Supplementary information

Two new monofunctional platinum(II) dithiocarbamate complexes: phenanthriplatin-type axial protection, equatorial-axial conformational isomerism, anticancer and DNA binding studies

Muhammad Imran[a], Zia-ur-Rehman[a*], Graeme Hogarth[b], Derek A. Tocher[c], Gul-e-Saba Chaudhry[d], Ian S. Butler[e], Francine Bélanger-Gariepy[f], Tamara Kondratyuk[g]

[a]Department of Chemistry, Quaid-i-Azam University, 45320, Islamabad, Pakistan.

[b]Department of Chemistry, King's College London, Britannia House, 7 Trinity Street, London, SE1 1DB, UK.

[c]Department of Chemistry, University College London, 20 Gordon Street, London, WC1 0AJ, UK.

[d]Institute of Marine Biotechnology, University Malaysia Terengganu, Kuala Terengganu, 21030 Malaysia.

[e]Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montreal, Quebec, Canada H3A 0B8.

[f]Département de Chimie, Université de Montréal, Montreal, Canada

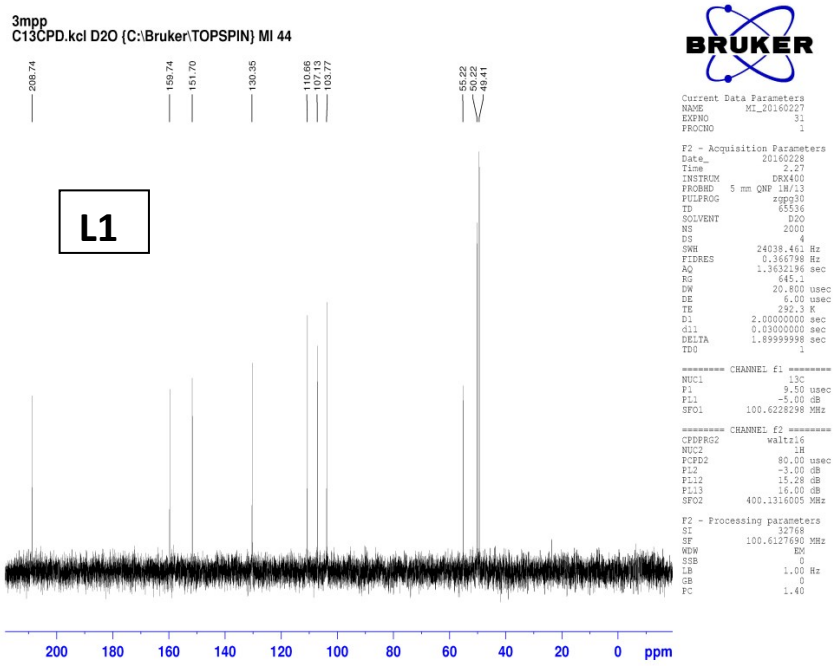
[g]University of Hawaii at Hilo, The Daniel K. Inouye College of Pharmacy, USA.

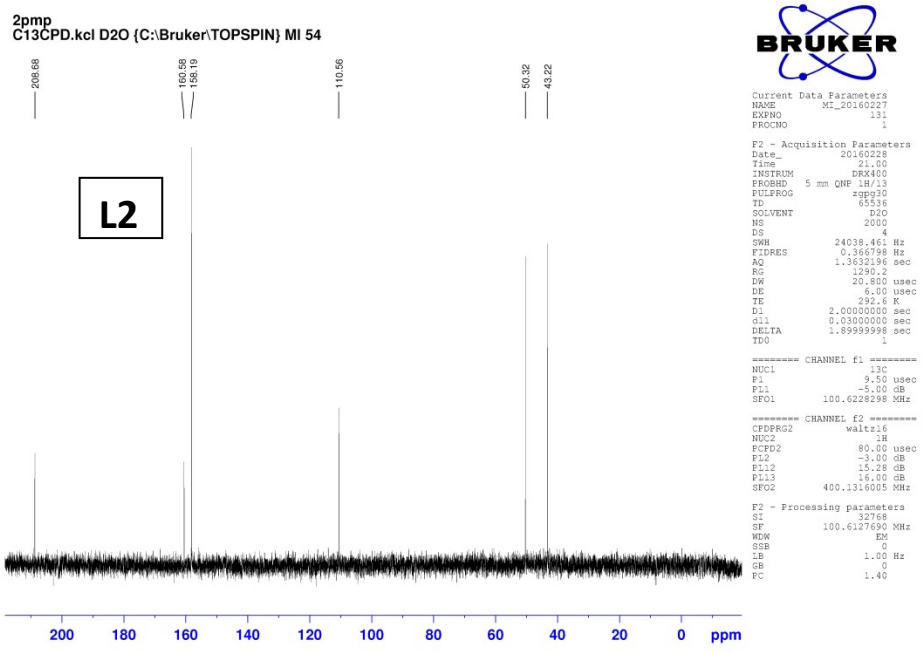
All correspondence should be addressed to zrehman@qau.edu.pk / hafizqau@ yahoo. com (Zia-ur-Rehman)

Materials and methods:

Reagents were purchased from; Sigma-Aldrich {1-(3-methoxyphenyl)piperazine and 1-(2-pyrimidyl)piperazine}, Wako Japan {tris(4-chlorophenyl)phosphine and platinum(II) chloride}, Riedel-de Ha¨en (CS_2) and sodium hydroxide from a local supplier. All the solvents were purchased from Daejung, Sigma-Aldrich and Scharlau. The chemicals used in the anticancer study (ethylenediaminetetraacetic acid disodium salt dihydrate (Na_2EDTA)), acetic acid, pyruvic acid, L-glutamine, sodium chloride, penicillin-G, sodium sarcosinate, sodium dodecyl sulfate (SDS), Triton X-100, streptomycin sulfate, and trizma-base were purchased from Sigma- Aldrich (USA). Fetal bovine serum (FBS) and Dulbecco's Modi-ed Eagle Medium (DMEM) were obtained from GibcoBRL, Gaithersburg, MD. Calf thymus (CT) DNA was procured from Sigma Aldrich. Cancer cell lines were purchased from American Type Cell Culture, USA. CellTiter 96 AQueous Non-Radioactive Cell Proliferation Assay (MTS) purchased from promega USA and ApoAlert^{TM} Annexin V assay, from Clontech, USA. A Gallenkamp (UK) electrothermal melting point apparatus was used for melting points determination. FT-IR spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR Spectrophotometer (4000–200 cm^{-1}). UV-visible measurements were carried out by UV-1601 UV-visible Spectrophotometer in a pair of quartz cells of 1 cm path length. Elemental analysis was carried out using a CE-440 Elemental Analyzer (Exeter Analytical, Inc.). 300 MHz Bruker instrument was used for obtaining ^{1}H- and ^{13}C-NMR spectra (TMS as an internal reference) and ^{31}P-NMR (85% H_3PO_4 in water as reference). Chemical shifts are given in *ppm* and multiplicities of proton signals are presented; s = singlet, d = doublet, t = triplet, dd = doublet of a doublets.

1.1 NMR spectra of ligands (L1, L2) and complexes 1 and 2.





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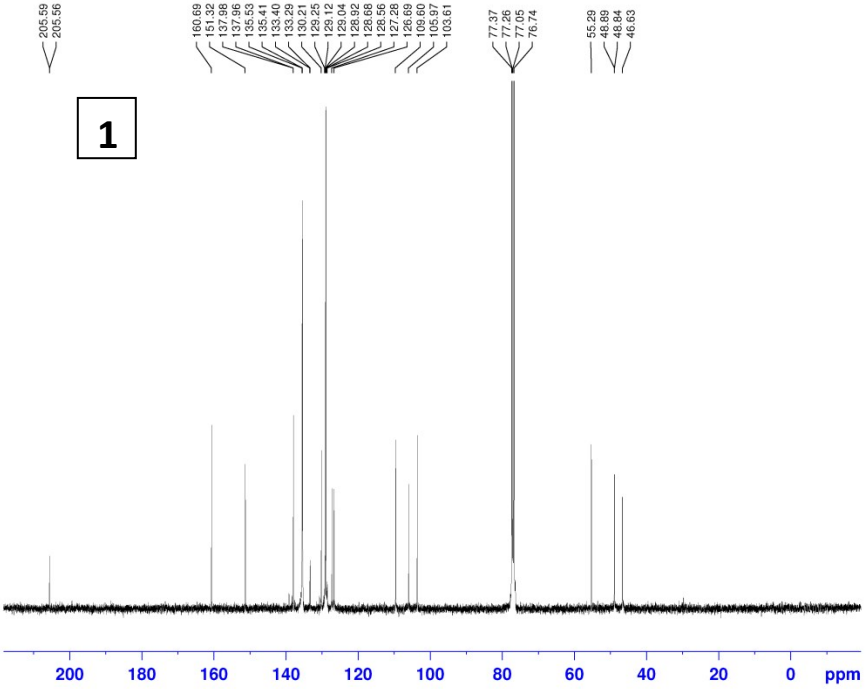

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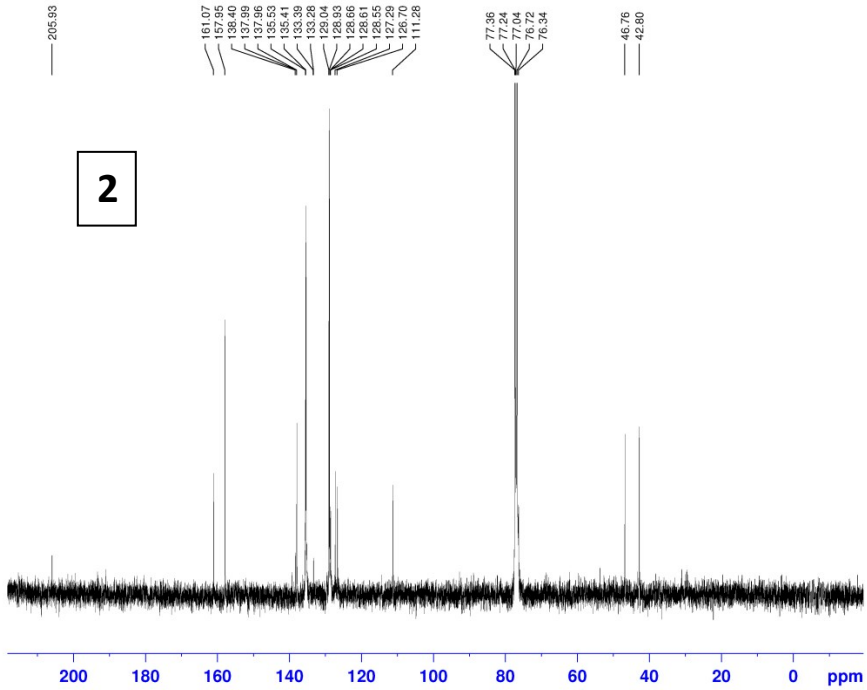

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AQ            1.3632196 sec
RG                574.7
DW               20.800 usec
DE                6.00 usec
TE                296.6 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.50 usec
PL1                 -5.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2               80.00 usec
PL2                 -3.00 dB
PL12                15.28 dB
PL13                16.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
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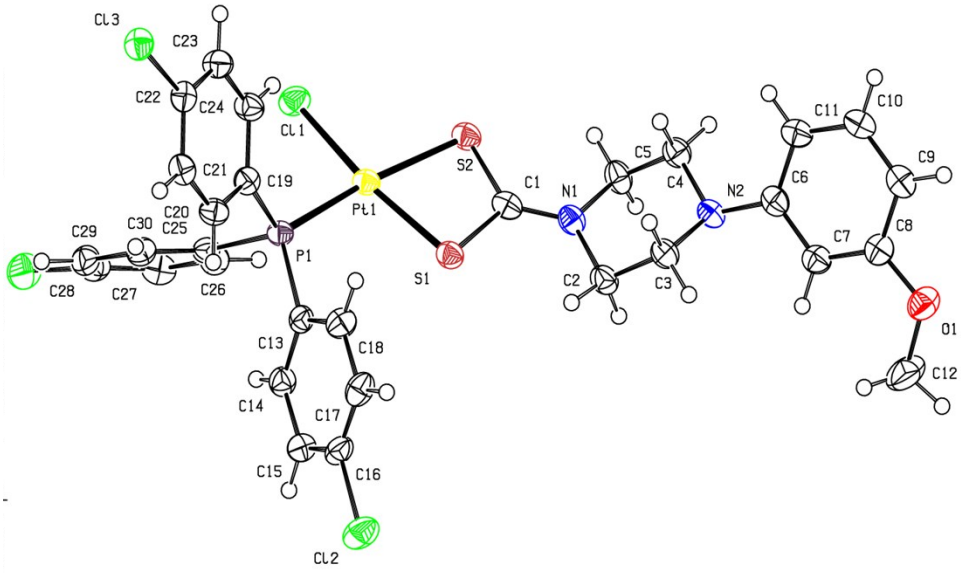
1.2 X-ray single crystal analysis

Suitable crystals of **1** ($C_{30}H_{27}Cl_4N_2OPPtS_2$) and **2** ($C_{27}H_{23}Cl_4N_4PPtS_2$) were selected and sealed (Nylon Loop) for examination on a SuperNova, Dual, Cu at zero, Atlas diffractometer. The crystals were kept at 150(1) K during data collection. Using Olex2 [**1**], the structures were solved with the ShelXS [**2**] and structure solution program using Direct Methods and refined with the ShelXL [**3**] refinement package using least-squares minimization.



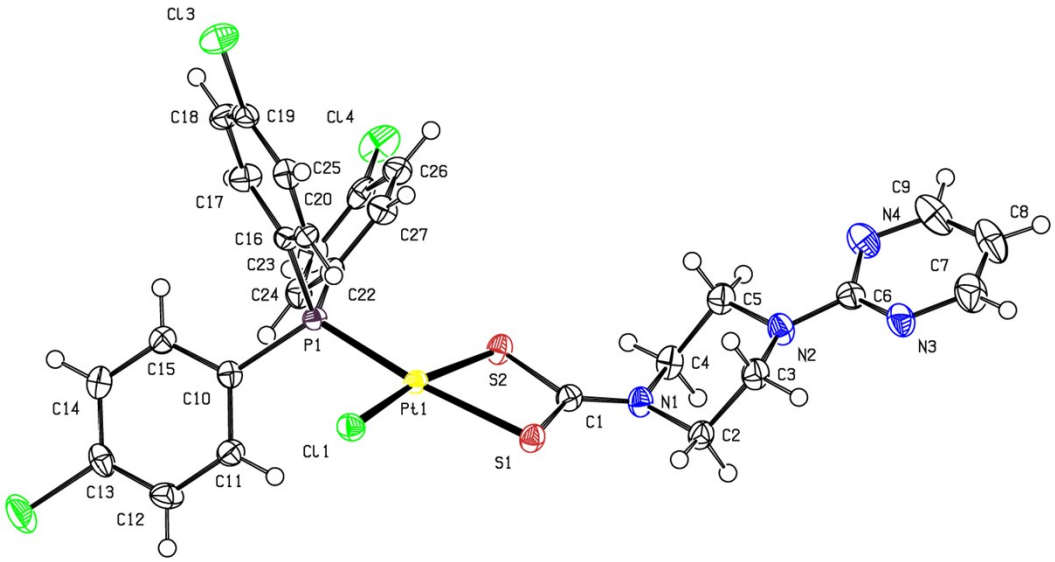


Fig. S1. ORTEP diagrams of crystal structure of both **1** and **2** complexes

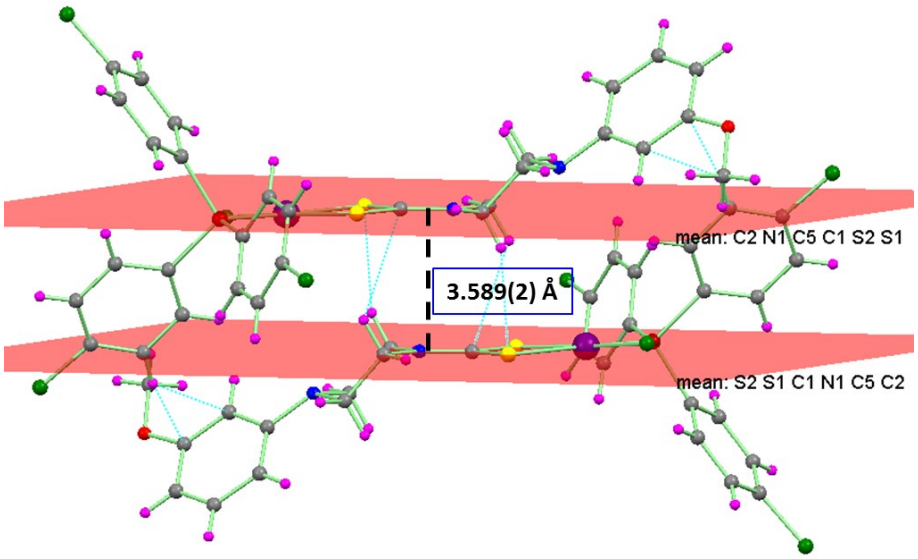


Fig. S2. Intermolecular distances in complex **1**

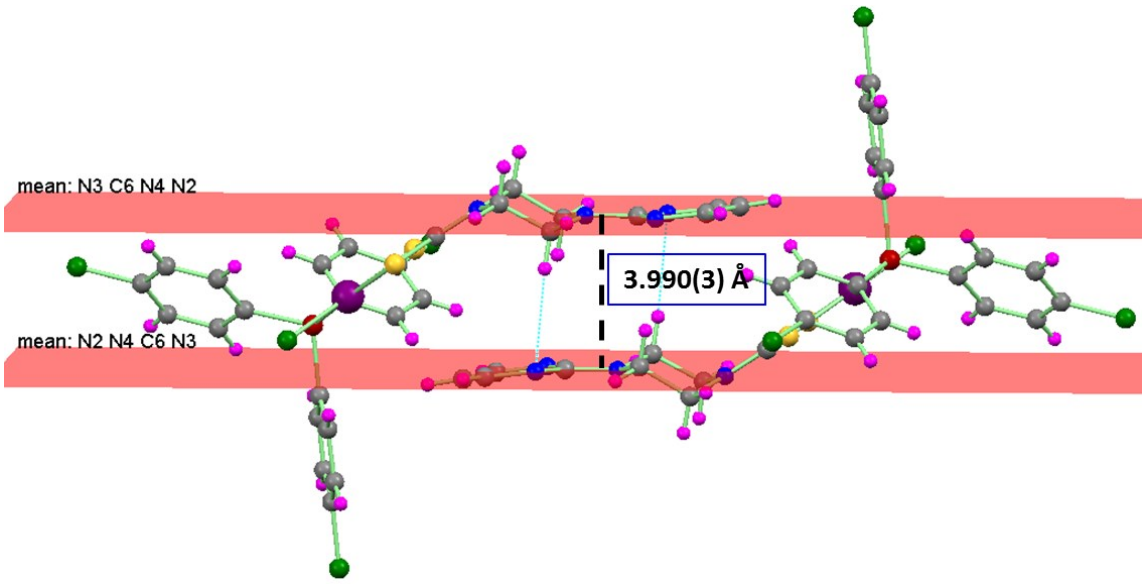


Fig. S3. Intermolecular distances in complex **2.**

1.3 Computational studies

DFT (density functional theory) calculations were performed by using the *Gaussian 09* suite of programs [**4**] and results were obtained using *Gauss View 5.0.8* software [**5**]. B3LYP density functional model with the basis set LANL2DZ (Los Alamos National Laboratory 2-double-ζ) [**6**]. The absence of negative frequencies in the vibrational analyses of the complexes confirmed the optimized geometries as the lowest energy structures. Gaussian checkpoint files of optimized geometries were used for further calculations. Net atomic charges were achieved by the Natural Bond Orbital (NBO) analysis of Weinhold and Carpenter [**7**] implemented in *Gaussian 09*. Molecular orbital data were acquired using additional keywords "pop = full formcheck."

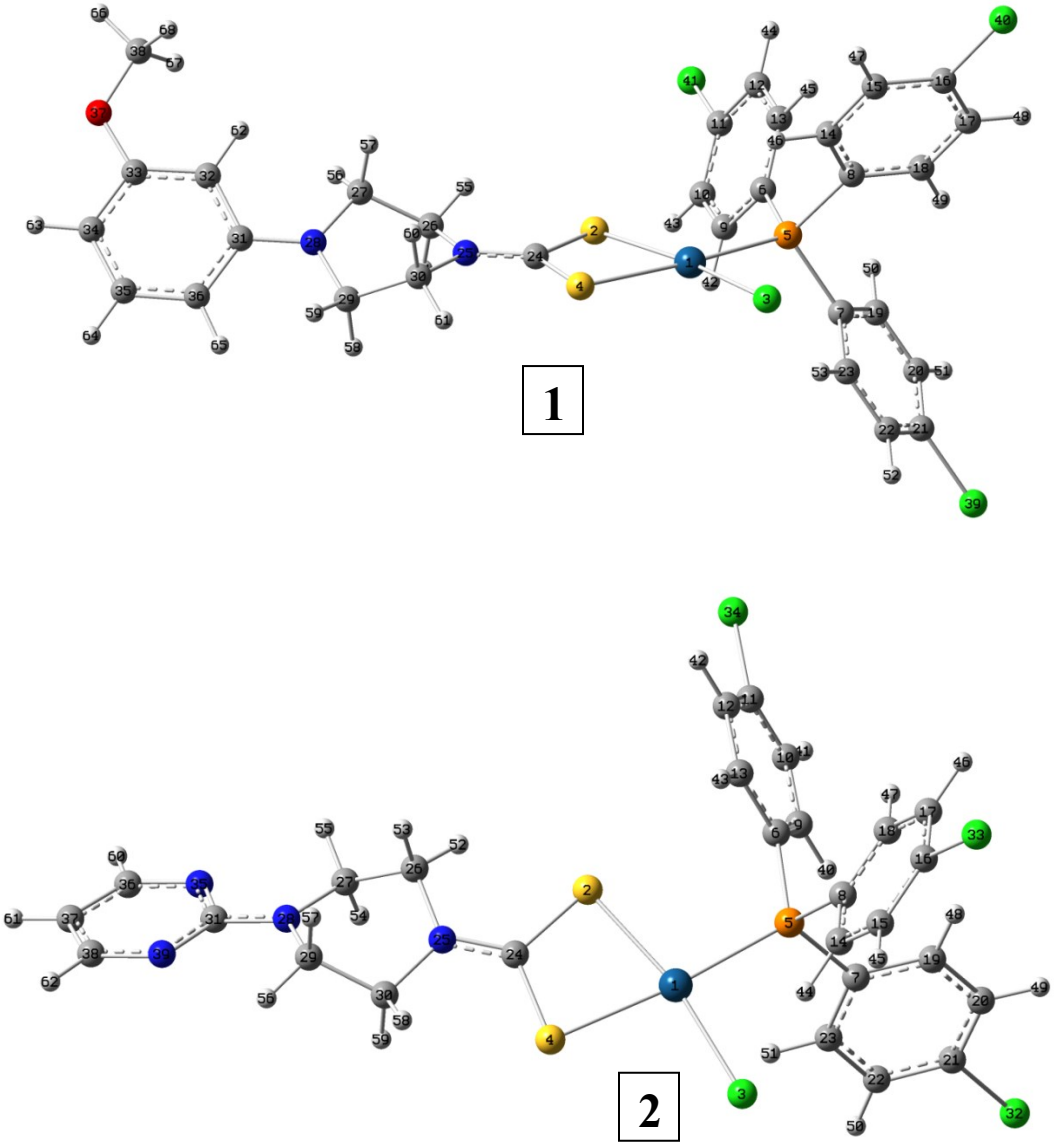


Fig. S4. DFT optimized structures for NBO analysis.

1.4 Stability in solution

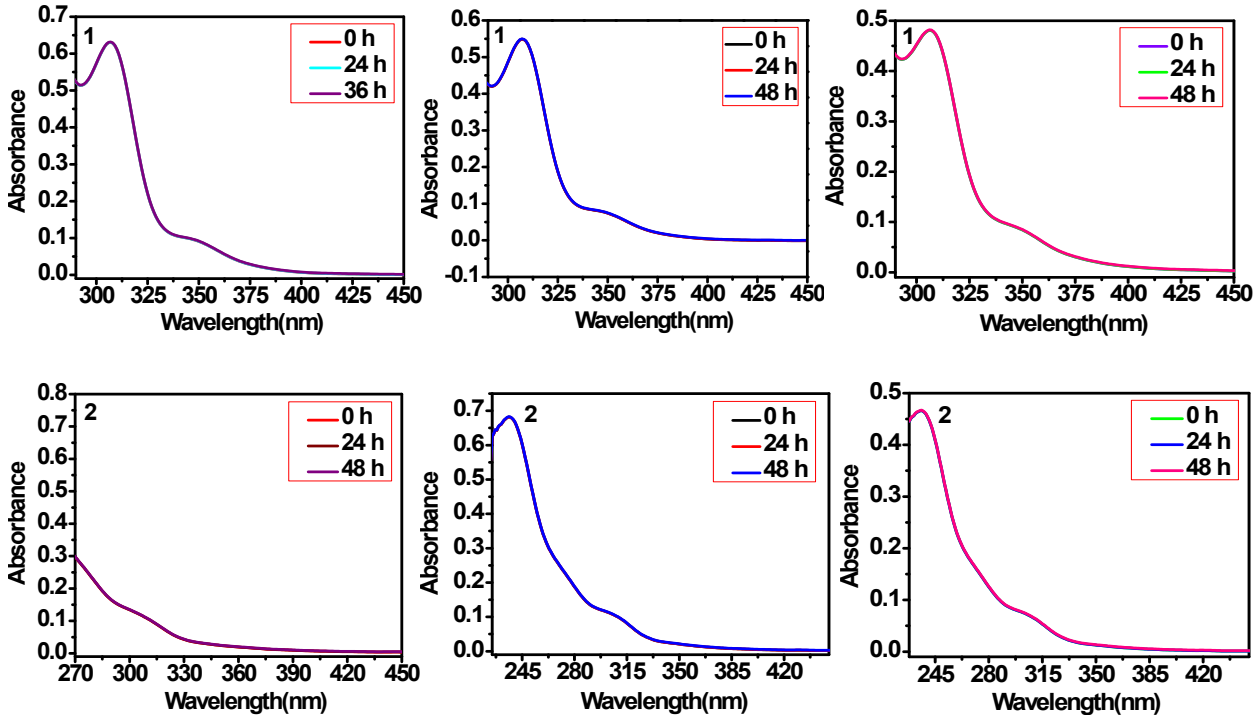


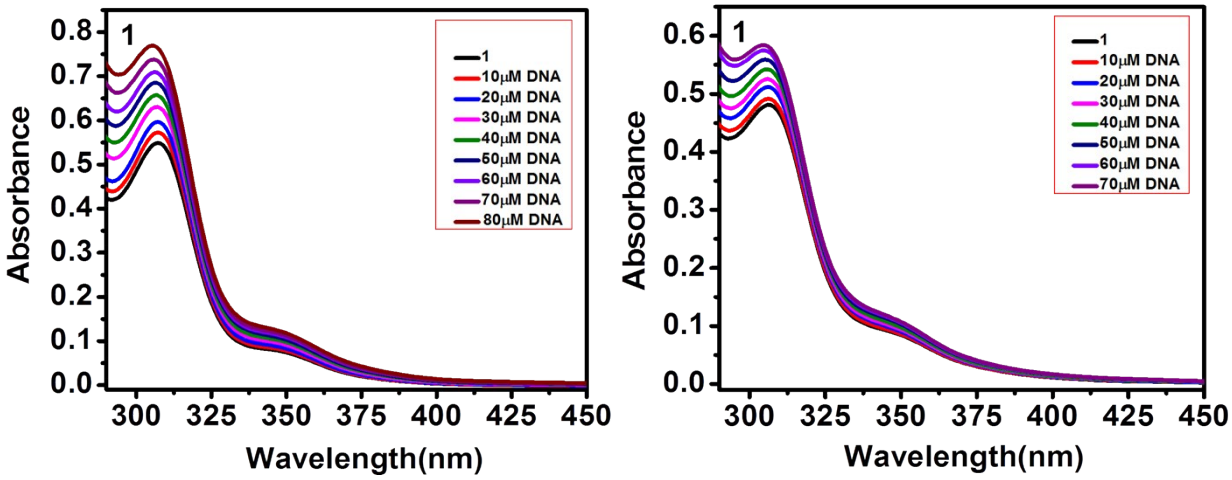
Fig. S5. Absorption spectra of **1** and **2** (50 μM) showing stability in DMSO, ethanol and saline solutions at 0, 24 and 48 h time intervals.

1.5 Lipophilicity and partition coefficient

To quantify the lipophilicity, partition coefficients of both complexes were calculated from the ratio of amount of complex in *n*-octanol/water by the shake flask method using the standard protocol [**8**].Two similar experiments were designed for each complex and the concentrations of both complexes in *n*-octanol were analyzed by electronic absorption measurements. Finally, the values of the partition coefficients, log P, were calculated from the logarithmic ratios of the amounts of complex between the organic and aqueous phases (log C_o / C_w).

1.6 DNA-binding studies using UV-visible spectroscopy

Calf thymus DNA (CT-DNA; 15 mg) interaction with the synthesized complexes was studied by using UV-visible spectroscopy. The stock solution of CT-DNA was prepared by dissolving 15 mg in doubly distilled water (pH 7) and stored at 4ºC. The protein free nature of the DNA was estimated by taking the ratio of A_{260}/A_{280} =1.8 [**9**]. The concentration of stock solution was measured at 260 nm by using an epsilon value of 6600 M^{-1} $cm^{-1}$and found to be 1.22 x 10^{-4} M [**10**]. The solutions of metal complexes incubated with and without DNA at 300 and 310 K separately and their maximum absorption values are reported. By applying the trial and error method, the maximum incubation time for complete interaction at 300 and 310 K separately was observed after 2.5 h and no absorbance changes were detected upon further incubation. To evaluate the quantitative binding potential of platinum complexes with DNA, the concentration of metal complex was kept constant while varying the DNA concentration [(10 to 80 μM) and (10 to 70 μM) for **1** and (10 to 60 μM) and (10 to 10 μM) for **2** at 300 and 310 K, respectively] and binding constant K_b and ΔG^o_b (molar Gibb's free energy of binding) have been calculated according to the reported methods [**11-13**].



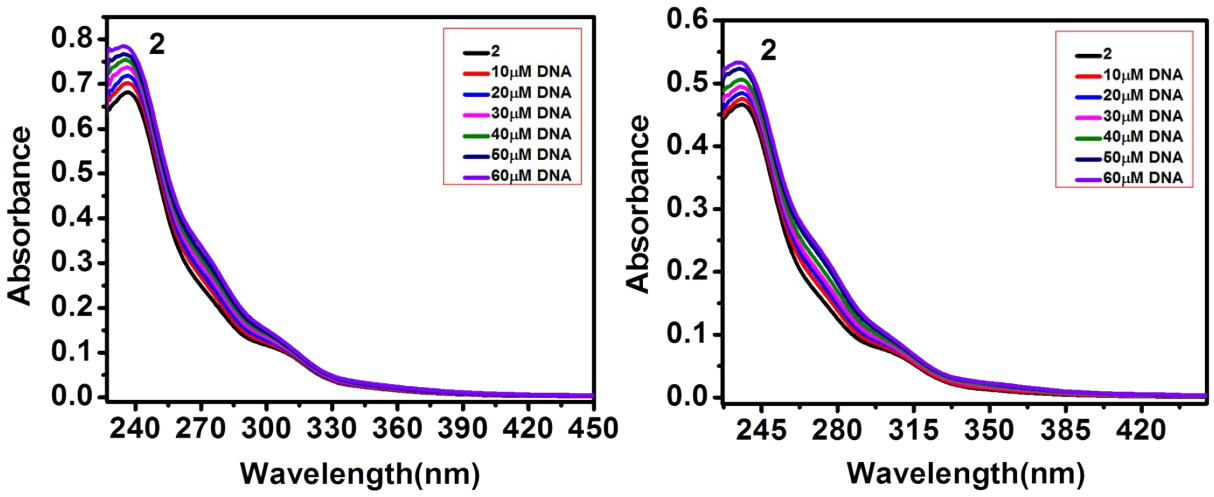


Fig. S6. Absorption spectra of constant concentration of complex **1** and **2** with varying DNA concentration at 300K (left) and 310K (right).

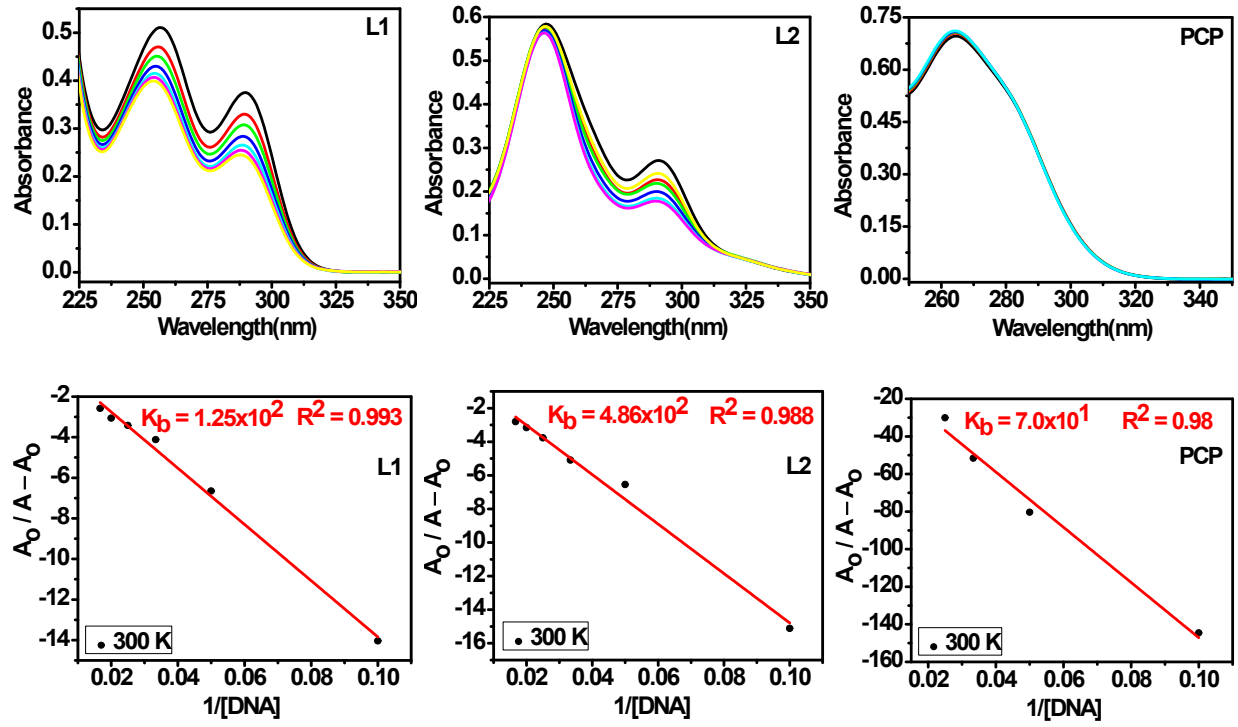


Fig. S7. Absorption spectra and DNA binding constant of ligands. **L1** and **L2** and PCP= tris(p-chlorophenyl)phosphine

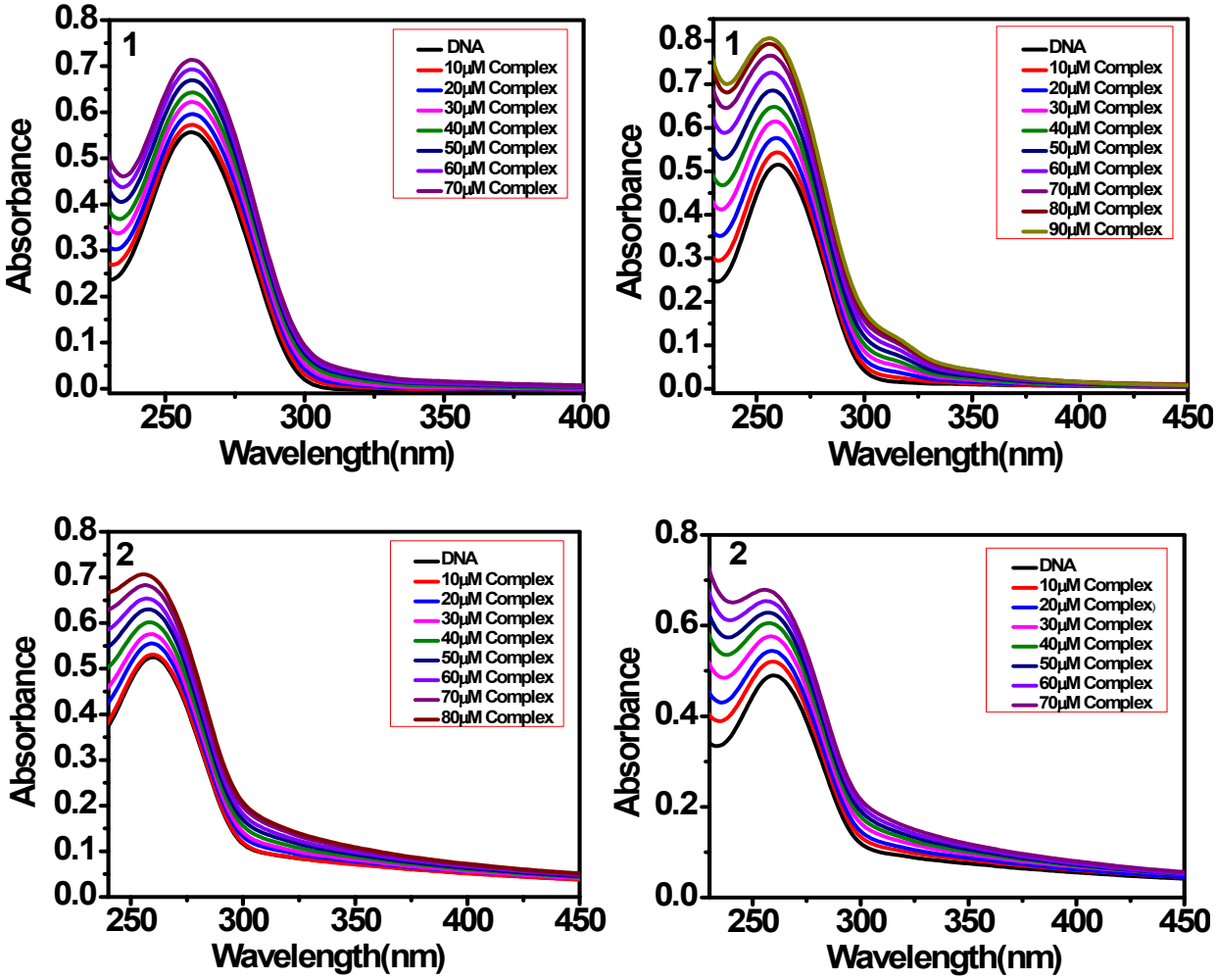
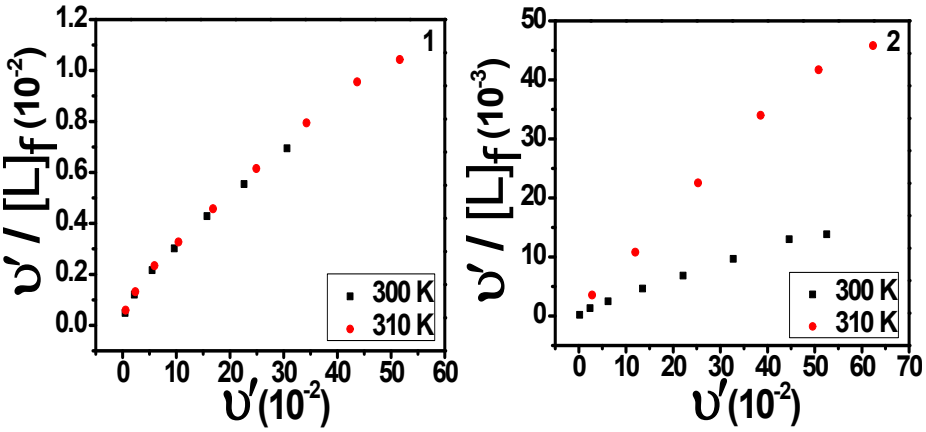


Fig. S8. Absorption spectra of constant DNA concentration with varying concentrations of complex **1** and **2** at 300K (left) and 310K (right).



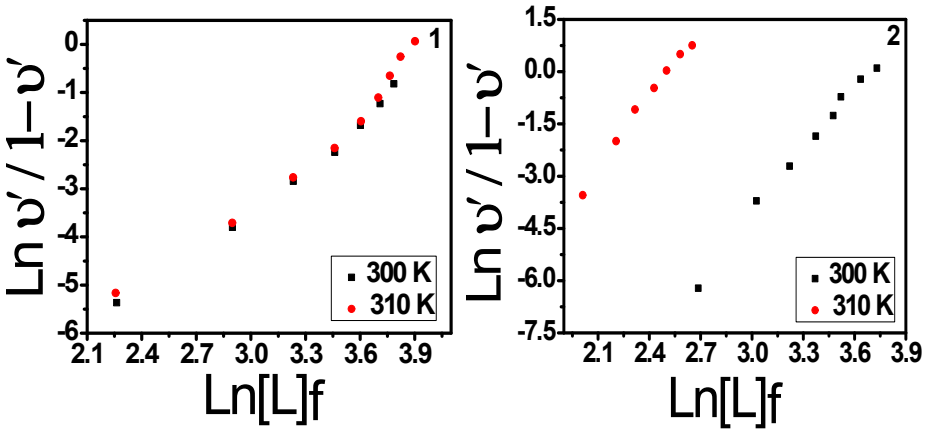


Fig. S9. Scatchard plot (upper) and Hill plot (lower) for complex **1** (left) and **2**(right)

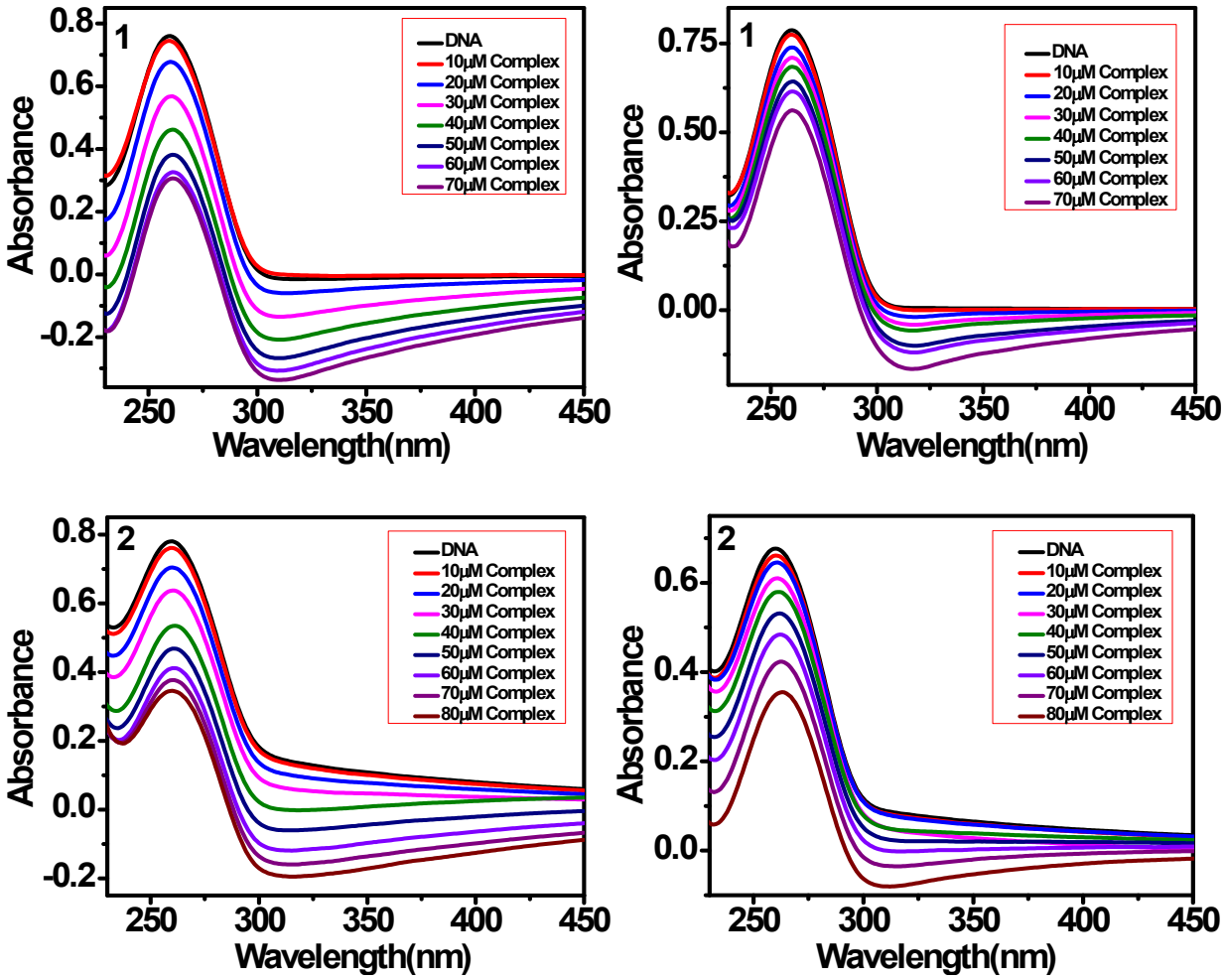


Fig. S10. Absorption spectra of complex **1** and **2** of DNA denaturation studies at 300K (left) and 310K (right)

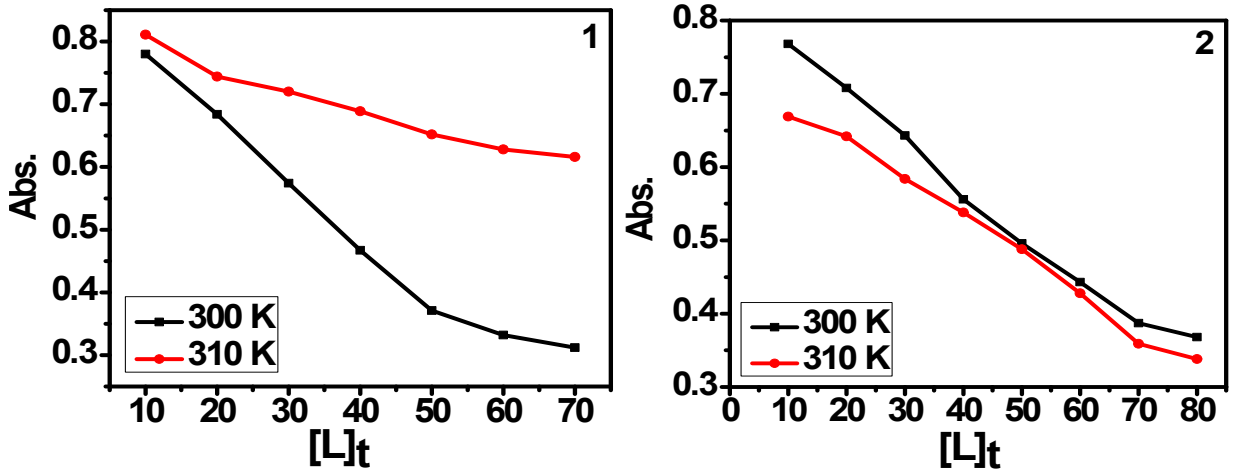


Fig. S11. Graph of DNA denaturation studies of complex **1** and **2** at 300K and 310K for $[L]_{1/2}$ value.

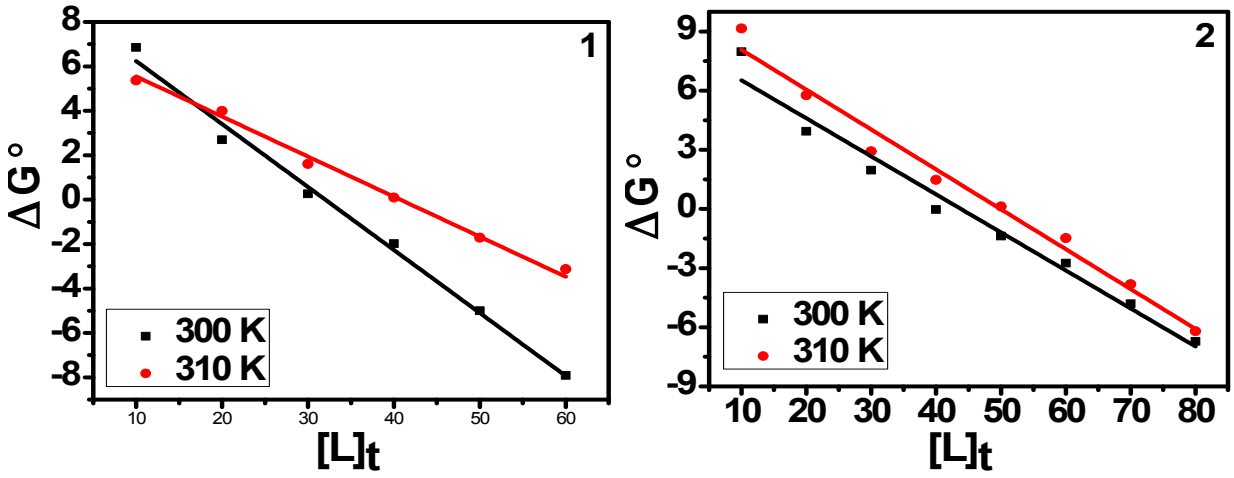


Fig. S12. Graph of ΔG° *vs*. complex concentrations $[L]_t$ in the transition region for complex **1** and **2**.

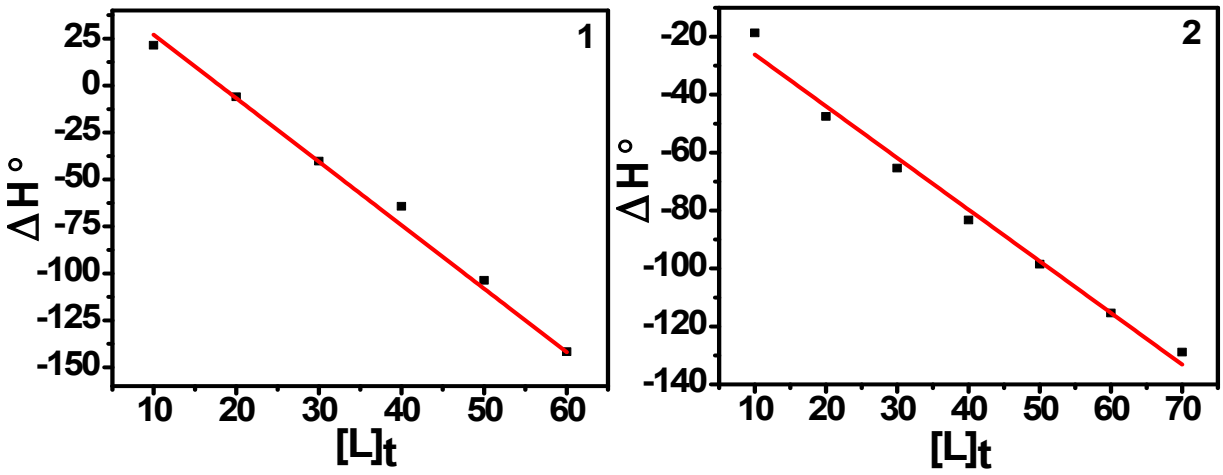


Fig. S13. Graph of ΔH^o *vs*. complex concentrations $[L]_t$ in the transition region for complex **1** and **2**.

1.7 Viscosity measurements

Viscosity measurements were performed using Ubbelohde viscometer at 25 ºC. The concentration of DNA (100 μM) was kept constant by gradually varying the concentrations of complex (10 to 60 μM) in all samples. The flow time was measured at least five times for each solution using a digital stopwatch and then the mean value was used. The relative viscosity of DNA (η) to solvent was estimated first and then the relative specific viscosities of DNA (η and η_o) were calculated in the presence and absence of title complexes by using $(t - t^o)/ t^o$, where t is the observed flow time of title compound and t^o is the flow time of the DNA alone. Finally, the graphs of the relative specific viscosities $(\eta/ \eta_o)^{1/3}$ *vs.* r , the ratio of [complex]/[DNA] were plotted.

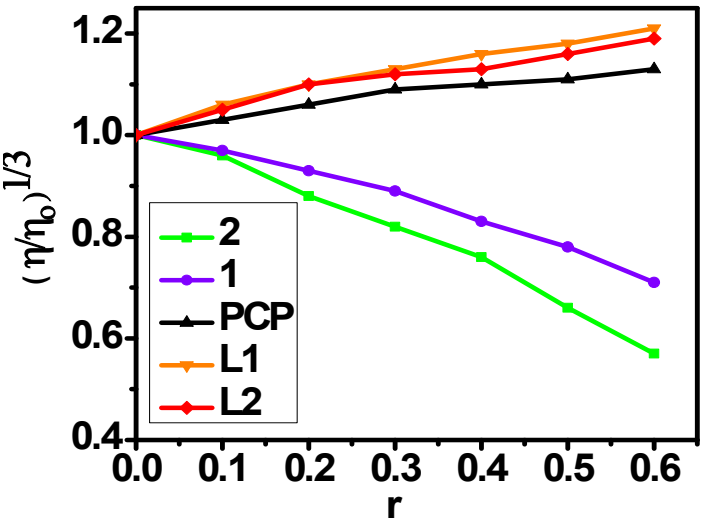


Fig. S14. Effect of increasing concentrations of complexes on the relative viscosity of CT-DNA at 25 ºC, where [DNA] = 100uM and r=[complex]/[DNA] and PCP = *tris(p-Chlorophenyl)phosphine*

1.8 Evaluation of cytotoxicity of compound 1 and 2 on selected cancer cell lines

The cytotoxicity of compounds evaluated by using CellTiter 96™ Aqueous Non-Radioactive Cell Proliferation Assay) MTS assay and sulforhodamine B (SRB) cellular protein staining method, as described earlier [**14-16**], was applied to test the cytotoxic potential of both **1** and **2** toward different cancer cell lines. Briefly, cancer cells (1×10^4 cells in 190 µl of the complete media) were plated in 96 well plates comprising tested compounds and incubated at 37°C, 5% CO_2 in humidified air for 72 h. The incubation was stopped with trichloroacetic acid and cells were washed, air-dried, stained with SRB solution and the optical densities (ODs) were determined at 515 nm using a microplate reader. A zero-day control was also performed in each case by adding an equivalent number of cells to several wells, incubating at 37°C for 30 min and

processing as described above. The percentage cell survival was calculated using the following formula:

$$\frac{OD_{cell\ +\ testedcompound} - OD_{day\ 0}}{OD_{cell\ +\ 10\%\ DMSO} - OD_{day\ 0}} \times 100$$

All the experiments were performed in triplicate.

1.9 NF-κB Assay

Human embryonic kidney cells 293 (HEK-293) from Panomics were employed for checking variations arising along the NF-κB pathway. Stable constructed cells were seeded into 96-well plates at 20 × 10^3 cells per well. The cells were kept in Dulbecco's modified Eagle's medium (DMEM) (Invitrogen Co.), supplemented with 10% fetal bovine serum (FBS), 100 units/mL penicillin, 100 µg/mL streptomycin, and 2 mM L-glutamine. Later 48 h of incubation, the medium was replaced and the cells were treated with several concentrations of the test substances. TNF-α (human, recombinant, E. coli, Calbiochem) was employed as an activator at a concentration of 2 ng/mL (0.14 nM) and the plate was incubated for 6 h. Consumed medium was discarded, and cells were washed twice with PBS. Subsequently, cells were lysed using 50 µL (for 96-well plate) of reporter lysis buffer from Promega, via incubating for 5 min on a shaker, and stored at -80 °C. The luciferase assay was accomplished using the Luc assay system from Promega. The gene product, luciferase enzyme, interacts with luciferase substrate by emitting light that was detected by using a luminometer (LUMIstar Galaxy BMG). However, the data for NF-κB inhibition are articulated as IC_{50} values (i.e., concentration required to inhibit TNF-α-induced NF-κB activity by 50%). As positive controls, TPCK (Nα-tosyl-L-phenylalanine chloromethyl ketone) known NF-κB inhibitor was used and IC50 values are given in Table S6. All experiments were executed in triplicate.

1.10 Determination of apoptosis

The Annexin V-FITC Apoptosis Detection Kit (APO Alert Annexin V, USA) was used to determine the mode of cell death (apoptosis) exerted by the compounds on the cancer cell lines [**17-18**]. The HeLa cells were seeded in 96 well plates and incubated in 5% (v/v) CO_2 at 37 ^oC for 24 h. Next, the media with IC_{50} compound concentrations after 72 h were added and incubated for 12 and 24 h. Afterward, the cells were washed with 1× binding buffer, 200 µL of binding buffer containing Annexin V-FITC and PI was added and placed at 37 °C for 15 min. The untreated cells (in the presence of only 1% DMSO (v/v) were designated as the negative control. Finally, the slides were then observed under Image Xpress Micro XLS Widefield High-Content Analysis System (HCS) (Sunnyvale, USA), for images.

Table S1. Crystal data and structure refinement for **1** and **2**

Crystal data	**1**	**2**
Identification code	REHMA93	xstr0592
Empirical formula	$C_{30}H_{27}Cl_4N_2OPPtS_2$	$C_{27}H_{23}Cl_4N_4PPtS_2$
Formula weight	863.51	835.47
Temperature/K	100	150(1)
Crystal system	Monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a/Å	19.8684(8)	11.74447(17)
b/Å	9.9816(4)	18.5199(2)
c/Å	17.7360(7)	14.4446(2)
α/°	90	90
β/°	113.1837(15)	109.7957(16)
γ/°	90	90
Volume/Å^3	3233.3(2)	2956.14(8)
Z	4	4
ρ_{calc}g/cm^3	1.774	1.877
μ/mm^{-1}	8.996	5.330
F(000)	1688.0	1624.0
Crystal size/mm^3	0.2 × 0.16 × 0.06	0.3 × 0.26 × 0.24
Radiation	GaKα (λ = 1.34139)	MoKα (λ = 0.71073)
2Θ range for data collection/°	8.424 to 109.988	5.74 to 51.998
Index ranges	-23 ≤ h ≤ 24, -12 ≤ k ≤ 12, -21 ≤ l ≤ 16	-14 ≤ h ≤ 14, -22 ≤ k ≤ 22, -17 ≤ l ≤ 17
Reflections collected	36327	44915
Independent reflections	6151 [R_{int} = 0.0558, R_{sigma} = 0.0378]	5781 [R_{int} = 0.0451, R_{sigma} = 0.0235]
Data/restraints/parameters	6151/0/371	5781/0/352
Goodness-of-fit on F^2	1.098	1.090
Final R indexes [I>=2σ (I)]	R_1 = 0.0321, wR_2 = 0.0842	R_1 = 0.0178, wR_2 = 0.0401
Final R indexes [all data]	R_1 = 0.0344, wR_2 = 0.0861	R_1 = 0.0198, wR_2 = 0.0410
Largest diff. peak/hole / e Å^{-3}	1.50/-1.69	0.54/-0.48

Table S2. Atomic NBO charges at B3LY P/LANL2DZ level.

Compound	NBO atomic charges							References
	Pt	Cl	P	S	S	$C(NCS_2)$	$N(NCS_2)$	
$C_{31}H_{33}ClN_3PPtS_2$	-0.185	-0.399	1.100	0.027	-0.002	-0.037	-0.460	[**19**]
$C_{31}H_{33}ClN_3PPtS_2$	-0.195	-0.387	1.074	0.034	-0.011	-0.038	-0.460	[**19**]
$C_{29}H_{25}ClF_3N_2OPPtS_2$	-0.193	-0.396	1.098	0.031	-0.006	-0.031	-0.455	[**20**]
$C_{29}H_{25}Cl_4N_2OPPtS_2$	-0.193	-0.395	1.097	0.032	-0.007	-0.031	-0.455	[**20**]
$C_{30}H_{30}ClN_2OPPtS_2$	-0.185	-0.397	1.097	0.020	0.006	-0.036	-0.459	[**20**]
$C_{32}H_{34}ClN_2OPPtS_2$	-0.184	-0.399	1.102	0.017	0.006	-0.037	-0.460	[**20**]
1	-0.193	-0.394	1.097	0.034	0.005	-0.031	-0.455	This work
2	-0.193	-0.396	1.097	0.036	0.004	-0.030	-0.455	This work

Table S3. Energies(ev) of HOMO, LUMO and Molecular properties of complexes **1** and **2**

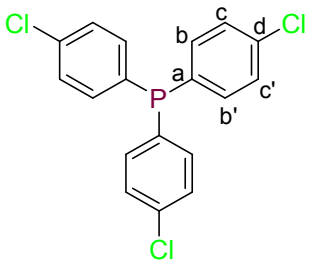
Comp.	E_{LUMO}	E_{HOMO}	$\Delta E=(E_{LUMO}-E_{HOMO})$	I.E	E.A	η	μ	ω
1	-2.2727	-5.58051	3.3078	5.5805	2.2726	1.6539	-3.9266	4.6611
2	-2.2158	-5.9954	3.7796	5.9954	2.2158	1.8898	-4.1056	4.4597

Table S4. IC_{50} values (μM) of complexes (**1** and **2**) against selected cancer cell lines and Vero (normal) cells.

Cell Lines	IC_{50} (μM)		
	Complex **1**	Complex **2**	**Cisplatin**
MCF-7	0.92	0.58	1.50
LU	6.80	3.30	4.80
ICIC-7	8.86	5.20	18.30
HeLa	0.24	0.33	24.10
Vero	80.20	85.40	75.50

Table S5. IC_{50} values (μM) of complexes (**1** and **2**) against NF-κB

Compound No	NF-κB [IC_{50} in μM]
1	0.48±0.08
2	9.8±1.1
TPCK	5.3 ± 0.9



Scheme S1: Numbering scheme of organophosphine,$P(C_6H_4Cl)_3$

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