Electronic Supplementary Information

An experimental and theoretical approach on kinetics and mechanism for formation of a four membered (S,S) chelated Pt(II) complex

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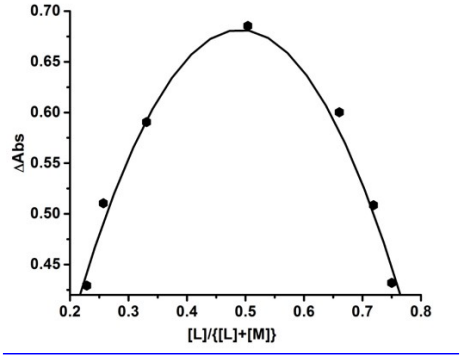

Fig. S1 Job's Plot of continuous variation

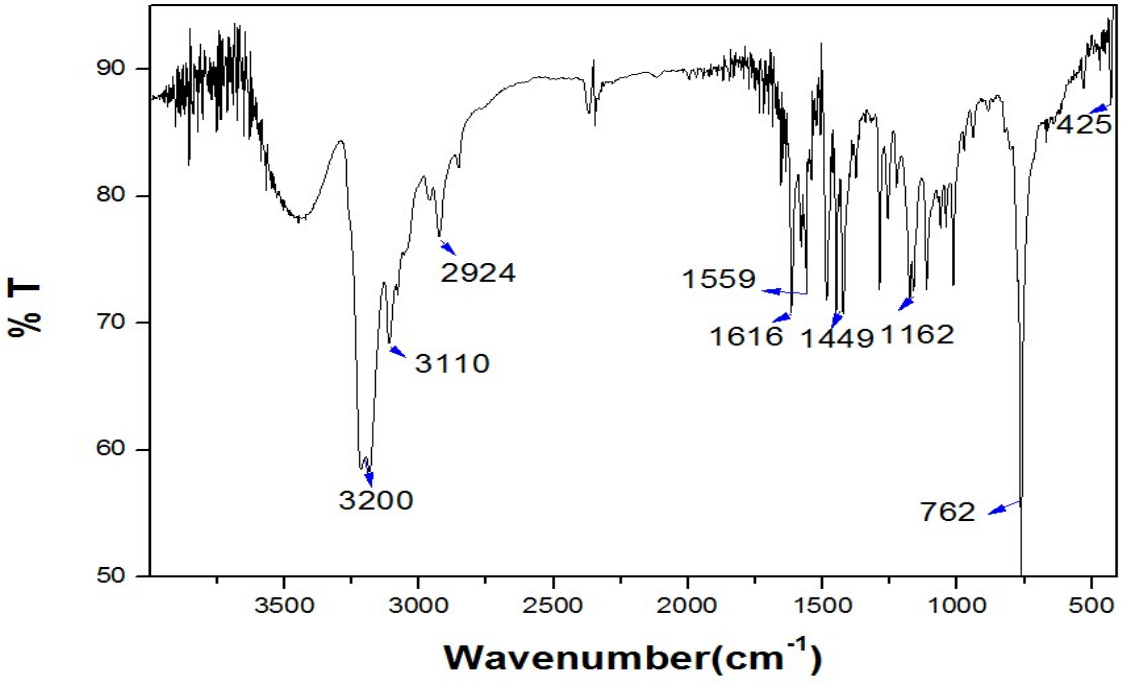

Fig. S2 FTIR spectra of Complex **1** in KBr disk (400 cm^{-1}-4000 cm^{-1})

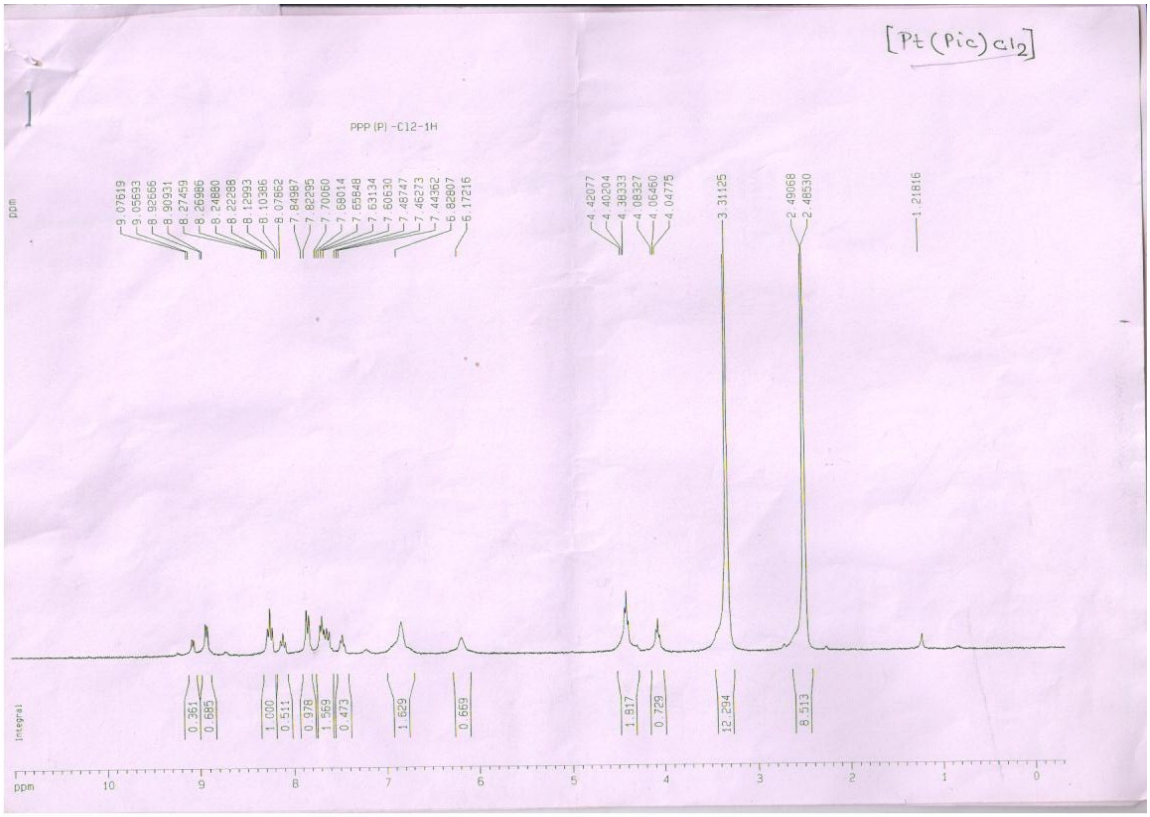

Fig. S3 ^{1}H NMR spectra of complex **1**

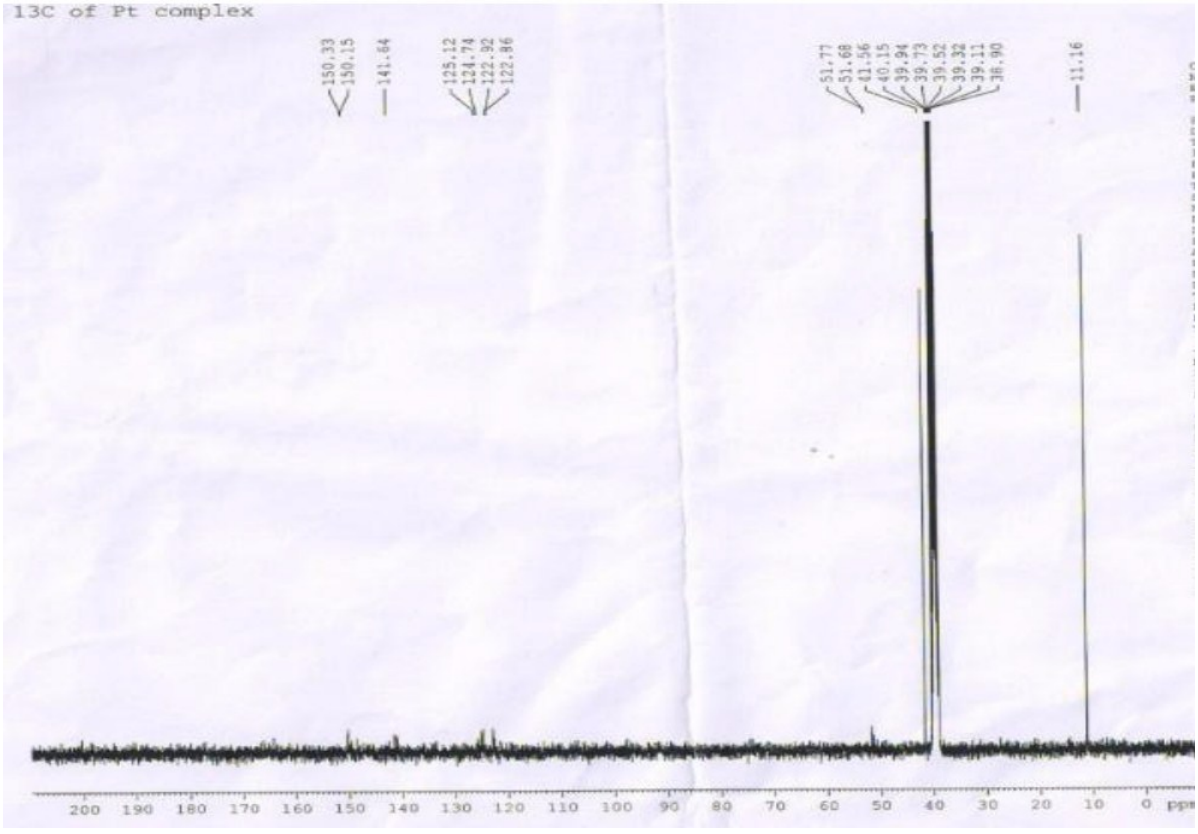

Fig. S4 ^{13}C NMR of complex**1**

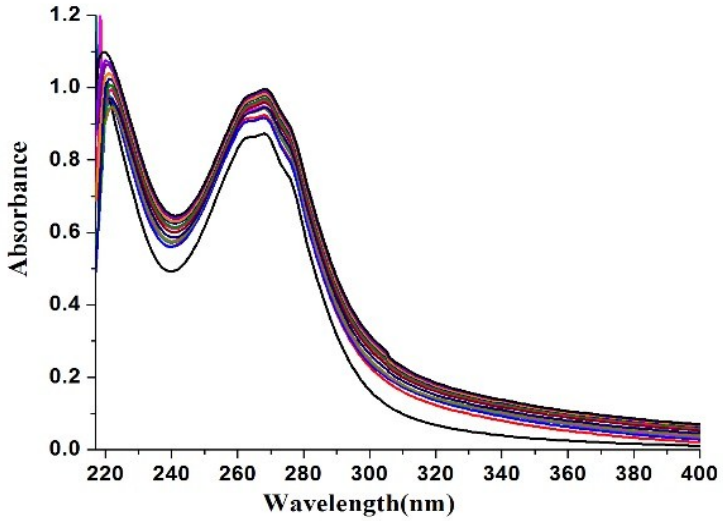

Fig. S5 Spectral difference between the reactant and product (1 cm quartz cell) (1): $[Pt(pic)(OH_2)_2]^{2+}$ = 2.43×10^{-4} mol.dm^{-3}, (2) $[Pt(pic)(OH_2)_2]^{2+}$ = 2.43×10-4 mol.dm^{-3}, [DDTC] = 2.43×10^{-3} mol.dm^{-3}, pH = 4.0

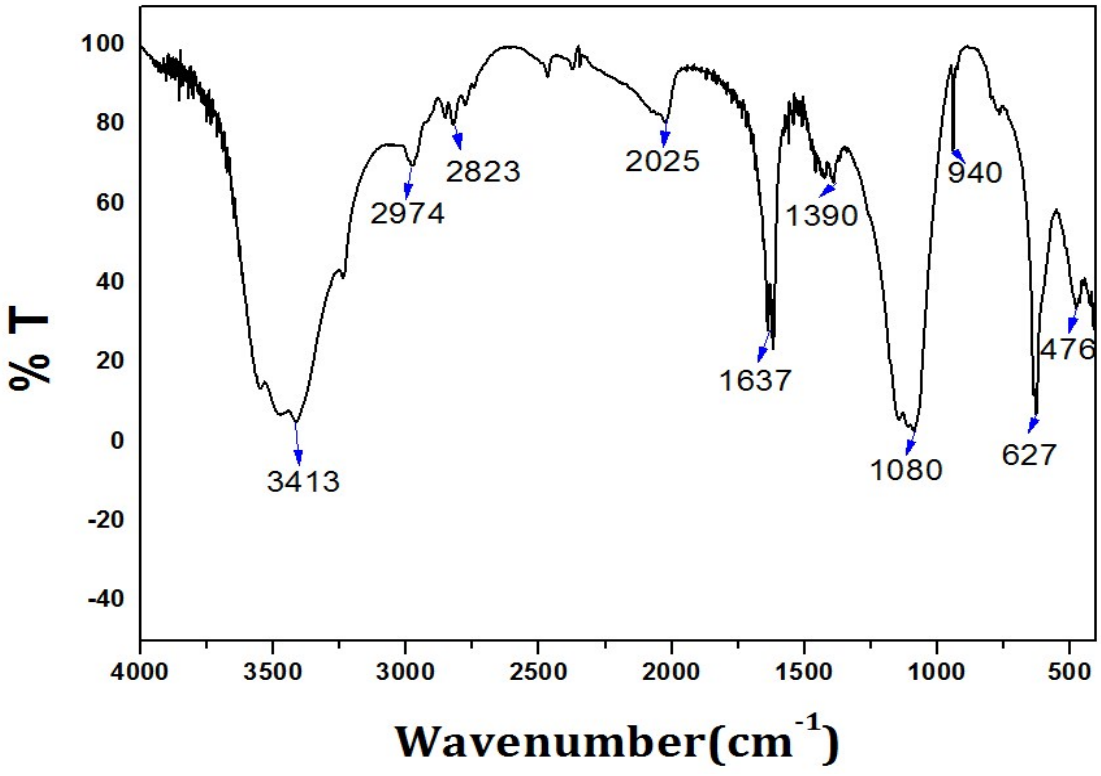

Fig. S6 FTIR spectra of Complex **3** in KBr disk (400 cm^{-1}-4000 cm^{-1})

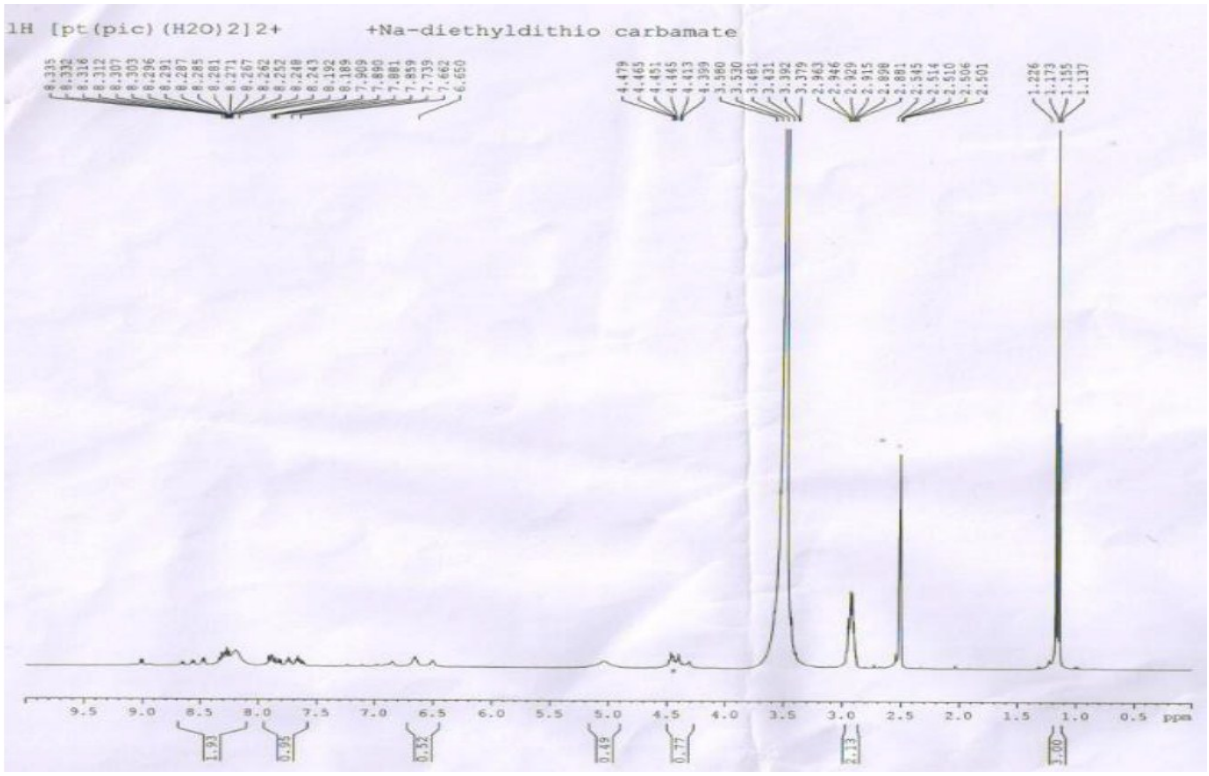

Fig. S7 ^{1}H NMR spectra of Complex **3** in DMSO d^{6} solvent

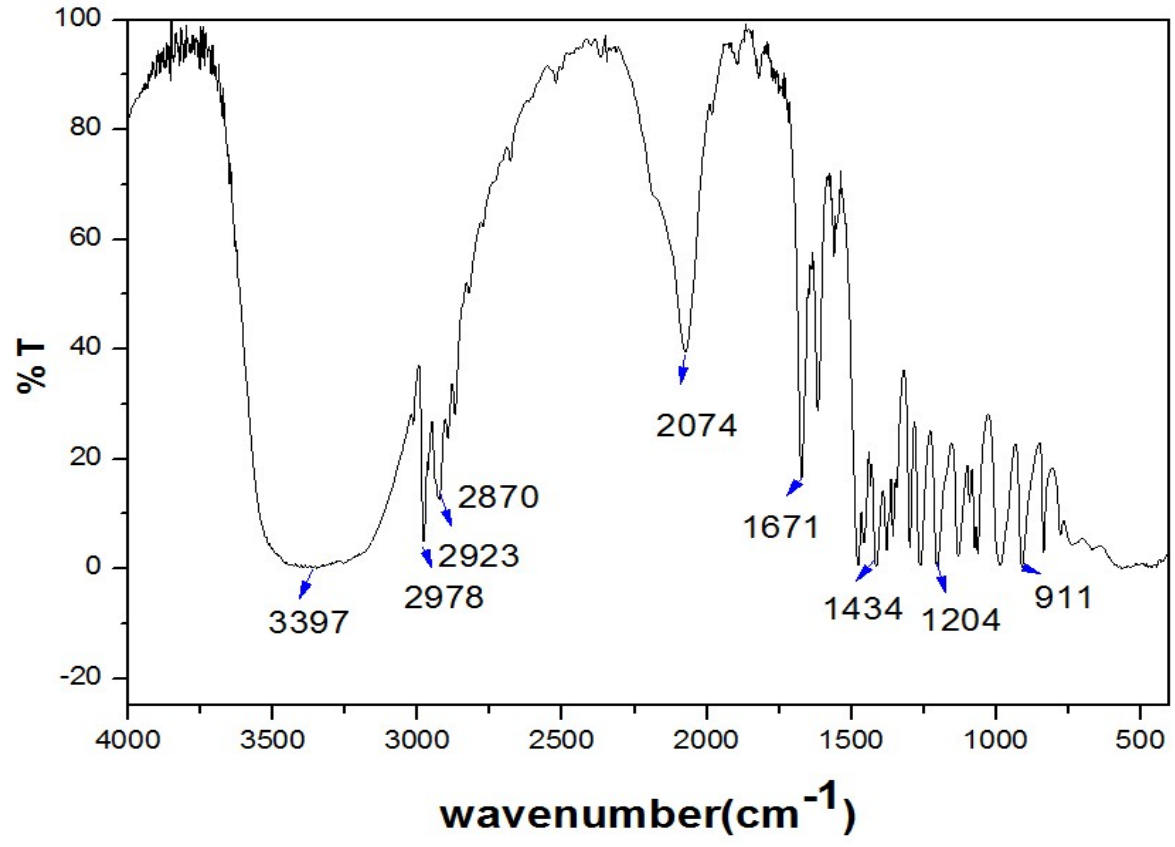

Fig S8 FTIR spectra of DDTC in KBr disk (400 cm^{-1}-4000 cm^{-1})

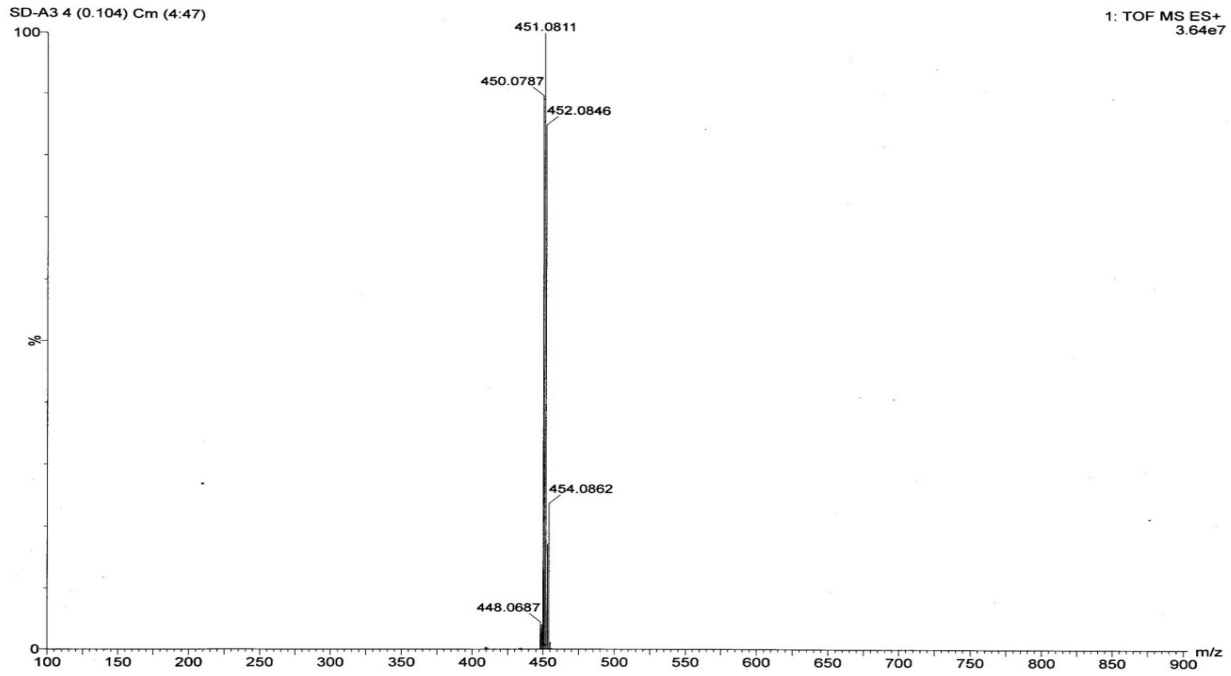

Fig. S9 ESI-Mass of Complex **3**

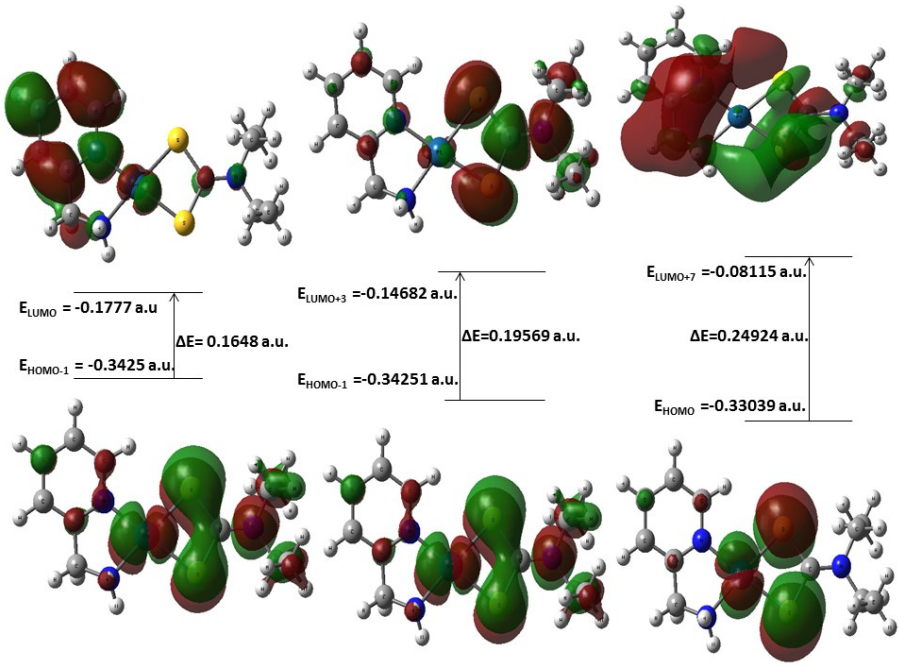

Fig. S10 Molecular orbitals involved in electronic transitions

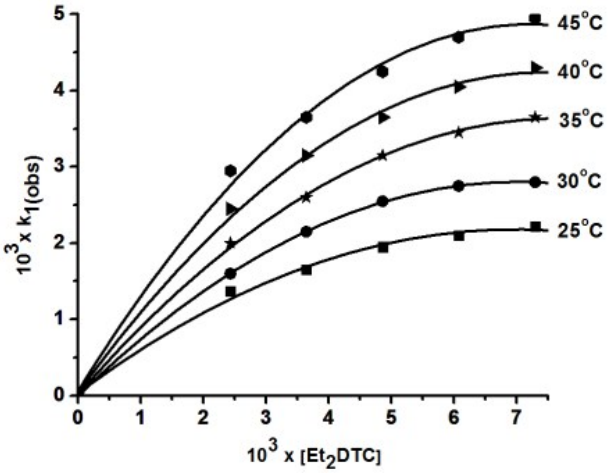

Fig. S11 Plot of 10^3[DDTC] versus $10^3k_{1(obs)}$ at different temperatures

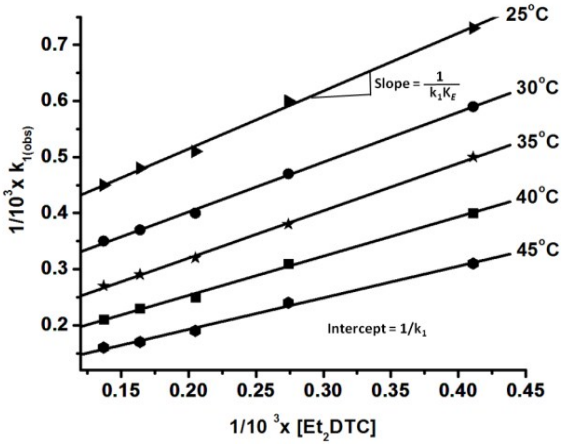

Fig. S12 Plot of 1/ $k_{1(obs)}$ versus 1/ [DDTC] at different temperatures

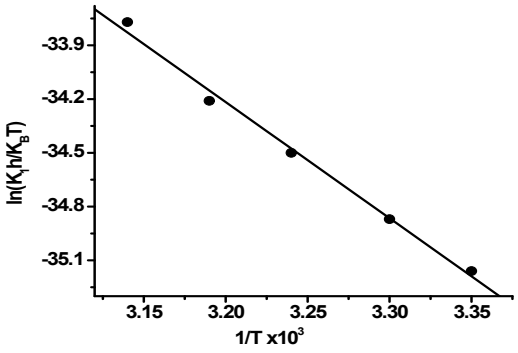

Fig. S13a Eyring plot

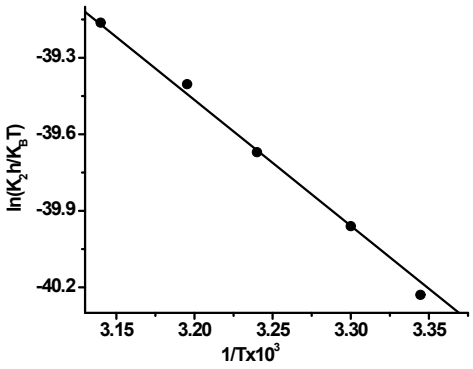

Fig. S13b Eyring plot

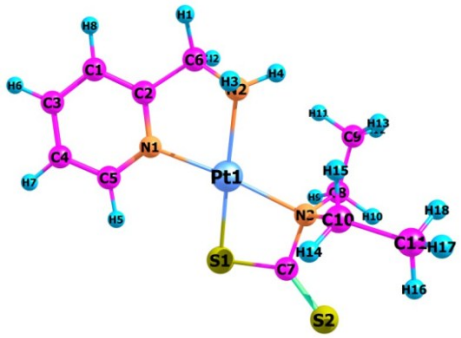

Fig. S14 Optimised structure of probable Complex **3'**

MTT ASSAY FOR ANTITUMOR PROPERTY DETERMINATION

Cells and culture conditions:

Human cervical carcinoma cells (HeLa), which were obtained from Bose institute, Kolkata, were used in this study. The Cells were allowed to grow in culture flask possessing DMEM medium (Hi-Media) containing 10% FBS (Hi-Media) with antibiotic concentration 1% of penicillin/streptomycin (50 IU/ml and 500 µg/ml) respectively in CO_2incubator with a humidified atmosphere (95% air/5%CO_2) at 37°C for 24 hours. After obtaining the expansion of cells around 70% confluence, these cells maintained in the same cultural conditions. The cells were counted by haemocytometer and diluted to the appropriate concentration for further seeding. The appropriate volume of cell suspension added to a new flask containing medium (DMEM with antibiotic). This experiment was performed on cultures from passages 3 to 4.

Cell counting:

The number of cells, cultured in culture flasks was evaluated by detaching with trypsin solution(0.05% trypsin–0.02% sodium EDTA) and counting using Haemocytometer and trypan blue solution (0.2% w/v final dye concentration).Viable HeLa cell number counts were obtained at 4,15, and 24-h incubation.

MTT cell viability assay

Cell viability was investigated using the MTT colorimetric assay. MTT is taken up into cells by endocytosis or protein-facilitated mechanism and reduced, mainly by mitochondrial enzymes. MTT assay is based on a reaction between mitochondrial enzyme dehydrogenase from viable cells with the yellow tetrazolium rings of MTT (3-(4, 5-dimethylthiazolyl-2)-2, 5-diphenyltetrazolium bromide) is reduced to generate reducing equivalents such as NADH and NADPH by metabolically active cells, by producing dark blue formazan crystals. These crystals are impermeable to cell membranes, thus resulting in its accumulation within healthy cells. The resulting intracellular purple formazan can be solubllized by adding a detergent, results in the liberation of the crystals. These were quantified by spectrophotometric means. The

number of the surviving cells is correlated to the level of the formazan product which is generated. The colour can then be quantified by using the colorimetric assay on a multi-well scanning spectrophotometric method by ELISA reader (Stat Fax™® 2100Microplate Reader, USA).

The ability of cells to reduce MTT provides an indication of the mitochondrial integrity and activity which, In turn, may be interpreted as a measure of cell number or proliferation or viability or survival or toxicity.
MTT Solution: (5 mg/ml) 250 mg of MTT dissolved in 50 ml of 1X Phosphate Buffer Solution

MTT Solvent: 4 mM HCl, 0.1% Nondet P-40 (NP40) all in isopropanol

In vitro assays

In order to determine the cytotoxic effect of complex **2**and **3** on HeLa cell viability, a rapid colorimetric MTT assay protocol was used. The *in vitro* assays the experiments were divided into three main sections; each of them was used to determine: a) the correspondence between the quantity of viable cells and resultant absorbance at 540 nm for plotting standard curves. b) *In vitro* growth features of cell lines by plotting curves to correlate absorbencies of viable cells against times (0, 24, 48, 72 and 96 h), i.e. plotting growth curves. c) Finally, chemo sensitivity characteristics of cell lines against serially diluted concentrations of Pt(pic) complexes.

In vitro cytotoxicity assay

a) Assays were carried out in 96-well culture plates. The cells (1×10^5 per ml) were allowed to settle by incubating the plates for 24 hrs before addition of the compound solution. After 48 hrs and 72 hrs continuous exposures to the compounds at 37^{o}C these plates were analyzed for cell viability using MTT assay. The effect of Pt(pic) compounds concentrations was assayed in 10 wells and within three independent experiments. The percentage of cell survival against platinum complex concentration was calculated by the following equation for HeLa cell lines**.**

$$\%\ of\ Survival\ = \frac{(At\ -\ Ab)}{(Ac\ -\ Ab)} x\ 100$$

Where;

At: Mean absorbance of the test compound

Ab: Mean absorbance of the blank

Ac: Mean absorbance of the negative control

b) HeLa cells were detached with trypsin EDTA (0.25%). The treated cells were counted and resuspended to a final concentration of 1×10^5 cells per ml. From cell lines, 100 µl of cell suspensions was added to each well of a 96-well plate. After 24 h of incubation, when cells were in the early exponential growth, the cells were treated with desired concentration of complexes by keeping blank and control. Cisplatin used in the same concentrations as positive control. The plates were incubated for 24 hrs. After that 20 µl MTT (5 mg/ml in PBS) was added to each well and incubated for another 3 hrs. Then 150 µl of DMSO was added to each well to dissolve the blue formazan product. The absorbance of this product was measured at 540 nm, using ELISA plate reader (Stat Fax™® 2100Microplate Reader, USA).

Docking methodology

In order to follow a docking study using Hex software, first we have to load a receptor(B-DNA) and complex **2** in pdb file format structure using the File pull-down menu. Then docking was carried out using the options, Controls → Docking → Activate. To save the Docking Results: The current docking orientation was written in a single pdb file by selecting the menu File → Save → Both.
Various steps involved in metal complex Docking are, initially Structure of complex 2 was optimised using Gaussian 09 and optimised structure was converted into pdb file using 'Open Babel' software. The structure of the receptor (B-DNA) was obtained from Protein Data Bank. Docking menu was clicked to carryout docking process. The results obtained after the completion of docking are shown in Fig. 8. The E-Total values of metal complex against B- DNA were calculated using Hex 8.0.0 docking software, and it can be concluded from the energy value Pt complex **2** stably binds with the B-DNA.

Table S1 The parameters used in the docking process

correlation type	shape only
FFT Mode	3D
Grid Dimension	0.7
Receptor range	180
ligand range	180
twist range	360
distance range	40

Table S2 Values of $10^3 \times k_{1(obs)}$ (s^{-1}) values at different [DDTC] at different temperatures. [Complex **2**] = 2.43×10^{-4} mol.dm^{-3}, pH= 4.0, ionic strength= 0.1 mol·dm^{-3}

$10^3\times$[DDTC] mol.dm^{-3}	Temperature (°C)				
	25	30	35	40	45
2.43	1.37±0.01	1.69±0.03	2.0±0.04	2.45±0.07	3.22±0.03
3.64	1.65±0.04	2.15±0.04	2.6±0.03	3.22±0.03	4.16±0.06
4.86	1.90±0.06	2.50±0.02	3.15±0.03	4.0±0.03	5.26±0.03
6.07	2.10±0.05	2.70±0.03	3.45±0.01	4.34±0.02	5.88±0.03
7.29	2.20±0.03	2.80±0.02	3.65±0.03	4.76±0.05	6.25±0.05

Table S3 $10^5 \times k_{2(obs)}$ (s^{-1}) values at different [DDTC] at different temperatures; [complex **2**] = 2.43×10^{-4} mol.dm^{-3}, pH= 4.0, ionic strength= 0.1 moldm^{-3}

[DDTC] mol.dm^{-3}	Temperature (°C)				
$10^3\times$	25	30	35	40	45
2.43	2.13±0.02	2.78±0.02	3.77±0.03	4.93±0.04	6.43±0.02
3.64	2.14±0.03	2.79±0.04	3.79±0.03	4.93±0.02	6.44±0.03
4.86	2.16±0.01	2.81±0.08	3.78±0.01	4.94±0.03	6.44±0.04
6.07	2.15±0.01	2.82±0.05	3.78±0.03	4.95±0.01	6.46±0.03
7.29	2.17±0.04	2.83±0.09	3.81±0.02	4.95±0.01	6.48±0.05

Table S4 Analogous systems of Pt(II) complexes

Systems	$\Delta H_1^{\ddagger}$ (kJmol^{-1})	$\Delta S_1^{\ddagger}$ (JKmol^{-1})	$\Delta H_2^{\ddagger}$ (kJmol^{-1})	$\Delta S_2^{\ddagger}$(JKmol^{-1})	Ref.
$[Pt(pic)(H_2O)_2]^{2+}$/ L-cysteine	34.91±0.97	-174.68±2.18	29.11±0.72	-233.74±2.4	25
$[Pt(pic)(H_2O)_2]^{2+}$/ N-acetyl-L- cysteine	21.12±0.35	-294.25±1.05	19.45±0.47	-267.68±1.6	
$[Pt(phen)(H_2O)_2]^{2+}$/ Thiourea	41.0 ± 2.0	-41.0 ± 6.0	37.3 ± 0.7	-61.0 ± 2.0	65
$[Pt(terpy)(H_2O)]^{2+}$/ Glutathione	23 ± 1	-116 ± 3	----	----	66
cis-$[Pt(pic)(H_2O)_2]^{2+}$ /Glutathione	52.37±2.10	-112.35±2.98	37.29±1.84	-130.12±3.16	67

[*cis*-Pt(en)$(H_2O)_2]^{2+}$/ L-aspargine	45.39±0.96	-116.98±2.9	33.78±0.51	-221.43±1.57	68
[*cis*-Pt(en)$(H_2O)_2]^{2+}$/ thiourea	61.90±1.6	-71±6	26.70±0.8	-186.80±2.7	69
[*cis*-Pt(en)$(H_2O)_2]^{2+}$/ L-thiosamecarbazide	35.60±0.8	-166±3	44.50±1.3	-182±4.0	70
[*cis*-Pt(dach)$(H_2O)_2]^{2+}$ /Glutathione	32.9±1.3	-187.20±4.2	30.50±0.1	-223.1±4.3	71
[*cis*-Pt(dach)$(H_2O)_2]^{2+}$ /DL-penicillamine	36.10±4.1	-175±12	44.4±1.1	-189±3.0	72

Table S5. Coordinates of different stationary states (Reactant intermediates, transition states and product intermediates) located on potential energy surface.

RI1

6	4.664598739	1.324054809	-0.869733112
6	3.588728739	0.473227809	-0.641222112
6	4.636744739	2.615762809	-0.342358112
6	3.520031739	3.024848809	0.385620888
6	2.471661739	2.130377809	0.564178888
7	2.505984739	0.876769809	0.072948888
6	3.552099739	-0.957435191	-1.129062112
7	2.129432739	-1.385549191	-1.297058112
1	3.998930739	-1.615455191	-0.376259112
1	4.110805739	-1.078226191	-2.062181112
78	0.986088739	-0.545727191	0.176024888
8	-0.274019261	0.169036809	1.688672888
1	-1.124699261	0.560469809	1.244888888
1	0.075103739	0.837561809	2.301853888
8	-0.368337261	-1.998705191	0.023988888
1	-1.272638739	-1.663984809	-0.081372888
1	-0.475368261	-2.363839191	0.920407888
1	2.026688739	-2.402650191	-1.253981112
1	1.761872739	-1.092670191	-2.206572112
1	1.570574739	2.410499809	1.097160888
1	5.469096739	3.292615809	-0.506585112
1	3.450294739	4.023364809	0.802624888
1	5.512428739	0.977688809	-1.452000112
16	-2.603883261	1.488948809	0.332570888
6	-3.812995261	0.347899809	-0.081861112
7	-5.082776261	0.718727809	-0.285403112
6	-6.147897261	-0.214363191	-0.718077112
6	-6.892675261	-0.854798191	0.456283888
1	-5.708692261	-0.975334191	-1.367141112
1	-6.836329261	0.369197809	-1.336133112
1	-6.220871261	-1.461887191	1.069717888
1	-7.687011261	-1.504040191	0.073419888
1	-7.356068261	-0.096670191	1.096311888
6	-5.532981261	2.114707809	-0.081276112
6	-5.437728261	2.956999809	-1.354557112
1	-4.932732261	2.551753809	0.717520888
1	-6.568474261	2.056314809	0.267587888
1	-4.399637261	3.041200809	-1.687199112
1	-5.818149261	3.964144809	-1.153693112
1	-6.033290261	2.529191809	-2.168462112
16	-3.477508261	-1.383891191	-0.288022112

TS1 negative frequency =-127.03 cm^{-1}

6	4.310761000	1.735300000	-0.751518000
6	3.419630000	0.675424000	-0.636274000
6	4.097956000	2.892395000	0.000077000
6	2.982450000	2.963320000	0.833183000
6	2.115417000	1.879207000	0.893844000
7	2.338512000	0.753952000	0.185331000
6	3.587004000	-0.635826000	-1.365321000
7	2.248768000	-1.277314000	-1.536595000
1	4.194237000	-1.318518000	-0.761451000
1	4.083776000	-0.495954000	-2.330780000
78	1.101755000	-0.853194000	0.150843000
8	0.263134000	-0.942756000	2.294089000
1	-0.508586000	-0.332366000	2.135249000
1	0.796643000	-0.574853000	3.020127000
8	-0.077031000	-2.536742000	-0.059487000
1	-1.090937000	-2.183754000	-0.234608000
1	-0.119404000	-2.975287000	0.812865000
1	2.333233000	-2.286503000	-1.672095000
1	1.763873000	-0.905261000	-2.357409000
1	1.214069000	1.895141000	1.495185000
1	4.787275000	3.727366000	-0.074015000
1	2.770681000	3.848353000	1.422694000
1	5.160331000	1.653222000	-1.421641000
16	-1.252672000	0.856892000	0.423696000
6	-2.743536000	0.068455000	-0.093513000
7	-3.844591000	0.823470000	-0.233625000
6	-5.129322000	0.264636000	-0.713841000
6	-6.012176000	-0.250020000	0.424795000
1	-4.913657000	-0.532370000	-1.426424000
1	-5.632715000	1.070140000	-1.257320000
1	-5.525891000	-1.076709000	0.949508000
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1	-3.662862000	4.201716000	-0.857159000
1	-4.272162000	2.955732000	-1.958124000
16	-2.820188000	-1.622830000	-0.440416000

PI1

6	4.371591000	1.671893000	-0.231080000
6	3.437078000	0.646662000	-0.146856000
6	3.946688000	2.997765000	-0.137756000
6	2.588286000	3.259122000	0.026737000
6	1.696776000	2.194791000	0.092003000
7	2.111534000	0.913740000	0.013105000
6	3.824672000	-0.812725000	-0.185838000
7	2.689971000	-1.613906000	-0.722919000
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1	4.737656000	-0.962667000	-0.770737000
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8	-1.029672000	-2.776042000	2.326907000
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1	-1.828387000	-3.296297000	2.510750000
8	-0.115175000	-2.546698000	-0.137000000
1	-0.923057000	-2.272198000	-0.686379000

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1	2.678892000	-1.600987000	-1.745255000
1	0.630157000	2.335013000	0.215812000
1	4.665009000	3.809037000	-0.200267000
1	2.211327000	4.273340000	0.098014000
1	5.420706000	1.430296000	-0.367438000
16	-1.013438000	0.332487000	0.899926000
6	-2.371633000	0.125833000	-0.270156000
7	-3.412117000	0.954170000	-0.088025000
6	-4.616757000	0.881367000	-0.950833000
6	-5.670837000	-0.083779000	-0.406491000
1	-4.304281000	0.588436000	-1.953218000
1	-5.015920000	1.898548000	-1.007457000
1	-5.283452000	-1.105888000	-0.381873000
1	-6.550811000	-0.067690000	-1.058005000
1	-5.994577000	0.196777000	0.602021000
6	-3.478532000	1.996527000	0.960035000
6	-2.996941000	3.363266000	0.468436000
1	-2.906101000	1.672950000	1.830409000
1	-4.525166000	2.051745000	1.274486000
1	-1.944329000	3.322318000	0.171963000
1	-3.101714000	4.101724000	1.270339000
1	-3.581886000	3.711123000	-0.389046000
16	-2.357625000	-1.050287000	-1.501405000

RI1'

6	3.726682000	2.724498000	0.678190000
6	2.756727000	1.779151000	0.364042000
6	5.040051000	2.305871000	0.896588000
6	5.350111000	0.950703000	0.779447000
6	4.339354000	0.055618000	0.451331000
7	3.068552000	0.461550000	0.257606000
1	3.455278000	3.772696000	0.750229000
1	5.810391000	3.028939000	1.145135000
1	6.360126000	0.586150000	0.930375000
1	4.524388000	-1.005550000	0.328048000
6	1.299180000	2.104247000	0.138294000
7	0.712795000	1.065795000	-0.759206000
1	1.166417000	3.104773000	-0.284770000
1	0.752277000	2.058978000	1.086128000
78	1.488663000	-0.756164000	-0.277911000
16	-2.622102000	-1.121086000	1.116581000
16	-2.419660000	0.531868000	-1.437953000
6	-3.302331000	0.039113000	-0.059920000
7	-4.536219000	0.477968000	0.206558000
6	-5.236026000	1.431266000	-0.686815000
6	-5.007538000	2.888184000	-0.283303000
1	-6.298856000	1.177023000	-0.634413000
1	-4.896755000	1.254241000	-1.707343000
1	-5.332338000	3.080113000	0.745266000
1	-5.582245000	3.544541000	-0.945246000
1	-3.950074000	3.151967000	-0.373322000
6	-5.326170000	0.039278000	1.380544000
6	-6.200765000	-1.180834000	1.083718000
1	-5.942940000	0.894169000	1.673052000
1	-4.650374000	-0.155860000	2.216170000
1	-6.900578000	-0.979959000	0.265914000
1	-6.785976000	-1.435012000	1.973734000
1	-5.590688000	-2.047398000	0.814336000
1	0.952693000	1.266762000	-1.734705000
1	-0.331156000	1.032003000	-0.730397000

8	-0.058830000	-1.959035000	-0.701936000
1	-0.516838000	-1.675105000	-1.513040000
1	-1.542626000	-1.473989000	0.350753000
8	2.185207000	-2.735713000	0.115836000
1	1.367796000	-3.125393000	-0.301367000
1	2.121972000	-2.947594000	1.065906000

TS1' negative frequency = -136.41 cm^{-1}

6	3.834250000	2.338232000	0.804936000
6	2.738313000	1.614373000	0.351435000
6	4.969451000	1.656202000	1.246060000
6	4.978290000	0.261534000	1.214140000
6	3.861129000	-0.411002000	0.735030000
7	2.766610000	0.254127000	0.312942000
1	3.794054000	3.422606000	0.816334000
1	5.832709000	2.206281000	1.606492000
1	5.839934000	-0.306700000	1.546701000
1	3.814587000	-1.491899000	0.679164000
6	1.431589000	2.228225000	-0.083926000
7	0.757608000	1.292579000	-1.029102000
1	1.568581000	3.212125000	-0.542680000
1	0.766742000	2.338110000	0.779948000
78	1.043069000	-0.602868000	-0.386832000
16	-1.480322000	-0.774091000	0.871125000
16	-2.321803000	0.847580000	-1.597047000
6	-2.673782000	0.159215000	-0.033197000
7	-3.882692000	0.341445000	0.515106000
6	-4.966087000	1.084780000	-0.172092000
6	-4.957127000	2.577133000	0.161987000
1	-5.905521000	0.623564000	0.147117000
1	-4.863581000	0.929839000	-1.246003000
1	-5.049229000	2.751092000	1.239754000
1	-5.802875000	3.067322000	-0.331731000
1	-4.034989000	3.045488000	-0.193109000
6	-4.258800000	-0.182960000	1.847667000
6	-4.888061000	-1.575806000	1.777494000
1	-4.963908000	0.536254000	2.275420000
1	-3.370648000	-0.192516000	2.480062000
1	-5.782038000	-1.584546000	1.144723000
1	-5.184249000	-1.894910000	2.782459000
1	-4.174252000	-2.304179000	1.382328000
1	1.144430000	1.387137000	-1.973148000
1	-0.282180000	1.439449000	-1.112726000
8	-0.411471000	-1.667839000	-1.897236000
1	-0.947202000	-0.885587000	-2.205486000
1	-1.039934000	-2.031726000	-1.237365000
8	1.428297000	-2.593114000	0.335172000
1	1.348723000	-3.214509000	-0.414008000
1	0.725134000	-2.833784000	0.970106000

PI1'

6	4.440063000	1.692590000	-0.066286000
6	3.160129000	1.268121000	0.275114000
6	5.314429000	0.792265000	-0.676530000
6	4.882762000	-0.508699000	-0.934479000
6	3.586520000	-0.867333000	-0.583675000
7	2.749399000	0.005000000	0.008268000
1	4.748243000	2.711250000	0.146412000
1	6.317652000	1.105350000	-0.948077000
1	5.532433000	-1.237508000	-1.406185000

1	3.185481000	-1.858144000	-0.763724000
6	2.176757000	2.144149000	1.018195000
7	0.777595000	1.652836000	0.822651000
1	2.261042000	3.190918000	0.710510000
1	2.391774000	2.090791000	2.091108000
78	0.742711000	-0.362394000	0.448306000
16	-1.523722000	-0.611008000	1.042606000
16	-1.624425000	0.921764000	-1.606327000
6	-2.423877000	0.244201000	-0.243090000
7	-3.749155000	0.333860000	-0.074408000
6	-4.622670000	0.978737000	-1.083920000
6	-4.817542000	2.472750000	-0.822687000
1	-5.580313000	0.450599000	-1.045447000
1	-4.183213000	0.815532000	-2.068217000
1	-5.241742000	2.659227000	0.170141000
1	-5.507780000	2.885557000	-1.565838000
1	-3.866224000	3.005313000	-0.906379000
6	-4.465216000	-0.193260000	1.109654000
6	-4.951185000	-1.632242000	0.920422000
1	-5.312356000	0.477032000	1.282598000
1	-3.810750000	-0.115430000	1.980196000
1	-5.619412000	-1.720000000	0.057267000
1	-5.505850000	-1.950791000	1.809168000
1	-4.109139000	-2.316298000	0.780156000
1	0.326046000	2.062381000	-0.005908000
1	0.191291000	1.894505000	1.623995000
8	-0.185109000	-1.907710000	-2.455280000
1	-0.619318000	-1.029480000	-2.313995000
1	-0.830722000	-2.456252000	-2.928279000
8	0.806564000	-2.392785000	-0.141383000
1	0.371088000	-2.349043000	-1.073297000
1	0.203138000	-2.906438000	0.426888000

RI2

6	-4.194612000	1.769967000	0.540991000
6	-3.335661000	0.714991000	0.256726000
6	-3.685614000	3.066058000	0.629229000
6	-2.319936000	3.266966000	0.441148000
6	-1.504740000	2.173926000	0.173256000
7	-2.001928000	0.922812000	0.076635000
1	-5.251749000	1.574276000	0.688554000
1	-4.345044000	3.900096000	0.847371000
1	-1.878478000	4.255305000	0.505081000
1	-0.436932000	2.267767000	0.021746000
6	-3.822399000	-0.704155000	0.085465000
7	-2.722890000	-1.652501000	0.416752000
1	-4.088471000	-0.872095000	-0.963958000
1	-4.713604000	-0.890894000	0.692901000
78	-0.892318000	-0.760276000	-0.227500000
16	1.062426000	0.299128000	-1.015217000
16	2.305506000	-1.539942000	1.118018000
6	2.393168000	-0.170657000	0.092407000
7	3.488033000	0.600024000	0.044912000
6	4.708972000	0.260154000	0.815667000
6	4.721370000	0.894497000	2.207300000
1	5.556840000	0.613419000	0.221142000
1	4.775682000	-0.826291000	0.885393000
1	4.649643000	1.986590000	2.154745000
1	5.660138000	0.644000000	2.712344000
1	3.894572000	0.516030000	2.814378000
6	3.606598000	1.828727000	-0.771338000
6	4.179329000	1.567962000	-2.166771000

1	4.255483000	2.509008000	-0.211661000
1	2.624140000	2.299690000	-0.838741000
1	5.168543000	1.101380000	-2.113856000
1	4.284068000	2.517613000	-2.702046000
1	3.520762000	0.917254000	-2.749420000
1	-2.874005000	-2.562717000	-0.019984000
1	-2.666753000	-1.814158000	1.424849000
8	0.057739000	-2.617886000	-0.452757000
1	0.907725000	-2.443528000	0.128937000
1	0.388106000	-2.698048000	-1.368123000

TS2negative frequency =-132.57 cm^{-1}

6	-4.467641000	0.934120000	-0.821876000
6	-3.313549000	0.179124000	-0.662473000
6	-4.506660000	2.245615000	-0.342562000
6	-3.377089000	2.767953000	0.289704000
6	-2.249527000	1.972028000	0.441044000
7	-2.216558000	0.692224000	-0.021401000
1	-5.324046000	0.499821000	-1.321644000
1	-5.399269000	2.845596000	-0.462987000
1	-3.364202000	3.780852000	0.668621000
1	-1.350707000	2.333304000	0.918313000
6	-3.154578000	-1.208968000	-1.234308000
7	-2.128438000	-1.975849000	-0.417227000
1	-2.748004000	-1.132548000	-2.248463000
1	-4.109547000	-1.740382000	-1.267037000
78	-0.670363000	-0.606941000	0.240287000
16	1.017842000	0.976841000	0.921120000
16	1.770892000	-1.373707000	-0.854615000
6	2.287080000	0.160038000	-0.095417000
7	3.485619000	0.688568000	-0.244000000
6	4.541870000	0.033672000	-1.087619000
6	5.430125000	-0.891641000	-0.239636000
1	5.124055000	0.841771000	-1.537906000
1	4.036903000	-0.526057000	-1.876142000
1	5.916883000	-0.340694000	0.571094000
1	6.207218000	-1.329001000	-0.874351000
1	4.830166000	-1.701096000	0.184564000
6	3.878869000	1.985049000	0.401299000
6	3.588793000	3.174230000	-0.529967000
1	4.945341000	1.909036000	0.627989000
1	3.330265000	2.078314000	1.340510000
1	4.135644000	3.076651000	-1.472586000
1	3.902722000	4.102802000	-0.042868000
1	2.518023000	3.232269000	-0.742739000
1	-1.695999000	-2.719957000	-0.978606000
1	-2.550030000	-2.402763000	0.420187000
8	0.226943000	-2.334098000	1.593038000
1	0.408500000	-1.938696000	2.487860000
1	1.108575000	-2.447066000	1.124658000

PI2

6	4.736246000	-0.425517000	0.218714000
6	3.445647000	0.084008000	0.110124000
6	4.920941000	-1.803214000	0.331469000
6	3.804024000	-2.638281000	0.322661000
6	2.542302000	-2.069873000	0.200058000
7	2.366543000	-0.737842000	0.099523000

1	5.583537000	0.252673000	0.216729000
1	5.920682000	-2.216761000	0.419220000
1	3.900802000	-3.715298000	0.403224000
1	1.643308000	-2.674615000	0.176249000
6	3.148376000	1.563606000	0.045285000
7	1.851541000	1.802129000	-0.641803000
1	3.964776000	2.107438000	-0.441503000
1	3.047094000	1.957651000	1.062870000
78	0.530865000	0.216040000	-0.167535000
16	-1.063003000	-1.459756000	0.355228000
16	-1.583293000	1.245319000	-0.441187000
6	-2.302389000	-0.283746000	0.014590000
7	-3.601417000	-0.513952000	0.082994000
6	-4.597287000	0.535651000	-0.230605000
6	-5.045609000	1.308876000	1.010841000
1	-5.444140000	0.030207000	-0.704049000
1	-4.162593000	1.205444000	-0.976675000
1	-5.497267000	0.647426000	1.757329000
1	-5.795623000	2.053109000	0.724199000
1	-4.203042000	1.830363000	1.474651000
6	-4.134720000	-1.841502000	0.467572000
6	-4.388420000	-2.742857000	-0.742168000
1	-5.060026000	-1.656418000	1.020903000
1	-3.429107000	-2.303683000	1.162402000
1	-5.105367000	-2.292832000	-1.436685000
1	-4.803255000	-3.697417000	-0.402709000
1	-3.459523000	-2.945098000	-1.283300000
1	1.975862000	1.841867000	-1.654817000
1	1.427956000	2.692553000	-0.327196000
8	0.443178000	3.906522000	0.592164000
1	-0.339704000	3.467147000	0.963026000
1	0.132138000	4.768698000	0.275620000

RI2’

6	-4.754546000	-0.415679000	-0.815903000
6	-3.389214000	-0.486228000	-0.558711000
6	-5.485716000	0.667392000	-0.327322000
6	-4.823934000	1.655707000	0.399951000
6	-3.455880000	1.529152000	0.608955000
7	-2.749921000	0.482352000	0.143498000
1	-5.237532000	-1.201065000	-1.388345000
1	-6.552301000	0.738369000	-0.515224000
1	-5.350586000	2.515501000	0.798877000
1	-2.905626000	2.278629000	1.165283000
6	-2.541212000	-1.660021000	-0.988619000
7	-1.116952000	-1.229344000	-1.132467000
1	-2.909248000	-2.101622000	-1.919870000
1	-2.566729000	-2.432433000	-0.212438000
78	-0.658219000	0.168548000	0.312255000
16	2.326792000	2.357954000	0.502163000
16	1.566032000	-0.611823000	0.371189000
6	2.724132000	0.732597000	0.151686000
7	3.953243000	0.380207000	-0.249591000
6	4.340326000	-0.995835000	-0.631509000
6	4.889215000	-1.812078000	0.541587000
1	5.096490000	-0.896559000	-1.416147000
1	3.473895000	-1.489206000	-1.076287000
1	5.763134000	-1.329509000	0.991142000
1	5.197376000	-2.801039000	0.185906000
1	4.131721000	-1.946786000	1.319220000
6	5.055569000	1.369359000	-0.321844000
6	5.153495000	2.044593000	-1.690704000

1	5.975467000	0.822955000	-0.093328000
1	4.900669000	2.109147000	0.464771000
1	5.307580000	1.313604000	-2.492183000
1	6.005503000	2.732492000	-1.695602000
1	4.248565000	2.618659000	-1.907245000
1	-0.958494000	-0.793478000	-2.044999000
1	-0.484236000	-2.032269000	-1.085875000
8	-0.217018000	1.604191000	1.769229000
1	-0.782791000	2.393576000	1.700075000
1	0.729413000	1.940184000	1.459886000

TS2'negative frequency = -134.14 cm^{-1}

6	-4.750227000	0.005001000	-0.845171000
6	-3.445229000	-0.408490000	-0.598987000
6	-5.170528000	1.250259000	-0.375466000
6	-4.263788000	2.054844000	0.313676000
6	-2.970009000	1.586980000	0.514238000
7	-2.572789000	0.376239000	0.079946000
1	-5.426302000	-0.639339000	-1.398013000
1	-6.185714000	1.589241000	-0.555704000
1	-4.543767000	3.035153000	0.683169000
1	-2.217472000	2.182222000	1.018761000
6	-2.911797000	-1.754002000	-1.031887000
7	-1.435569000	-1.666353000	-1.241293000
1	-3.416365000	-2.108517000	-1.936915000
1	-3.077790000	-2.488491000	-0.236623000
78	-0.622122000	-0.392195000	0.207392000
16	1.383179000	1.674161000	0.006279000
16	1.549107000	-1.288074000	0.134666000
6	2.370892000	0.257273000	-0.072341000
7	3.686852000	0.288719000	-0.271848000
6	4.511518000	-0.937607000	-0.340132000
6	5.068721000	-1.350794000	1.024106000
1	5.322876000	-0.729624000	-1.043985000
1	3.907229000	-1.738092000	-0.774193000
1	5.687856000	-0.559718000	1.459979000
1	5.693890000	-2.242280000	0.908775000
1	4.261712000	-1.586167000	1.724217000
6	4.422854000	1.564648000	-0.423786000
6	4.539691000	2.000925000	-1.885014000
1	5.411666000	1.407639000	0.017908000
1	3.909611000	2.325039000	0.167402000
1	5.046182000	1.244184000	-2.493842000
1	5.123231000	2.925564000	-1.944050000
1	3.551242000	2.190913000	-2.312799000
1	-1.217647000	-1.282333000	-2.163682000
1	-1.008136000	-2.592714000	-1.199198000
8	-0.130915000	0.374275000	2.374922000
1	-0.853009000	0.812822000	2.856273000
1	0.524968000	1.069659000	2.148393000

PI2'

6	-4.736205000	0.425412000	0.219492000
6	-3.445591000	-0.084058000	0.110625000
6	-4.920935000	1.803122000	0.331897000
6	-3.804063000	2.638265000	0.322460000
6	-2.542354000	2.069906000	0.199624000
7	-2.366568000	0.737839000	0.099446000
1	-5.583448000	-0.252839000	0.217976000
1	-5.920665000	2.216653000	0.419855000

1	-3.900905000	3.715297000	0.402722000
1	-1.643394000	2.674678000	0.175336000
6	-3.148228000	-1.563652000	0.046037000
7	-1.851653000	-1.802198000	-0.641523000
1	-3.964781000	-2.107665000	-0.440296000
1	-3.046491000	-1.957436000	1.063676000
78	-0.530891000	-0.216038000	-0.167730000
16	1.062934000	1.459865000	0.354853000
16	1.583312000	-1.245322000	-0.441138000
6	2.302366000	0.283780000	0.014635000
7	3.601372000	0.513983000	0.083214000
6	4.597296000	-0.535651000	-0.230135000
6	5.045422000	-1.308765000	1.011456000
1	5.444227000	-0.030244000	-0.703474000
1	4.162726000	-1.205508000	-0.976220000
1	5.496934000	-0.647234000	1.757958000
1	5.795505000	-2.052999000	0.724998000
1	4.202790000	-1.830234000	1.475165000
6	4.134617000	1.841583000	0.467712000
6	4.388544000	2.742768000	-0.742112000
1	5.059821000	1.656563000	1.021234000
1	3.428872000	2.303862000	1.162341000
1	5.105611000	2.292633000	-1.436433000
1	4.803328000	3.697369000	-0.402709000
1	3.459744000	2.944939000	-1.283436000
1	-1.976363000	-1.841973000	-1.654486000
1	-1.427903000	-2.692605000	-0.327074000
8	-0.442722000	-3.906565000	0.591412000
1	-0.131871000	-4.768799000	0.274845000
1	0.340304000	-3.467284000	0.962100000

Supporting references:

65 U. Fekl, and R Van Eldik, *Eur. J. Inorg. Chem*., 1998, 389.
66 D. Ž. Bugarčić, T. Soldatovic, R. Jelic, B. Algues and A. Grandas, *Dalton Trans.,* 2004, 3869.
67 G. K. Ghosh, K. Misra, W. Linert, and S. C. Moi, Synth. React. *Inorg. Met.-Org. Chem*., 2013,**43**,714.
68 S.K. Bera, S.K. Chandra, and G.S. De*, Int J. Chem. Kinet*., 2003, **35,** 252.
69 P.S. Sengupta, S. Ghosh and G.S. De, *Transition Met. Chem*., 2000, **25**, 279.
70 S. Ghosh, P.S. Sengupta, and G.S. De, *Indian J. Chem.,* 2000, **38A,** 453.
71 R. Sinha, A. K. Choudhary and G.S. De, *Indian J. Chem*., 2003, **42A,** 473.
72 P. *Karmakar*, B. K. Bera, K.L. Barik, S. Mukhopadhay and A.K. Ghosh*, J Coord. Chem.*, 2010, **63** , 2158.