1)-S(1)-C(1)	103.48(18)
O(1)-S(1)-Pt(1)	111.79(11)
C(1)-S(1)-Pt(1)	96.42(13)
C(2)-C(1)-S(1)	109.2(3)
C(2)-C(1)-H(1C)	109.8
S(1)-C(1)-H(1C)	109.8
C(2)-C(1)-H(1D)	109.8
S(1)-C(1)-H(1D)	109.8
H(1C)-C(1)-H(1D)	108.3
C(1)-C(2)-N(1)	108.3(3)
C(1)-C(2)-H(2A)	110.0
N(1)-C(2)-H(2A)	110.0
C(1)-C(2)-H(2B)	110.0

N(1)-C(2)-H(2B)	110.0
H(2A)-C(2)-H(2B)	108.4
N(2)-C(3)-C(4)	122.3(3)
N(2)-C(3)-H(3)	118.9
C(4)-C(3)-H(3)	118.9
C(5)-C(4)-C(3)	119.6(3)
C(5)-C(4)-H(4)	120.2
C(3)-C(4)-H(4)	120.2
C(4)-C(5)-C(6)	118.8(3)
C(4)-C(5)-H(5)	120.6
C(6)-C(5)-H(5)	120.6
C(7)-C(6)-C(5)	119.6(3)
C(7)-C(6)-H(6)	120.2
C(5)-C(6)-H(6)	120.2
N(2)-C(7)-C(6)	121.7(3)
N(2)-C(7)-C(8)	115.0(3)
C(6)-C(7)-C(8)	123.3(3)
N(3)-C(8)-C(9)	121.1(3)
N(3)-C(8)-C(7)	115.2(3)
C(9)-C(8)-C(7)	123.6(3)
C(10)-C(9)-C(8)	119.1(3)
C(10)-C(9)-H(9)	120.4
C(8)-C(9)-H(9)	120.4
C(11)-C(10)-C(9)	119.4(3)
C(11)-C(10)-H(10)	120.3
C(9)-C(10)-H(10)	120.3
C(10)-C(11)-C(12)	119.2(3)
C(10)-C(11)-H(11)	120.4
C(12)-C(11)-H(11)	120.4
N(3)-C(12)-C(11)	122.1(3)
N(3)-C(12)-H(12)	118.9
C(11)-C(12)-H(12)	118.9
H(2C)-O(2)-H(2D)	108(4)
H(3C)-O(3)-H(3D)	109(7)

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Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for C12H18ClN3O3PtS. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\,h^2\,a^{*2}U^{11} + ... + 2\,h\,k\,a^*\,b^*\,U^{12}\,]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pt(1)	18(1)	15(1)	21(1)	0(1)	1(1)	1(1)
N(1)	27(2)	18(2)	31(2)	-4(1)	0(1)	0(1)
N(2)	19(1)	17(1)	21(1)	3(1)	3(1)	1(1)
N(3)	18(1)	18(1)	20(1)	1(1)	2(1)	1(1)
O(1)	24(1)	35(2)	55(2)	9(1)	6(1)	3(1)
S(1)	25(1)	21(1)	34(1)	2(1)	1(1)	6(1)
C(1)	34(2)	21(2)	63(3)	2(2)	8(2)	4(2)
C(2)	43(2)	23(2)	54(3)	3(2)	-5(2)	1(2)
C(3)	18(2)	25(2)	27(2)	1(1)	2(1)	1(1)
C(4)	21(2)	31(2)	29(2)	-3(2)	2(1)	-4(1)
C(5)	26(2)	23(2)	28(2)	-4(1)	7(2)	-4(1)
C(6)	25(2)	20(2)	24(2)	0(1)	6(1)	2(1)
C(7)	19(2)	21(2)	15(2)	0(1)	4(1)	2(1)
C(8)	21(2)	22(2)	16(2)	1(1)	4(1)	2(1)
C(9)	26(2)	19(2)	25(2)	3(1)	7(1)	1(1)
C(10)	22(2)	27(2)	26(2)	6(1)	4(1)	7(1)
C(11)	19(2)	35(2)	22(2)	0(2)	0(1)	-1(2)
C(12)	22(2)	23(2)	25(2)	-1(1)	1(1)	-2(1)
Cl(1)	29(1)	23(1)	35(1)	-2(1)	3(1)	-4(1)
O(2)	29(2)	30(2)	68(2)	1(2)	1(2)	-1(1)
O(3)	50(2)	31(2)	55(2)	7(2)	14(2)	3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2x 10 ^{3}) for C12H18ClN3O3PtS.

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	x	y	z	U(eq)
H(1A)	5959	348	7270	31
H(1B)	6547	189	5586	31
H(1C)	8512	-397	6205	47
H(1D)	8822	-748	8258	47
H(2A)	7128	-345	9187	49
H(2B)	6887	-837	7309	49
H(3)	9791	2013	8696	28
H(4)	10475	3218	9243	32
H(5)	9305	4251	8495	30
H(6)	7450	4038	7194	27
H(9)	5800	3773	5852	27
H(10)	4042	3377	4449	30
H(11)	3667	2093	4132	31
H(12)	5031	1231	5230	28
H(2C)	2460(30)	1115(19)	7660(40)	0(8)
H(2D)	1340(40)	1160(30)	7520(70)	46(14)
H(3C)	7920(50)	7420(40)	8480(90)	90(20)
H(3D)	7970(80)	8070(60)	9840(160)	210(50)

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